POLYMER SYNTHESIS USING RUTHENIUM AND OTHER CATALYSTS AND DEVELOPMENT OF FUNCTIONAL POLYMERS

TORU KATSUMATA

Department of Polymer Chemistry

Graduate School of Engineering

Kyoto University

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Contents

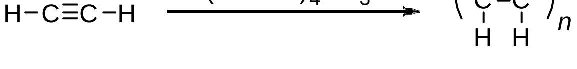
General Introduction

Research Background

Organometallic polymerization catalysts have been extensively studied since the most important method using transition metal catalysts for polymer synthesis was discovered by Ziegler and Natta in the 1950s.[1] The features of polymerization with transition metal catalysts include the control of regioregularity, tacticity, geometric structure, and branched structure of formed polymers by selection of the steric structure and electronic property of ligands and/or cocatalysts.

Transition metal-catalyzed polymerization of acetylenic compounds started when titanium (Ti) catalysts were used for unsubstituted acetylene in 1958.[2] The polymerization reaction proceeded via the coordination-insertion mechanism in a manner similar to the polymerization of olefins using the same type of catalysts to afford polyacetylene which possesses the alternating carbon–carbon double bond in the main chain. In 1974, Shirakawa and coworkers succeeded in the preparation of a uniform polyacetylene film by using a solvent-soluble Ziegler-Natta catalyst, $Ti(O\text{-}n\text{-}Bu)_4–Et_3Al$ (Scheme 1).[3] While the formed polyacetylene film found limited applications due to its insolubility in solvents and instability in air, it showed metallic conductivity upon doping with iodine.[4] This research stimulated studies on other conjugated polymers such as substituted polyacetylenes.

Scheme 1



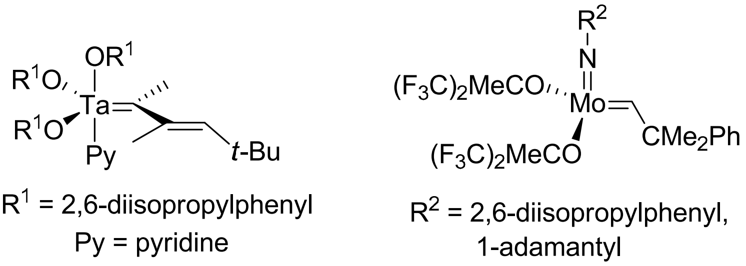
Substituted polyacetylenes can also be obtained with Ziegler-Natta catalysts, although the formed polymers are often insoluble in common organic solvents and their molecular weights are usually rather low. Masuda and coworkers revealed that simple halides of molybdenum (Mo) and tungsten (W) catalyze the polymerization of phenylacetylene (PA) and provide high molecular weight poly(PA) ($M_n > 10^4$) in high yields in 1974.[5] Both aliphatic and aromatic, and further not only monosubsituted[6] but also disubstituted acetylenes[7] polymerized with these catalyst systems, and monomers bearing certain heteroatoms also underwent polymerization.[8] Group 5 transition metal halides, e.g., pentahalides of tantalum (Ta) and niobium (Nb), were found to be effective in the polymerization of monomers carrying sterically bulky substituents such as 1-trimethylsilyl-1-propyne, 1-phenyl-1-propyne, and diphenylacetylenes.[9] The M_ws of some polymers reached several million.

Concerning the control of polymer molecular weight, the first example of living polymerization of substituted acetylenes was reported by Percec[10] and Masuda[11] independently in 1987. According to Percec's report, $TaCl_5$ and $MoCl_5$ induced living polymerization of 1-trimethylsilyl-1-propyne and *tert*-butylacetylene, and the obtained polymers had broad molecular weight distribution (MWD, $M_w/M_n > 1.9$). Masuda and coworkers found that a ternary catalyst, $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5), polymerizes 1-chloro-1-octyne and [*o*-(trimethylsilyl)phenyl]acetylene in a living fashion with low initiation efficiencies (2–16%). Further, they revealed that similar Mo-based ternary catalyst systems achieved the living polymerization of [*o*-(trifluoromethyl)phenyl]acetylene and *tert*-butylacetylene,[12] where R_3Al–EtOH[13], R_2Zn–EtOH[14], and RLi[13a,b,14a,15] were used as cocatalysts. Use of anisole as solvent improved the initiation efficiency up to 45%, and the polydispersity (M_w/M_n) of poly[{*o*-(trifluoromethyl)phenyl}acetylene] obtained in anisole was as small as 1.02.[16] The living polymerization of [*o*-(trifluoromethyl)phenyl]acetylene was also achieved by W-based binary or ternary catalysts, such as $WOCl_4$–*n*-Bu_4Sn–*t*-BuOH (1:1:1), $WOCl_4$–*n*-BuLi (1:1), and $WOCl_4$–EtMgBr (1:1).[17]

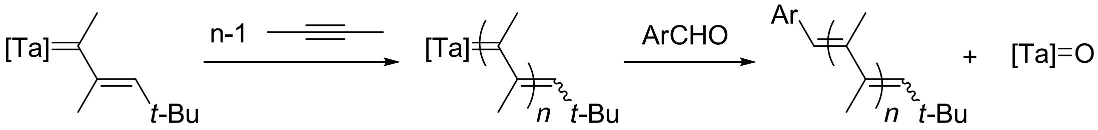
In 1989, Schrock and coworkers reported the living polymerization of substituted acetylenes using isolated well-defined catalysts.[18] Solvent-soluble poly(2-butyne) with 1.03 of M_w/M_n was obtained with a Ta carbene complex shown in

Chart 1 at –30 °C in toluene; then the degree of polymerization (DP_n) of polymer was below 200, and the initiation efficiency was quantitative. The polymerization using well-defined catalysts has a feature that the polymer ends can be functionalized easily by Wittig-like reaction (Scheme 2). Various molybdenum carbene complexes were developed, which polymerized *ortho*-substituted phenylacetylenes[19] and 1,6-deptadiynes[20] in a living manner (Chart 1). These catalysts showed higher activity and efficiency than the Ta catalyst did, and initiated polymerization in almost 100% initiation efficiencies.

Chart 1

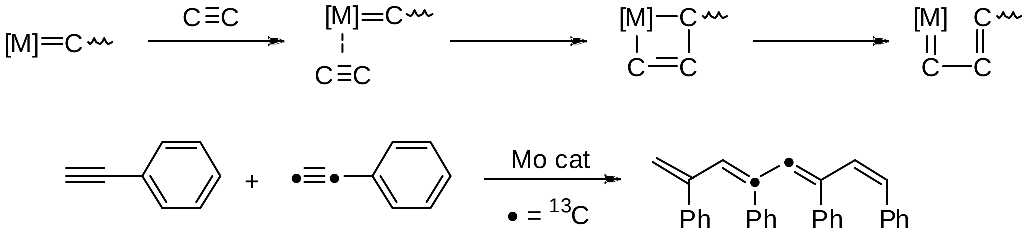


Scheme 2



The mechanism of polymerization of substituted acetylenes using the catalyst systems described above has been discussed. Although the active species of ill-defined catalysts had not been elucidated clearly, Masuda et al. proposed that this kind of polymerizations are initiated by metal carbene species generated in situ, followed by the propagation reaction via metathesis mechanism (Scheme 3).[21] This

Scheme 3

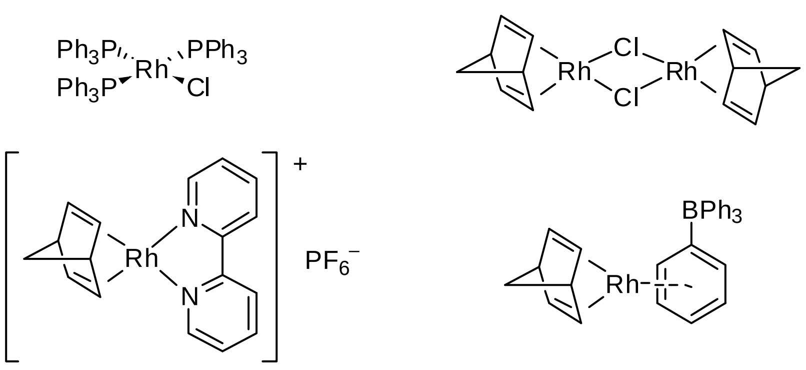


hypothesis was supported by experimental evidence.[22] Substituted acetylenes can be regarded as cycloolefins with the two-membered ring, and copolymerize with cycloolefins, indicating that alkyne polymerization proceeded by metathesis mechanism.[20d,23] Finally, the discovery of well-defined carbene catalysts that polymerize alkynes clearly proved that the metal carbene is the active species.[24]

Catalysts based on rhodium (Rh), which is a late transition metal, efficiently polymerize only monosubstituted acetylenes (e.g., *N*-propargylamide,[25] propiolic acid ester,[26] phenylacetylene, and its derivatives[27]), whereas group 5 and 6 transition metal complexes are active in the polymerization of various mono- and disubstituted ones. Rh complexes exhibit excellent functional group tolerance, and hence they have been used for hydroxy-[25a,28] carboxylic acid-[29], amide-[30], and radical-containing monomers.[31] In contrast to the early transition metal complexes which are generally quite sensitive to air and moisture and difficult to handle in air, the late transition metal complexes such as Rh are much more stable to air and moisture because of their low oxophilicity. This feature enables Rh complexes to work as catalysts in not only relatively nonpolar solvents including dichloromethane and tetrahydrofuran but also highly polar and protic solvents such as alcohols and amines and water.[29,30a,b,32]

The first example of the polymerization using Rh catalyst was reported by Kern et al. in 1969, which is concerned with the synthesis of poly(PA) using Wilkinson catalyst.[33] According to this paper, $RhCl(PPh_3)_3$ produced a yellow-orange poly(PA) with low molecular weight (M_n = 1100). In the following decades, dimeric Rh(I)

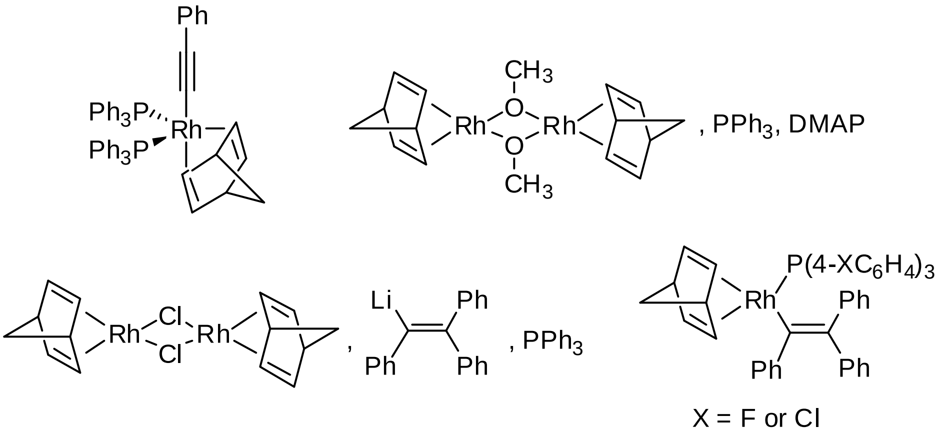
Chart 2



complex [RhCl(diene)]$_2$ [diene = cyclooctadiene (cod) or norbornadiene (nbd)],[34] cationic Rh(I) complex [Rh(diene)(N–N)]X (diene = cod or nbd; N–N = nitrogen-based bidentate ligand; X = Cl, PF$_6$, or ClO$_4$),[34b,35] and zwitterionic Rh(I) complex Rh$^+$(diene)[(η^6-C$_6$H$_5$)B$^-$(C$_6$H$_5$)$_3$] (diene = cod or nbd)[36] were developed as catalysts for the polymerization of PA under mild conditions (Chart 2).

Rh-catalyzed living polymerization of PA was first accomplished by Noyori and coworkers in 1994.[37] An isolated Rh acetylide complex shown in Chart 3 induced the living polymerization of PA in the presence of *N*,*N*-dimethylaminopyridine (DMAP) and produced a polymer with narrow MWD (M_w/M_n ~ 1.1). It was found in 1996 that a ternary catalyst, [(nbd)Rh(OMe)]$_2$–PPh$_3$–DMAP is also effective in the living polymerization, where the initiation efficiency (72%) was higher than that (37%) of the acetylide complex.[38] Later, Masuda et al. revealed that [(nbd)RhCl]$_2$–Ph$_2$C=(Ph)Li–PPh$_3$ provided the polymer whose M_w/M_n was about 1.1 and that its initiation efficiency with respect to Rh was virtually quantitative.[39] Further, a well-defined Rh(I) catalyst, Rh[C(Ph)=CPh$_2$](nbd)[(4-XC$_6$H$_4$)$_3$P] (X = F or Cl) was synthesized and isolated from a reaction mixture of [(nbd)RhCl]$_2$, Ph$_2$C=(Ph)Li, and (4-XC$_6$H$_4$)$_3$P, and the F-derivative was fully characterized by X-ray analysis.[40] The polymerization of PA with the F-derivative in the presence of 5 equivalents of (4-FC$_6$H$_4$)$_3$P proceeded with quantitative initiation efficiency to give poly(PA) with polydispersity as low as 1.05. The living character of this

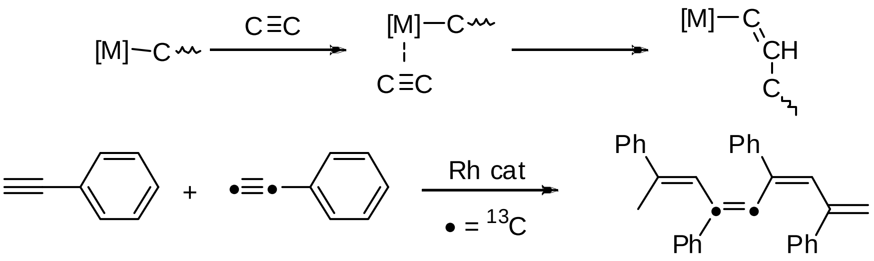
Chart 3



polymerization was confirmed by time-molecular weight relationship and multistage polymerization. This catalyst system could be used for the polymerization of *N*-propargylamide, and the presence of a long-lived active species was confirmed.[41] Recently, it was reported that an improved Rh(I) vinyl complex bearing tetrafluorobenzobarrelene (tfb) as a diene ligand provided a high molecular weight polymer with $M_w/M_n = 1.12$ even when the monomer-to-catalyst ratio ($[M]_0/[Rh]$) was as high as 4000.[42]

In general, the polymerization of substituted acetylenes with Rh catalysts proceeds via the coordination-insertion mechanism in a manner similar to that with Ziegler-Natta catalyst to give substituted polyacetylenes composed of all-*cis* or *cis*-rich alternating double bonds in the main chain. Noyori and coworkers elucidated this polymerization mechanism by using ^{13}C-labeled PA (Scheme 4).[43] This was also supported by the following two studies; one is the observation of quantitative initiation efficiency of a well-defined vinyl complex,[40,42] and the other is functionalization of the initiating polymer end by introduction of functional groups into the vinyl ligand of Rh(I) complex.[44]

Scheme 4



Other late transition metal catalysts including palladium (Pd),[45] nickel (Ni),[46] and platinum (Pt)[47] were reported to show activity for the polymerization of alkynes. Not only PA but also diethynylbenzene and polar monomers such as propargyl alcohol and *N*,*N*-dimethylpropargylamine were used as monomers. In the case of Pd catalysts, copolymerization of PA with either an oxanorbornene derivative[48] or a diazo compound was also achieved.[49]

Olefin metathesis is one of the most important and useful methods for organic reaction, and polymer synthesis such as ring-opening polymerization of cycloolefins and polycondensation of acyclic α,ω-dienes. Since the scramble reaction of double bonds was discovered in the 1950s,[50] several similar reactions were reported: e.g., ring-opening polymerization of norbornene by Truett et al. in 1960,[51] synthesis of 2-butene from propylene catalyzed by heterogeneous W catalyst ($W(CO)_6–Al_2O_3$) by Baily et al. in 1964,[52] and rearrangement of deuterated 2-butene catalyzed by a homogeneous catalyst ($WCl_6–EtOH–EtAlCl_2$) by Calderon in 1968.[53] In 1967, this kind of reaction, redistribution of double bonds, was called "metathesis" for the first time.[54] Olefin metathesis was accomplished with heterogeneous and homogeneous catalyst systems where transition metals were combined with alkylating agent or deposited on solid supports, e.g., $WCl_6–Bu_4Sn$, $WOCl_4–EtAlCl_2$, $MoO_3–SiO_2$, and $Re_2O_7–Al_2O_3$. These systems occupy an important position in application of olefin metathesis due to their low cost and simple preparation.

Although the mechanism of olefin metathesis had not been clear until 1970, Chauvin and coworkers proposed the metal carbene mechanism involving the interconversion of an olefin and a metal alkylidene via a metalacyclobutane intermediate by alternating [2+2] cycloadditions and cycloreversion (Scheme 5).[55] This proposal was gradually accepted and supported by experimental results.[56]

Scheme 5

The discovery of catalytic activity of a well-defined, coordinatively saturated metal carbene complex, $(CO)_5W=CPh_2$ in metathesis in the 1970s[57] motivated the development of coordinatively unsaturated more active Ta, Mo, and W carbene catalysts.[58] The developed catalysts showed high activity for olefin metathesis and faster initiation than those ever reported under mild conditions, which enabled to study the relationship between the structure and activity of the catalysts. Among them, the Mo and W alkylidenes represented as (ArN)(OR′)$_2$M=CHR displayed very high activity not only towards terminal olefins but also towards internal olefins and low-strain cycloolefin monomers (ROMP) as well as sterically demanding and electron-poor α,ω-dienes (ring-closing reaction).[59] The incorporation of optically active substituents as alkoxy ligands achieved the applications to asymmetric catalysts[60] and synthesis of stereoregular ROMP polymers.[61]

The development of ruthenium (Ru) metathesis catalyst originates from the synthesis of polynorbornene derivatives by $RuCl_3$(hydrate).[62] Several decades later, $Ru(H_2O)_6(tos)_2$ (tos = toluene-*p*-sulfonate) was found to be active in the polymerization of norbornene, 7-oxanorbornene, and norbornadiene.[63] In general, catalysts based on Ru, a late transition metal of group 8, can be used in air and applied to substrates having polar functional groups, such as hydroxy, carboxy, and amide groups, and/or in polar and protic solvents including water because of its excellent tolerance to functional groups (Figure 1).[64]

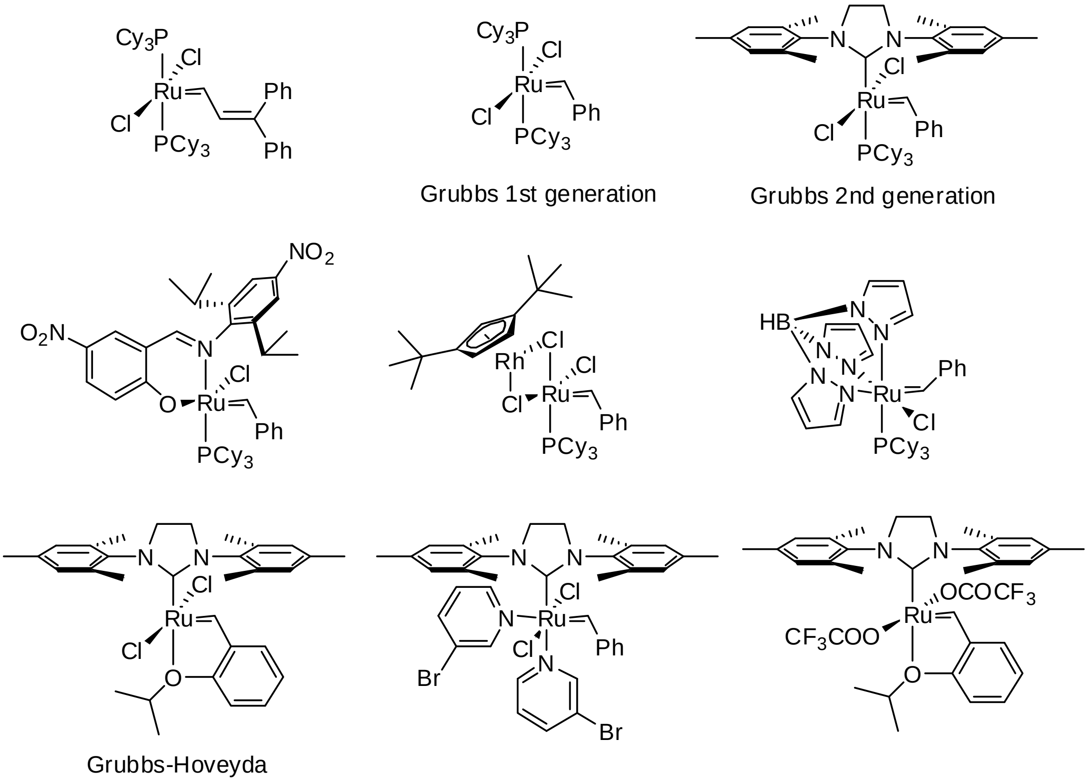
Figure 1

Titanium	Tungsten	Molybdenum	Ruthenium
Acids	Acids	Acids	**Olefins**
Alcohols, Water	Alcohols, Water	Alcohols, Water	Acids
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
Ketones	Ketones	**Olefins**	Aldehydes
Esters, Amides	**Olefins**	Ketons	Ketons
Olefins	Esters, Amides	Esters, Amides	Esters, Amides

↑ Increasing Reactivity

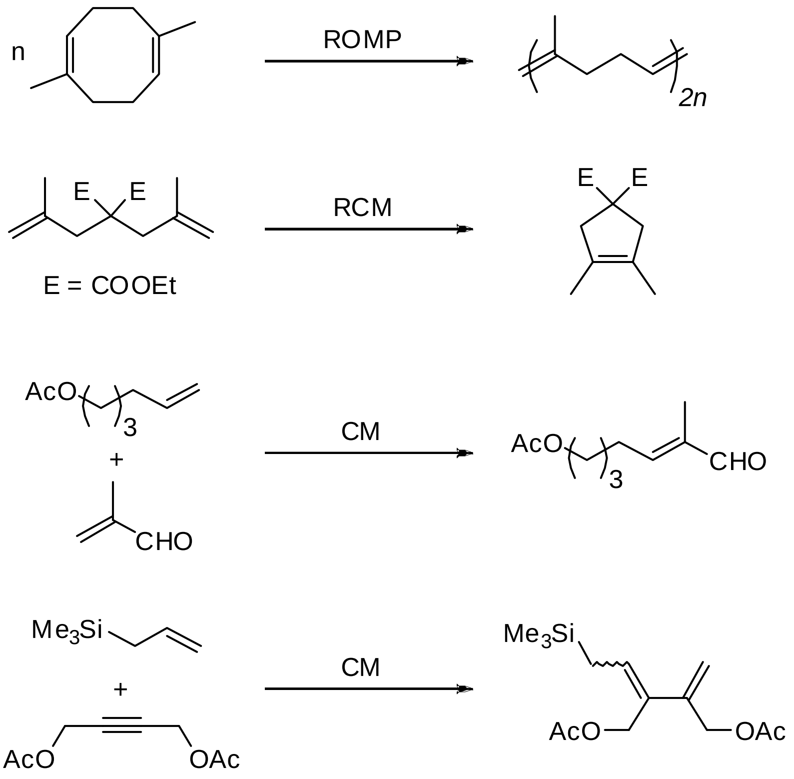
Ruthenium metathesis catalysts have been rapidly developed since the first well-defined alkylidene complex obtained by the reaction of $RuCl_2(PPh_3)_3$ with diphenylcyclopropane[65] and the succeeding benzylidene complexes shown in Chart 4 were synthesized.[66] In particular, the benzylidene complex with two tricyclohexylphosphine (PCy_3) is relatively active to efficiently initiate reactions due to the bulky and strong electron-donating property of the phosphine ligand. Halide ligands also affect the catalyst activity to decrease it as they become larger and less electron-withdrawing in the order Cl > Br >> I. Many benzylidene complexes have been reported after the discovery of $(PCy_3)_2Cl_2Ru{=}CHPh$ (Grubbs 1st generation catalyst), which include phenoxyimine,[67] heterobimetallic,[68] and tris(pyrazolyl)borate complexes,[69] but they are less active than Grubbs 1st generation catalyst.

Chart 4



The chemistry of Ru benzylidene catalysts has been largely developed by adoption of *N*-heterocyclic carbene (NHC) ligand. The complexes with 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene[70] and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[71] were synthesized, and especially the latter one (Grubbs 2nd generation) showed extremely high activity. This complex even remained effective at concentrations as low as 0.05 mol% for ring-closing metathesis (RCM) reactions and 0.0001 mol% for ROMP, and can be used for sterically hindered olefins: e.g., ROMP of trisubstituted cycloolefins such as 1,5-dimethyl-1,5-cyclooctadiene,[72] RCM of sterically demanding olefins to form tri- and tetrasubstituted olefins, cross metathesis (CM) to yield trisubstituted olefins, and CM of olefins with internal alkynes (Scheme 6).[70,71] Highly active Ru catalysts enable the synthesis of macrocyclic olefins via RCM reactions, playing an important role in the field of total synthesis.[73]

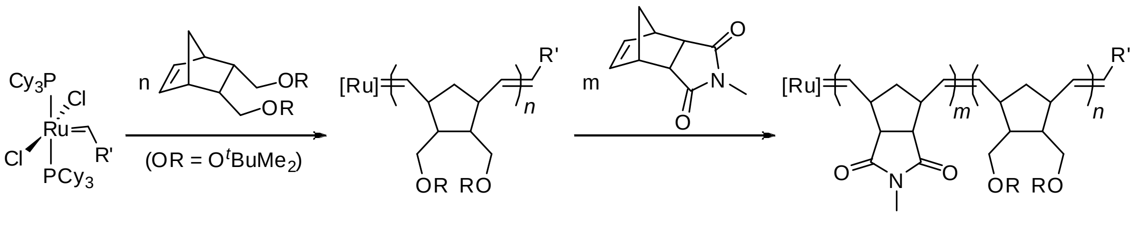
Scheme 6



In 2000, Hoveyda et al. reported a novel Ru benzylidene catalyst having a benzylidene bridged with an isopropoxy group at *ortho* position.[74] This chelate catalyst showed slow initiation reaction, but possessed high stability against heat. It has been applied as a recyclable catalyst recoverable up to 98%. The activity was enhanced by introducing either an NO_2 group on the benzylidene [75] or a biphenylidene[76] moiety instead of benzylidene. This is explained by the activation of oxygen/metal interaction, favoring a faster access to the key 14-electron species in propagation.

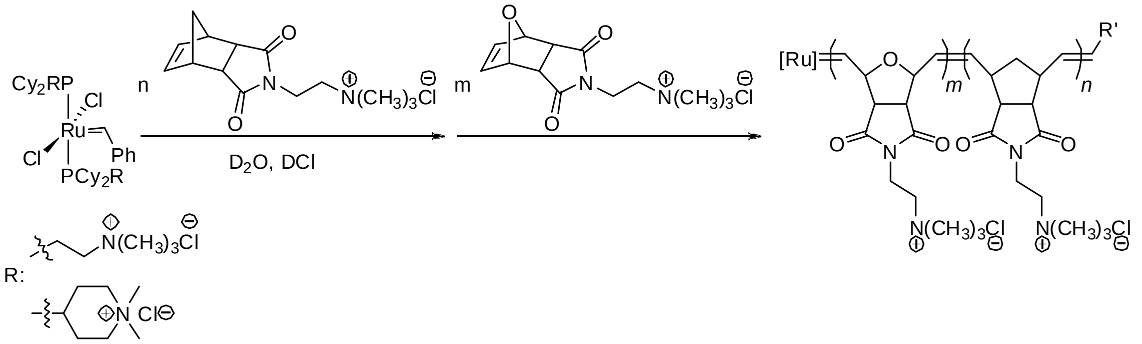
It has been reported that the Ru carbene catalysts shown above display extremely high activity for ROMP and that some of them achieve living polymerization in ROMP. Although Grubbs 1st and 2nd generation catalysts were active in the ROMP of the unsubstituted norbornene, these polymerization did not show living nature, and produced polymers with broad MWD ($M_w/M_n > 2$) because of chain transfer reaction.[77] In contrast, the less reactive norbornene monomers bearing two *tert*-butyldimethylsiloxymethyl and methylimide groups polymerized in a living fashion with these two catalysts, and they produced a block copolymer (Scheme 7).[78] The benzylidene complex bearing two 3-bromopyridine ligands instead of PCy_3 in Grubbs 2nd generation catalyst induced living polymerization of norbornene derivatives, yielding a polymer with narrow MWD ($M_w/M_n \approx 1.05$).[79] The incorporation of CF_3COO in place of Cl ligand in Hoveyda-type catalyst enhanced catalytic activity to accomplish living cyclopolymerization of 1,6-heptadiynes.[80]

Scheme 7



The Ru benzylidene catalysts which possess good tolerance to polar functional groups can be used in water. Complexes containing water-soluble phosphine ligands are generally soluble in water and effect metathesis reaction in water. Although these complexes did not bring about living polymerization, the addition of strong Brønsted acids such as HCl to the polymerization solution prevented catalyst decomposition and eventually enabled the living polymerization of water-soluble norbornenes and the synthesis of block copolymers from them (Scheme 8).[81]

Scheme 8



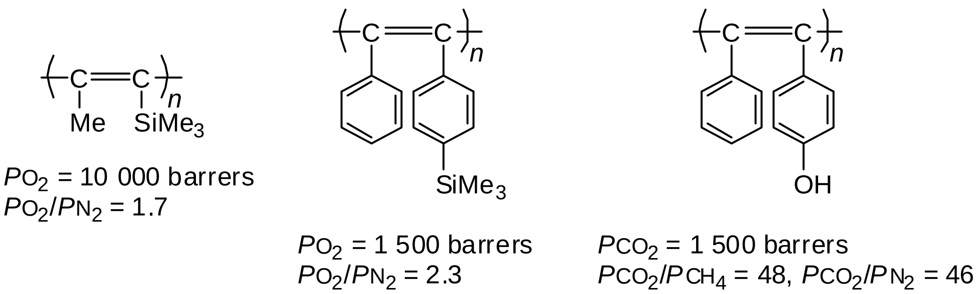
Recently, a variety of functional polymers have been reported. In particular, conjugated polymers including substituted polyacetylenes,[82] poly(phenyleneethynylenes),[83] and poly(phenylenevinylenes)[84] have been extensively studied with respect to their optical and electronic properties based on the conjugated main chain.

Substituted polyacetylenes possessing a variety of pendants and a stiff main chain composed of alternating double bonds exhibit interesting properties such as energy transfer, energy migration, high gas permeability, and formation of helical conformation.[82] While the unsubstituted polyacetylene is insoluble in any organic solvents and easily decomposes in air, substituted polyacetylenes feature excellent solubility, high thermal stability, facile fabrication of membranes, and high gas permeability.

For example, poly(1-trimethylsilyl-1-propyne) (PTMSP) showed extremely high gas permeability, and its oxygen permeation coefficient (P_{O_2}) reached 6000–10000 barrers (Chart 5).[85] Poly[1-pheyl-2-(4-trimethylsilyl)phenyl]acetylene]

(PTMSDPA) also exhibited fairly high gas permeability ($P\mathrm{O}_2$ = 1500 barrers) with relatively high gas separation factor of oxygen and nitrogen ($P\mathrm{O}_2$ /$P\mathrm{N}_2$ = 2.3), which had high thermal stability and its onset temperature (T_0) of weight loss was 420 °C.[86] Hydroxy-containing poly(diphenylacetylene) exhibited outstanding CO_2 permeability as well as excellent separation performance for CO_2 against methane and nitrogen ($P\mathrm{CO}_2$ = 110 barrers; $P\mathrm{CO}_2$/$P\mathrm{CH}_2$ = 48, $P\mathrm{CO}_2$/$P\mathrm{N}_2$ = 46), which can be explained by the increase of solubility of CO_2 in the polymer membranes, resulting from strong interaction between CO_2 molecules and the hydroxyl groups.[87] These polymers are expected to be applied to oxygen-enriching membranes and CO_2 separation membrane.

Chart 5



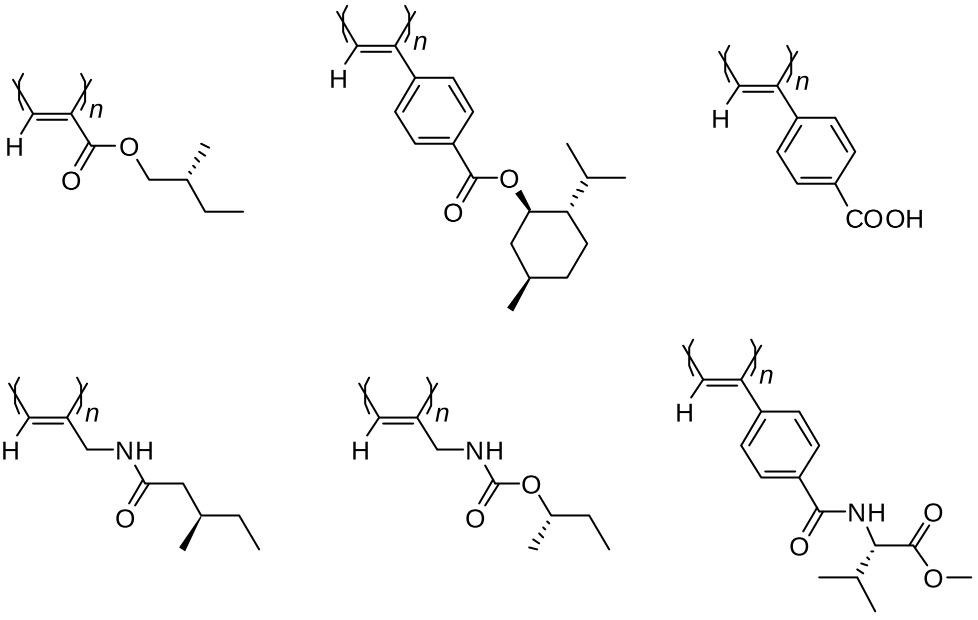
$P\mathrm{O}_2$ = 10 000 barrers
$P\mathrm{O}_2$/$P\mathrm{N}_2$ = 1.7

$P\mathrm{O}_2$ = 1 500 barrers
$P\mathrm{O}_2$/$P\mathrm{N}_2$ = 2.3

$P\mathrm{CO}_2$ = 1 500 barrers
$P\mathrm{CO}_2$/$P\mathrm{CH}_4$ = 48, $P\mathrm{CO}_2$/$P\mathrm{N}_2$ = 46

There are many reports concerning the formation of helical conformation in substituted polyacetylenes (Chart 6). Rh catalysts are capable of producing stereoregular substituted polyacetylenes with all-*cis* or *cis*-rich main chain, which enables the formation of predominantly one-handed helical structure by incorporation of chiral groups into polymer side chains. Among such helical polymers, the examples of helices induced by steric repulsion include poly(propiolic esters)[26b–e] and poly(phenylacetylene) derivatives.[88] In contrast, Masuda and coworkers found in 2001 that helical structure of poly(*N*-propargylamides) was mainly induced by the intramolecular hydrogen bonding between amide groups in the side chain, which was stabilized in relatively low polar solvents including $CHCl_3$ and THF, but destroyed in polar solvents such as MeOH.[25e] After this discovery, several polymers whose helicity stabilized by intramolecular hydrogen bonding were reported: e.g., poly(*N*-propargylamides),[25] poly(*N*-propargylcarbamates),[89] and poly(phenylacetylenes).[90] Furthermore, poly(4-carboxyphenylacetylene) with no chirality formed a preferred-handed conformation upon complexation with chiral primary amines and amino alcohols.[91]

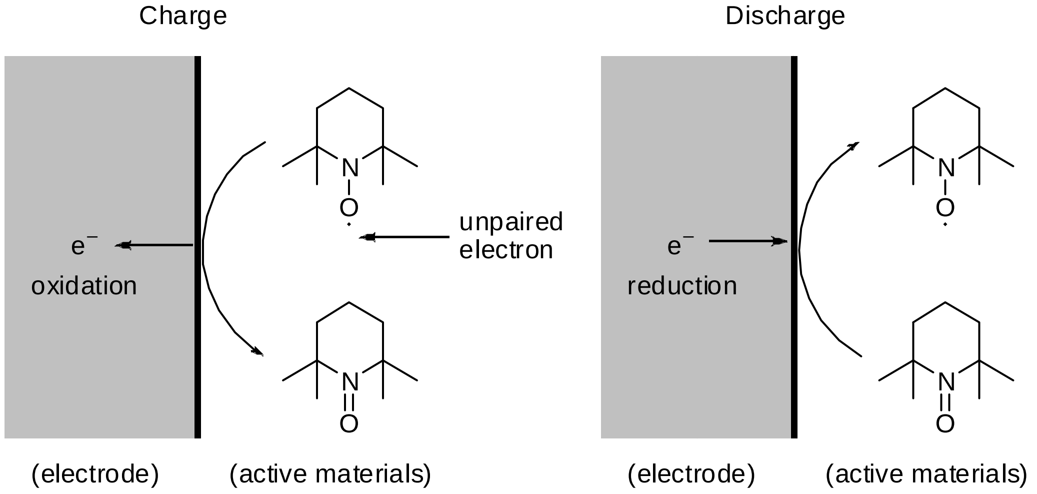
Chart 6.



The organic radical battery, whose electrodes are composed of organic radical materials instead of heavy metals, is now under intensive research, because it does not need precious metals widely used for lithium ion batteries and is environmentally friendly. Electrodes consisting of only organic compounds have been studied since long ago by using conjugated polymers including polyacetylene, polyaniline, polypyrrole, and polyazulene or by applying the dimerization reaction between thiolate and disulfide.[92]

2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and its derivatives are well known as stable nitroxy radicals and have found applications in a variety of fields such as spin labels,[93] scavengers of unstable radical species,[94] and oxidizing agents of alcohols.[95] Polymers carrying stable radicals like TEMPO have been intensively studied in the fields of electron-spin resonance[96] and molecular motion.[97] In recent years, it has been investigated whether TEMPO-containing polymers can be applied to the cathode of organic radical battery that uses the redox reaction of nitroxy radical (Figure 2). Nakahara et al. synthesized poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMA) which can be utilized as a cathode-active material and found that it exhibits a capacity of 77 A h/kg at 3.5 V of discharge voltage.[98] This value corresponded to 77% of its theoretical one, which is attributable to the incomplete polymer reaction to introduce the radical moiety. However, the organic radical battery has a large advantage to charge and discharge in a very short time due to fast redox reaction of nitroxy radicals.

Figure 2



Objective of This Thesis

As described above, substituted polyacetylenes have been attracting attention for their interesting properties and functions. However, the known catalyst systems have limitation; e.g., early transition metal catalysts cannot be used for polar functional group-containing monomers and in polar and protic media, and late transition metals such as Rh can hardly show activity for disubstituted acetylenes. Therefore, it is important to develop catalyst systems that have no limitation for monomers and solvents. The author examined the polymerization of substituted acetylenes with Ru carbene catalysts which possess excellent tolerance for polar functional groups and show high activity for olefin metathesis reactions. Further the general properties (e.g., solubility, thermal stability, and so forth) and functions (e.g., gas permeability, thermochromism based on the change of secondary structure, etc.) were investigated.

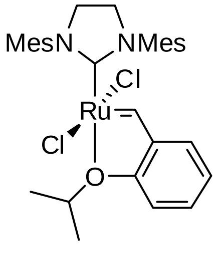
Among functional polymers, free radical-containing polymers gain attention because they can be applied to organic radical battery materials. The synthesis of polyacetylenes and polynorbornenes bearing free radical moieties was studied by using Rh and Ru catalysts, respectively, and the possibility to apply the polymers to the cathode active materials of organic radical battery.

Outline of This Thesis

This thesis is composed of two parts. **Part I** (Chapters 1–5) deals with the synthesis of functional polymers based on substituted polyacetylenes and poly(norbornenes). The activity of ruthenium carbene complexes for the polymerization of substituted acetylenes has been described. The synthesis of polyacetylenes and polynorbornenes bearing functional groups and their gas permeability have also been investigated. **Part II** (Chapters 6–8) concerns the polymerization of radical-containing monomers and the organic radical battery properties of the formed polymers.

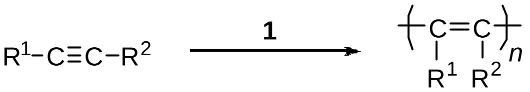
Chapter 1 discusses the polymerization of various mono- and disubstituted acetylenes with Grubbs-Hoveyda catalyst (**1**). Catalyst **1** polymerized hexyl propiolate (**2**) and 1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**3**) to give polymers in moderate yields. The polymerization of monomer **2** provided the corresponding polymer with M_n = 25 500, M_w/M_n = 2.63, and relatively high cis content (75%) at

[M]$_0$/[Ru] = 100 and 80 ºC for 24 h with no solvent. The optimal polymerization conditions examined in this time for the polymerization of monomer **3** were 80 ºC, 24 h, and [M]$_0$/[Ru] = 25 providing poly(**3**) with M_n = 60 700 and M_w/M_n = 2.22. According to UV-vis spectra, the Ru-based poly(**3**) displayed a narrower conjugation than those obtained with conventional catalysts. The ^{13}C NMR spectra in solid and solution states suggested that this polymer had a different geometric structure of main chain from those with other catalysts.



1

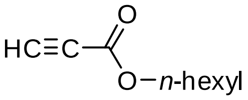
Mes = 2,4,6-trimethylphenyl



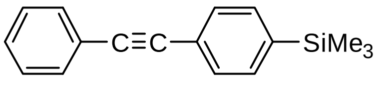
$$\mathrm{R^1{-}C{\equiv}C{-}R^2} \xrightarrow{\mathbf{1}} \left(\underset{\mathrm{R^1}}{\mathrm{C}} = \underset{\mathrm{R^2}}{\mathrm{C}} \right)_n$$

2 or **3**

poly(**2**) or poly(**3**)

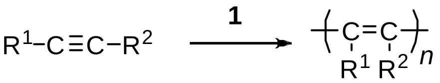


2

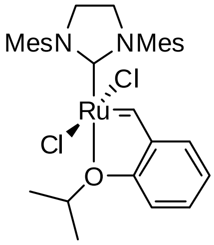


3

Chapter 2 describes the activity of catalyst **1** in the polymerization of various diphenylacetylenes possessing nonpolar and polar groups. Catalyst **1** displayed activity for the polymerization of diphenylacetylene (**4**) and diphenylacetylene derivatives bearing silyl (**3**), siloxy (**5** and **6**), ester (**7** and **8**), amide (**9**–**11**), and carbamate (**12**) groups. The homopolymerization of ester group-carrying monomers

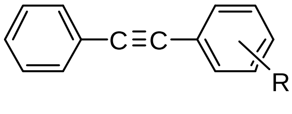


$$\mathrm{R^1{-}C{\equiv}C{-}R^2} \xrightarrow{\mathbf{1}} \left(\underset{\mathrm{R^1}}{\mathrm{C}} = \underset{\mathrm{R^2}}{\mathrm{C}} \right)_n$$

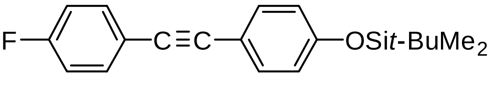


1

Mes = 2,4,6-trimethylphenyl



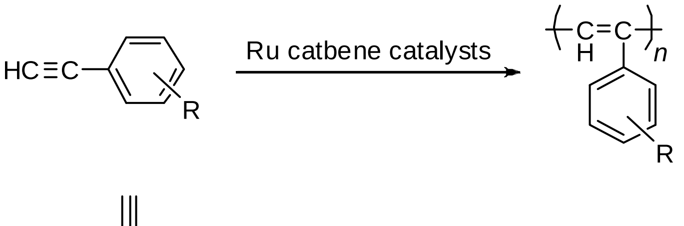
3: R = p-SiMe$_3$
4: R = H
5: R = p-OSit-BuMe$_2$
7: R = p-COOEt
8: R = m-COOEt
9: R = p-CONHC$_7$H$_{15}$
10: R = m-CONHC$_7$H$_{15}$
11: R = m-NHCOC$_7$H$_{15}$
12: R = p-NHCOOt-Bu

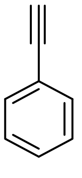


6

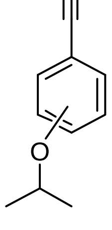
6 and **7** hardly proceeded, whereas these monomers copolymerized with nonpolar monomer **3** to give the copolymers whose content of ester groups was larger than that of the monomer feed ratio. The oxygen permeability of the Ru-based poly(**6**) ($P\mathrm{O}_2$ = 180 barrers) was higher than that of the Ta-based poly(**6**) ($P\mathrm{O}_2$ = 100 barrers), and the same tendency was observed with all other gases. This is attributed to the more twisted main chain of Ru-based polymer to prevent packing of its side chains more than in the Ta-based polymer.

Chapter 3 delineates the relationship between the activity of Ru carbene catalyst and the structure of phenylacetylenes as monomers (**13**–**17**). Phenylacetylene (**13**) did not polymerize with any ruthenium catalysts, whereas *o*-isopropoxyphenylacetylene (**14**) did in a moderate yield. No polymer was obtained from *m*- and *p*-isopropoxyphenylacetylenes (**15** and **16**). It is assumed that the isopropoxy group at the *ortho* position coordinates to the Ru center to prohibit the decomposition of active species. The UV-vis spectrum of the Ru-based poly(**14**) appeared similarly to that of the W-based one, but quite differently from that of the Rh-based one. The CD spectroscopic analysis revealed that the Ru-based *trans*-rich poly(phenylacetylene) derivative bearing chiral groups [poly(**17**) and poly(**18**)] took a helical conformation with predominantly one-handed screw sense.

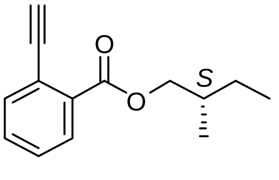




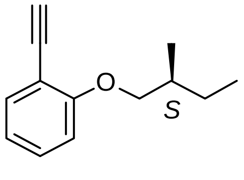
13



14: *ortho*
15: *meta*
16: *para*

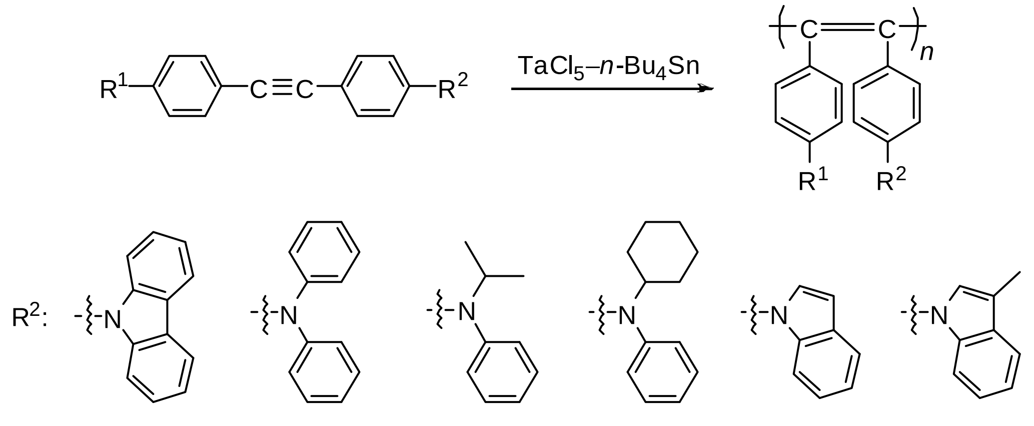


17



18

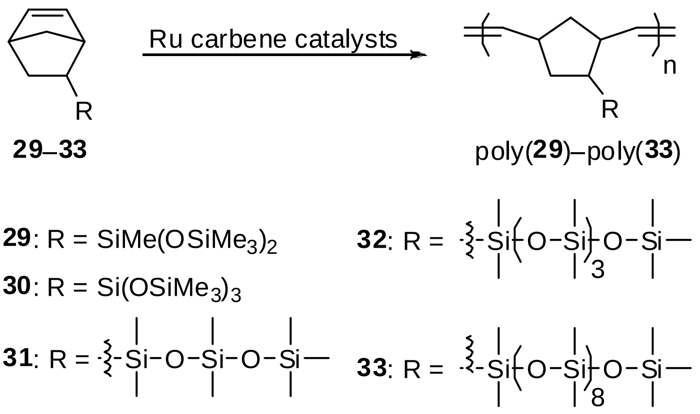
Chapter 4 deals with the synthesis of nitrogen-containing poly(diphenylacetylenes), their permeability and other properties. Diphenylacetylene derivatives possessing *tert*-amine moieties such as *N*-substituted carbazole (**19** and **25**), triphenylamine (**20** and **26**), and indole (**23**, **24**, **27**, and **28**) polymerized with TaCl$_5$–n-Bu$_4$Sn (1:2) to provide the corresponding polymers in moderate to high yields. However, isopropylphenylamine and cyclohexylphenylamine-carrying monomers (**21** and **22**) hardly polymerized due to their relatively high basicity of amine moieties. A polymer with high molecular weight was obtained from monomer carrying diphenylamine (**20**), and the free-standing membranes of these polymers were fabricated by casting toluene solution of these polymers. Although their permeability was not so high, the permselectivity of CO$_2$ was relatively high. The increment of molar absorptivity (ε) of poly(**20**) and poly(**26**) at ~ 700 nm was observed with increasing applied voltage in the UV-Vis spectrum.



R^1 = H	**19**	**20**	**21**	**22**	**23**	**24**
R^1 = SiMe$_3$	**25**	**26**			**27**	**28**

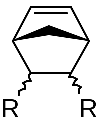
In **Chapter 5**, the synthesis of polynorbornenes bearing oligomeric siloxane moieties and their properties including gas permeability and thermal properties were examined. The ROMP of norbornenes having various length of oligomeric siloxane was carried out in the presence of ruthenium carbene catalysts. Polymers were obtained in high yields, and their onset temperatures of weight loss (T_0) were

180–250 °C. The glass transition temperatures (T_g) of poly(**31**)–poly(**33**) bearing linear siloxane linkages were much lower (–115 ~ –23 °C), and decreased with increasing length of the siloxane linkages. The ROMP-polymers, poly(**29**) and poly(**30**), could be hydrogenated completely, and the hydrogenated polymers had lower T_g values than those of precursor ROMP polymers. The free-standing membranes of poly(**30**) possessing branched siloxane group showed high gas permeability, which is the most permeable to various gases among ROMP-polynorbornene derivatives reported so far.

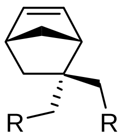


Chapter 6 delineates the synthesis and charge/discharge properties of TEMPO-containing polynorbornenes. Polymerization of norbornene monomers (**34**–**41**) proceeded smoothly in the presence of Grubbs-Hoveyda 2nd generation catalyst. The resulting polymers were thermally stable up to ca. 240 °C according to the TGA measurements. All polymers obtained in this chapter could be applied to cathode materials of the organic radical battery. Concerning isomers including *endo* and *exo*, poly(**34**)–poly(**36**), the charge/discharge capacities of the polymer-based cells increased with an increment in the distance between the two TEMPO radical moieties along the polymer backbone. The capacity of the poly(**35**)-based cell reached its theoretical value (109 A h/kg) and a large capacity (>90 A h/kg) was retained even at high current densities up to 6 A/g. The deterioration of charge capacity in

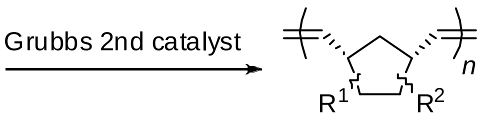
poly(**35**)-based cell was hardly observed even after 500 cycles.



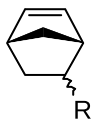
34: R = COOTEMPO (*exo*,*exo*)
35: R = COOTEMPO (*endo*,*exo*)
36: R = COOTEMPO (*endo*,*endo*)
37: R = $CH_2OCOTEMPO$ (*exo*,*exo*)
38: R = $CH_2OCOTEMPO$ (*endo*,*endo*)



39: R = $CH_2OCOTEMPO$

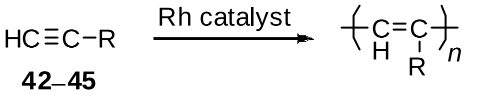


poly(**34**)–poly(**41**)



40: R = COOTEMPO (*endo* and *exo* mixture)
41: R = $CH_2OCOTEMPO$ (*endo* and *exo* mixture)

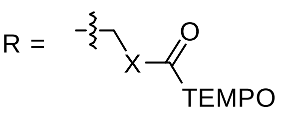
Chapter 7 concerns the polymerization of acetylenic monomers **42**–**45** having TEMPO moieties and the application of the formed polymers to the organic radical battery. Propargylamide, propiolic ester, and phenylacetylene derivatives carrying TEMPO radicals polymerized with Rh catalyst in good to high yields. All the TEMPO-containing polymers demonstrated reversible charge/discharge processes, whose discharge capacities were 21.3–108 A h kg^{-1}. In particular, the capacity of a poly(**44**)-based cell reached their theoretical value.



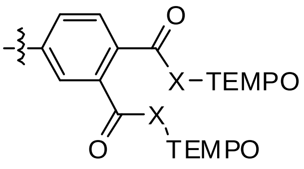
$$HC\equiv C{-}R \xrightarrow{\text{Rh catalyst}} \left(\underset{H}{C}{=}\underset{R}{C}\right)_n$$

42–**45**

poly(**42**)–poly(**45**)

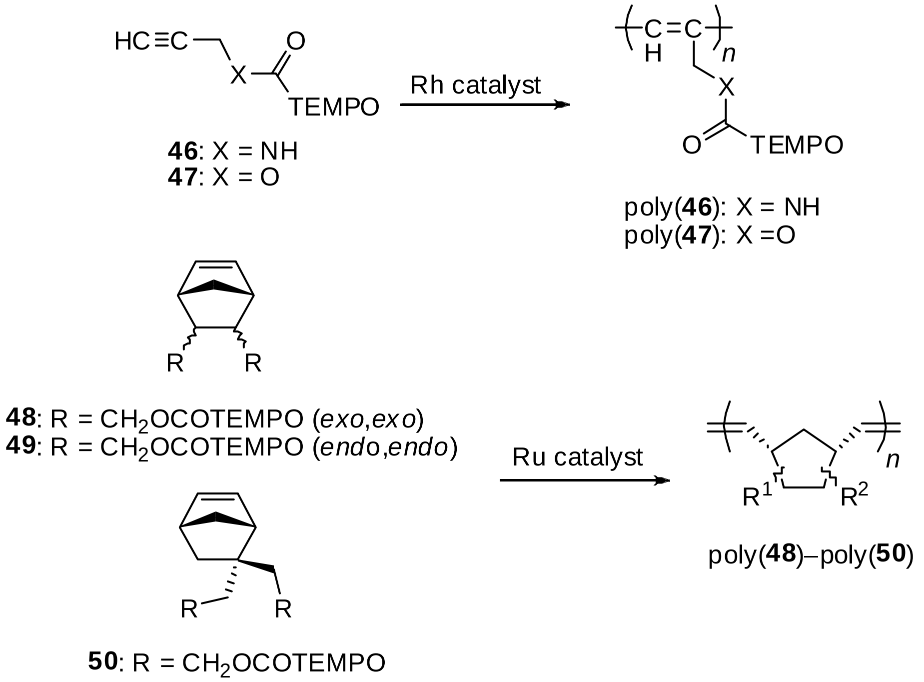


42: X = NH
43: X = O



44: X = NH
45: X = O

In **Chapter 8**, PROXY-containing polyacetylenes and polynorbornenes was synthesized and their charge/discharge properties were investigated. Acetylenic and norbornene monomers **46**–**50** polymerized with Rh and Ru catalyst in good to high yields, respectively, to afford novel polymers containing the PROXY radical at high densities. All the polymers demonstrated the reversible charge/discharge processes, whose capacities were larger than 85 A h/kg. In particular, the maximum capacity of poly(**47**)- and poly(**48**)-based cells reached nearly their theoretical capacity values.



In conclusion, this thesis has delineated the synthetic methodologies of functional polymers such as substituted polyacetylenes and polynorbornenes and their properties and functions. The author studied the activity of ruthenium carbene complexes for the polymerization of substituted acetylenes. The polymerization of substituted acetylenes and norbornenes with various catalysts including ruthenium, rhodium and tantalum were also examined in order to develop functional polymers. Polymer properties including solubility and thermal stability and functions such as gas separation and organic radical battery were investigated. The author hopes that the present thesis will contribute to the synthetic strategy of functional polymers and development of their functions such as gas separation and organic radical battery.

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Part I

Polymerization of Substituted Acetylenes and Norbornenes with Ru Carbene and Other Catalyst

Chapter 1

Polymerization of Substituted Acetylenes by the Grubbs-Hoveyda Carbene Catalyst

Abstract

Polymerization of various mono- and disubstituted acetylenes was investigated by using Grubbs-Hoveyda catalyst (**1**). Hexyl propiolate (**2**) and 1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**3**) polymerized in moderate yields. Bulk polymerization of **2** at $[M]_0/[Ru] = 100$ and 80 ºC for 24 h afforded poly(**2**) having $M_n = 25\ 500$ and $M_w/M_n = 2.63$. This polymer possessed relatively high cis content (75%) according to NMR. Monomer **3** polymerized in bulk to yield poly(**3**) with $M_n = 60\ 700$, $M_w/M_n = 2.22$ under conditions of 80 ºC, 24 h, $[M]_0/[Ru] = 25$. The Ru-based poly(**3**) displayed a narrower conjugation than those obtained with other catalysts. The ^{13}C NMR spectra of this polymer in solid and solution states showed quite different signal patterns from those with conventional catalysts, suggesting a different geometric structure of main chain.

Introduction

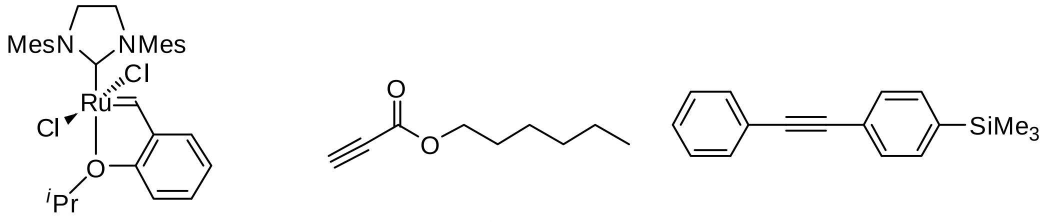
Substituted polyacetylenes have been gathering much attention due to their potential applications to material-separation membranes, and optoelectronic and related fields.[1] These polymers have been obtained by polymerization of corresponding acetylenic monomers in the presence of transition metal catalysts. Catalysts including group 5 and 6 transition metal and Rh have traditionally been employed to induce their polymerization. Among them, halides of early transition metals such as $TaCl_5$, $NbCl_5$, $MoCl_5$, and WCl_6 in conjunction with organometallic cocatalysts polymerize various mono- and disubstituted acetylenes to give high molecular weight polymers in good yield. Some well-defined Ta, Mo, and W carbenes, so-called Schrock carbenes, induce living polymerization of substituted acetylenes.[2] This implies that the group 5 and 6 transition metal-catalyzed polymerization proceeds by the metathesis mechanism. One of the drawbacks of the early transition metal is that they are readily deactivated by polar groups in the monomer and polymerization solvents because of their high oxophilicity.

Another type of catalysts frequently used for the polymerization of substituted acetylenes are rhodium (Rh) catalysts. Rh catalysts can polymerize only monosubstituted acetylenes such as phenylacetylene and its ring-substituted derivatives,[3] *N*-propargylamides,[4] and propiolic esters.[5] The Rh-catalyzed polymerization proceeds by the insertion mechanism, and features excellent tolerance to polar substituents in the monomer[6] and protic solvents[7]. The Rh-based polymers generally possess high cis stereo-regularity, which is indispensable for the formation of helical structures of poly(*N*-propargylamide)s.[4]

A huge number of studies on the synthesis and catalysis of ruthenium (Ru) carbene complexes have been reported in these several years. Ru carbene complexes represented by Grubbs' first- and second-generation catalysts exhibit high activity in olefin metathesis reactions such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), cross metathesis (CM).[8] Compared to early transition metal-based metathesis catalysts, Ru carbene complexes display tolerance against protic functional groups in these metathesis reactions as well as considerable stability to oxygen and moisture. It should also be noted that many Ru complexes have well-defined carbene structures, which enables to directly generate carbene-type active species without adding cocatalysts. The Grubbs' second-generation complex reportedly reacts with diphenylacetylene stoichiometrically to afford η^3-vinylcarbene complex, which is regarded as an intermediate of the polymerization of acetylenes.[9] Ru-catalyzed polymerizations of acetylene[10] and diyne compounds[11] have recently been reported. Though an Ru carbene complex bearing 3-bromopyridine polymerizes not only acetylene but also its several derivatives, the substituted polyacetylenes formed have not been mentioned in detail.[10] Buchmeiser and coworkers developed living polymerization systems by using diethyl dipropargylmalonate as monomer and mainly Ru carbenes containing trifluoroacetate ligands as catalysts.[11] These facts prompted the author to examine the polymerization of various mono- and disubstituted acetylenes by an active Ru carbene catalyst.

This chapter describes on the polymerization of the substituted acetylenes using the Grubbs-Hoveyda Ru carbene (**1**)[12] which is one of the most active Ru catalysts in metathesis reactions (Chart). Hexyl propiolate (**2**), 1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**3**), phenylacetylene, 1-octyne, etc. were used as monomers. Among these monomers, **2** and **3** afforded polymers in moderate yields in bulk polymerization. The geometric structure and properties of poly(**2**) and poly(**3**) were elucidated by NMR and other analytical methods.

Chart. Catalyst and Monomers.



Grubbs-Hoveyda catalyst **1**
(Mes = 2,4,6-trimethylphenyl)

2

3

Results and Discussion

Polymerization of Monomer 2. Bulk polymerization of monomer **2** was at first studied in detail (Table 1). The effect of polymerization temperature was examined keeping at $[M]_0/[cat] = 100$ and time = 24 h. At 60 ºC, polymer was obtained in 12% yield, whose M_n was 43 400 (run 1). With increasing temperature, the polymer yield tended to increase, while the M_n of polymer decreased. Thus, the polymer yield increased to 24% at 80 ºC, while only methanol-soluble oligomers formed at 120 ºC (runs 2, 3). Next, the $[M]_0/[cat]$ ratio was varied while keeping the polymerization temperature at 80 ºC. Even though $[M]_0/[cat]$ ratio was increased to 200, no significant difference was observed in polymer yield and molecular weight (run 6). On the other hand, decreases in the $[M]_0/[cat]$ ratio resulted in lower yields and M_n's (runs 4, 5). This suggests that methanol-soluble oligomers are mainly formed at high catalyst concentrations. The polymerization seems to level off after a certain period of time, because the polymer yield did not obviously increase even after 7 days (run 7).

Table 1. Bulk Polymerization of 2 by Catalyst 1

				polymer[a]		
run	temperature, °C	$[M]_0/[Ru]$	time, h	yield, %	M_n[b]	M_w/M_n[b]
1	60	100	24	12	43 400	2.48
2	80	100	24	24	25 500	2.63
3	120	100	24	0	(1 900)[c]	(1.11)[c]
4	80	25	24	0	(1 500)[c]	(1.05)[c]
5	80	50	24	5	20 900	1.86
6	80	200	24	23	21 500	2.65
7	80	200	168	28	23 800	2.35

[a] Methanol-insoluble part. [b] Measured by GPC. [c] Methanol-soluble part.

Table 2. Solution Polymerization of 2 by Catalyst 1[a]

run	temperature, °C	polymer[b]		
		yield, %	M_n[c]	M_w/M_n[c]
1	50	0	—	—
2	55	trace	—	—
3	60	6	1 400 000 (14%)[d] 32 900 (86%)[d]	1.15 1.87
4	65	4	41 000	3.47
5	70	13	37 500	2.61
6	80	18	19 900	2.60
7	90	0	—	—

[a] Polymerized in toluene for 24 h; [Ru] = 10 mM, $[M]_0$ = 0.50 M. [b] Methanol-insoluble part. [c] Measured by GPC. [d] Peak area ratio in GPC.

Solution polymerization catalyzed by **1** proceeded with monomer **2.** Among toluene, THF, 1,2-dichloroethane, acetonitrile, ethyl acetate, and DMSO as polymerization solvents, toluene usually achieved the highest polymer yields. Detailed results using toluene as solvents are shown in Table 2. Whereas only trace or no polymer was obtained at 55 ºC and below in toluene (runs 1, 2), polymerization proceed at 60 ºC to give in 6% yield a polymer having bimodal molecular weight distribution (M_n = 1 400 000 and 32 900, run 3). The polymer yield was improved by raising the polymerization temperature, while an adverse effect was observed for molecular weight. With increasing temperature, the bimodal peak in GPC chart changed into a single peak bearing a shoulder with wide polydispersity at 65 ºC and a unimodal peak at 70 ºC (runs 4, 5). The polymer yield increased to 18% at 80 ºC (run 6) as in bulk polymerization, while no methanol-insoluble polymer was obtained at 90 ºC (run 7).

Structure and Properties of Poly(2). It has been reported that monomer **2**

can be polymerized by Rh, Mo, W catalyst systems and that the formed polymers possess different geometric structures depending on the catalysts used.[5e] More specifically, the poly(propiolic ester)s obtained with Rh catalysts have high cis contents, while trans-rich polymers are obtained with Mo and W catalysts. Actually poly(**2**) samples were prepared in this study by using $[(nbd)RhCl]_2$, $MoOCl_4/n\text{-}Bu_4Sn$, and $WOCl_4/n\text{-}Bu_4Sn$ to compare the geometric structure with that obtained with Ru catalyst **1** (Table 3), and the ^{1}H NMR spectra of the poly(**2**)s were depicted in Figure 1. In general, it is known that the polymerization of monosubstituted acetylenes using Rh catalysts provide the cis-transoidal polyacetylenes.[13] The poly(**2**) formed with catalyst **1** had relatively high cis content comparable to the Rh-based polymer (runs 1, 4), while those with Mo and W catalysts had much lower *cis* contents (runs 2, 3). It is noteworthy that, although the polymerizations with Ru, W, and Mo catalysts should all proceed via the metathesis mechanism, the *cis* content of the Ru-based polymer was

Table 3. Polymerization of 2 by Various Catalysts

		polymer[d]			
run	catalyst	yield, %	M_n[e]	M_w/M_n[e]	*cis* content, %[f]
1[a]	$[(nbd)RhCl]_2$	36	237 000 (88%)[g] 8 800 (12%)[g]	2.34 1.20	83
2[b]	$MoOCl_4/n\text{-}Bu_4Sn$	45	9 900	1.53	—[h]
3[b]	$WOCl_4/n\text{-}Bu_4Sn$	35	4 500	1.30	—[h]
4[c]	**1**	24	25 500	2.63	75

[a] In CH_3CN at 30 ºC for 24 h; [Rh] = 10 mM, $[M]_0$ = 1.0 M. [b] In toluene at 60 ºC for 24 h; [Cat] = 20 mM, [n-Bu_4Sn] = 20 mM, $[M]_0$ = 0.50 M. [c] At 80 ºC for 24 h; neat, $[M]_0/[Ru]$ = 100. [d] Methanol-insoluble part. [e] Measured by GPC. [f] Determined by ^{1}H NMR (in $CHCl_3$, at 50 ºC). [g] Peak area ratio in GPC measurement. [h] The signals of the main-chain olefinic proton were too broad and small; the *cis* contents are assumed to be lower than 60 %.

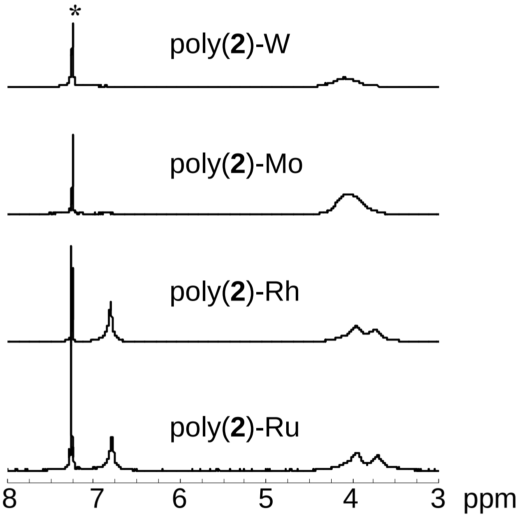


Figure 1. ^{1}H NMR spectra of poly(**2**)s obtained with various catalysts (samples from Table 3; measured in $CDCl_3$ at 50 ºC). Asterisked peaks are due to impurities.

significantly higher than those of W- and Mo-based counterparts. This difference may be accounted for by the presence of bulky ligands in Ru catalyst **1**, which should control the geometric structure more strongly.

Polymerization of Monomer 3. Although the polymerization of monomer **3** did not proceed in any of toluene, THF, 1,2-dichloroethene, acetonitrile, ethyl acetate, and DMSO as solvents, its bulk polymerization took place, and so it was examined under various conditions (Table 4). When $[M]_0/[Ru] = 100$, polymer was hardly obtained at 60 ºC, while polymer with $M_n = 96\ 900$ was formed in 16% yield at 80 ºC (run 2). With increasing temperature to 120 ºC, the polymer yield did not change, but the molecular weight decreased to 12 300 (run 3). This is a similar tendency to the case of monomer **2**, and the optimal polymerization temperature is concluded to be 80 ºC. When the $[M]_0/[Ru]$ ratio was varied with keeping the polymerization temperature at 80 ºC, the polymer yield improved to 42% at $[M]_0/[Ru] = 25$ (run 5). When the polymerization time was extended to 7 days at $[M]_0/[Ru] = 100$ and 200, the polymer yield increased up to 48% and 39%, respectively (runs 8, 9).

The time course of the polymerization of monomer **3** by **1** is shown in Figure

2. Both monomer conversion and polymer yield leveled off after 24 h. The M_n reached 99 000 in 1 h and then somewhat decreased, while the polydispersity slightly increased.

Table 4. Bulk Polymerization of 3 by Catalyst 1[a]

				polymer[b]		
run	temperature, ˚C	$[M]_0/[Ru]$	time, day	yield, %	M_n[c]	M_w/M_n[c]
1	60	100	1	trace	—	—
2	80	100	1	16	96 900	2.56
3	120	100	1	16	12 300	2.15
4	80	10	1	25	26 100	2.05
5	80	25	1	42	60 700	2.22
6	80	50	1	35	95 500	1.91
7	80	200	1	10	107 400	2.39
8	80	100	7	48	83 300	1.98
9	80	200	7	39	92 400	2.01

[a] For 24 h. [b] Methanol-insoluble part. [c] Measured by GPC.

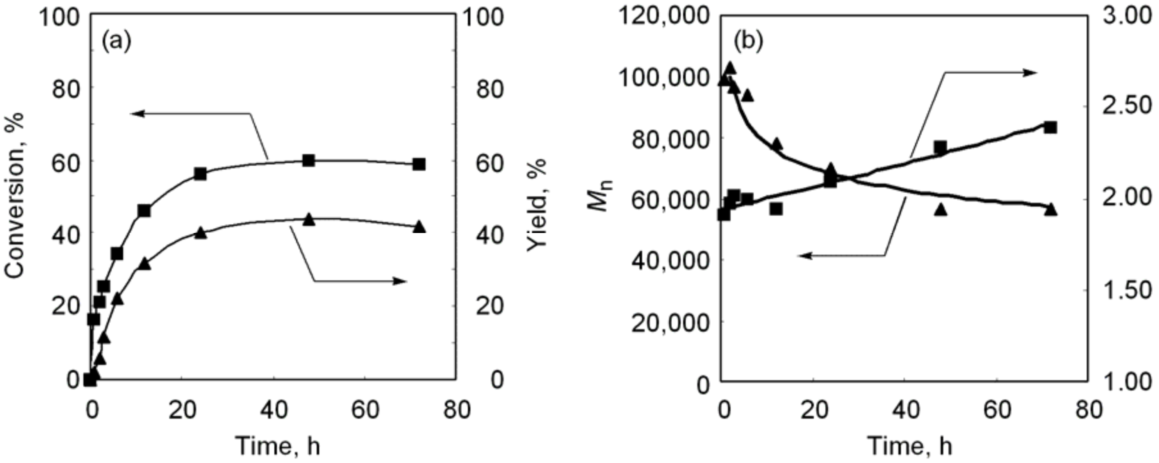


Figure 2. Time profile of the bulk polymerization of monomer **3** by **1**. (polymerized in toluene at 80 °C; $[M]_0/[Ru] = 25$; the polymer yield denotes the yield of methanol-insoluble part.)

Table 5. Polymerization of 3 and DPA by Various Catalysts

			polymer[d]			
run	monomer	catalyst	yield, %	M_n[e]	M_w/M_n[e]	color
1[a]	**3**	$TaCl_5$/*n*-Bu_4Sn	80	70 200	3.14	orange-yellow
2[a]	**3**	$MoCl_5/Ph_4Sn$	21	48 900	10.5	dark yellow
3[a]	**3**	WCl_6/Ph_4Sn	29	11 200	2.31	bright yellow
4[b]	**3**	**1**	42	60 700	2.22	white
5[a]	DPA	$TaCl_5$/*n*-Bu_4Sn	47	insoluble[f]	—	yellow
6[c]	DPA	**1**	22	insoluble[f]	—	white

[a] In toluene at 80 ºC for 24 h; [Cat] = 20 mM, [Sn] = 40 mM, $[M]_0$ = 0.20 M. [b] At 80 ºC for 24 h; neat, $[M]_0$/[Ru] = 25. [c] At 80 ºC for 24 h; neat, $[M]_0$/[Ru] = 100. [d] Methanol-insoluble part. [e] Measured by GPC. [f] Insoluble in any organic solvents including $CHCl_3$, toluene, and THF.

Structure and Properties of Poly(3). Poly(**3**) samples were synthesized by using various catalysts to study the polymer structure; the results of the polymerizations are shown in Table 5.[14] Whereas the Ta-, Mo-, and W-based polymers had colors of yellow to orange-yellow, only the Ru-based samples was virtually white in the powdery state. For the sake of comparison, poly(DPA) (DPA: diphenylacetylene) samples were also prepared, as is listed in Table 5.

Figure 3 shows the IR spectra of monomer **3** and the four poly(**3**) samples. A peak at 1530 cm^{-1} which is absent in the spectrum of monomer **3** appears in those of poly(**3**)s. This peak is assignable to the stretching vibration of alternating C=C bonds in the main-chain which are generated by polymerization of the acetylene moiety. Slight differences are seen in the ranges of 500–700, 900–1100 and 1300–1750 cm^{-1} in the four spectra of poly(**3**)s, which appears to reflect differences in the structure of the polymers.

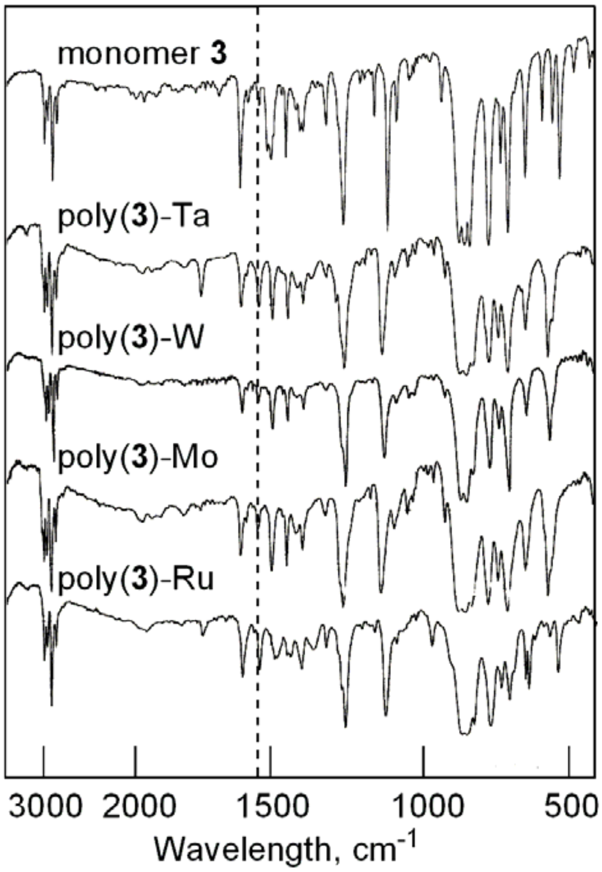


Figure 3. ^{13}C NMR spectra of poly(**3**)s obtained with various catalysts (samples from Table 5; measured in $CDCl_3$ at room temperature).

As seen in Figure 4, the ^{13}C NMR spectra of Ta-, W-, and Mo-based poly(**3**)s in $CDCl_3$ solution display seven peaks in the C_{sp2} region; i.e. sharp peaks at 126, 127 and 128 ppm, a large peak with a shoulder at 131 ppm, a small peak at 136 ppm and two sharp peaks at 144 and 146 ppm. These spectra are very similar to one another. On the other hand, the spectrum of the Ru-based poly(**3**) is quite different from those of the other three polymers. This indicates that the Ru-based polymer has a different structure from those of the other polymers, but the detailed difference is not clear from these spectra.

Whereas the UV/vis spectra of poly(**3**)s obtained with the conventional catalysts display two peaks around 375 and 435 nm, that of the polymer with catalyst **1** possessed only one peak at 290 nm (Figure 5a). This indicates that the conjugation

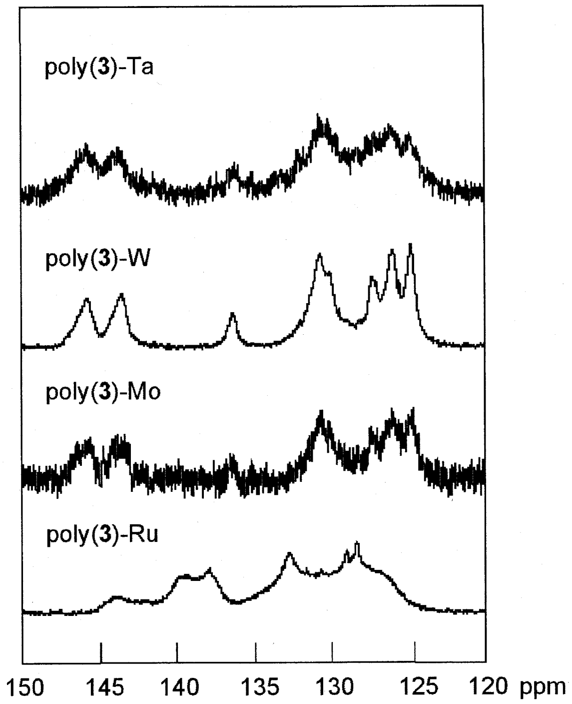


Figure 4. ^{13}C NMR spectra of poly(**3**)s obtained with various catalysts (samples from Table 5; measured in $CDCl_3$ at room temperature).

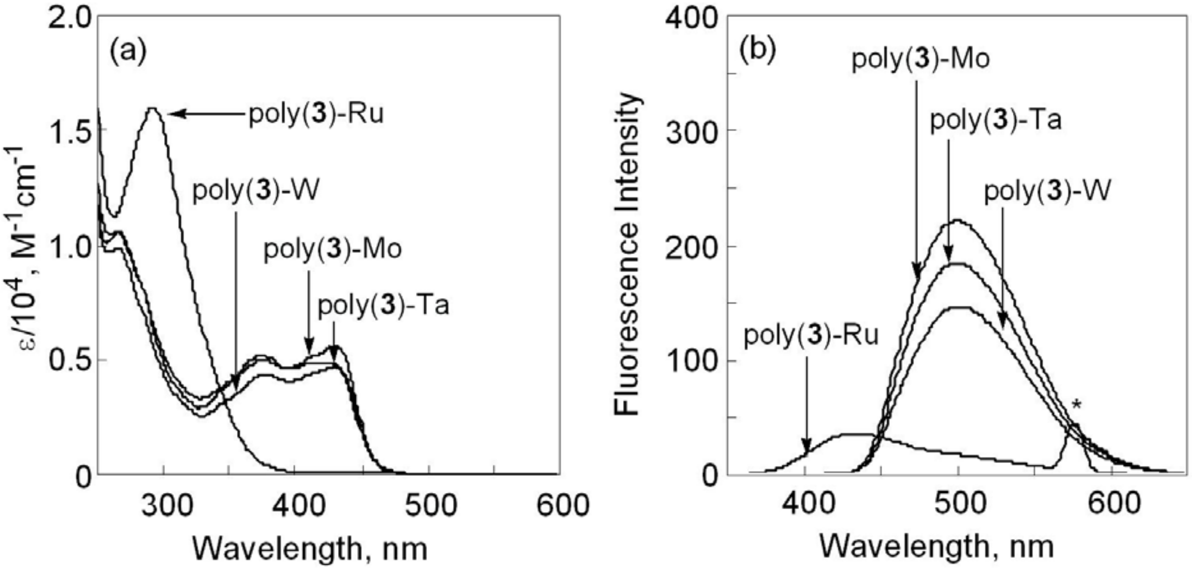


Figure 5. (a) UV-vis spectra of poly(**3**)s obtained with various catalysts (samples from Table 5; measured in $CHCl_3$, $c = 1.0\times10^{-4}$ M). (b) Fluorescence spectra of poly(**3**)s obtained with various catalysts (samples from Table 5; measured in $CHCl_3$; excited at 292 nm (Ru), 374.5 nm (Mo), or 376 nm (Ta, W); $c = 1.0 \times 10^{-5}$ M). Asterisked is an optical ghost peak.

length of the latter polymer is much shorter than those of the former polymers. The fluorescence spectra of poly(**3**)s exited at their absorption maxima were shown in Figure 5b. The fluorescence spectra of the former three polymers are similar to one another, while that with catalyst **1** is quite different.

The TGA curves of these poly(**3**)s measured in air are more or less different from one another. According the onset temperature (T_0) of weight loss, the polymers with Ta and Mo (~450 ºC) are more stable than those with Ru and W (~350 ºC) (Figure 6). Furthermore, the Ru-based polymer loses weight steeply with increasing temperature. While the rather low T_0 of the Ru-based polymer should be due to the difference in polymer structure from other polymers, that of the W-based polymer may stem from its low molecular weight. The residue at around 700 ºC is attributed to SiO_2 whose weight is theoretically 24% of the polymer.

All of the poly(**3**) samples were totally soluble in toluene, THF, and chloroform (Table 6). Among these samples, some differences were observed; the Ta-based polymer was insoluble in hexane, the Mo-based one was partly soluble, and the W- and Ru-based ones were completely soluble.

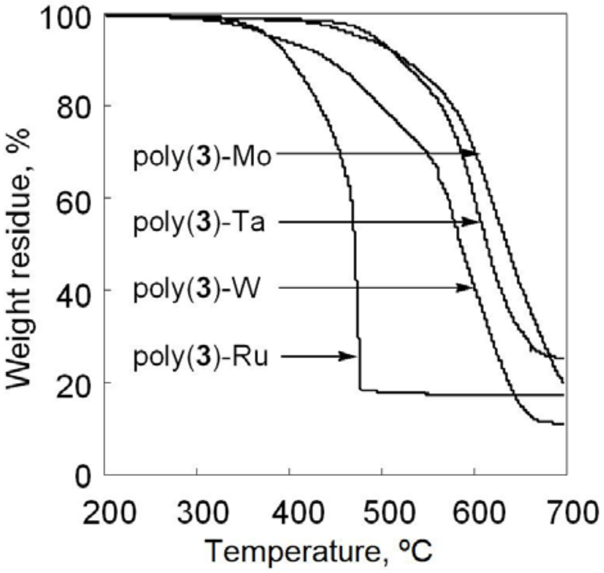


Figure 6. TGA curves of poly(**3**)s obtained with various catalysts (samples from Table 5; measured in air; heating rate 10 °C/min).

Table 6. Solubility of Poly(3) Obtained with Various Catalysts

	poly(**3**)			
solvent	$TaCl_5$/*n*-Bu_4Sn	$MoCl_5/Ph_4Sn$	WCl_6/Ph_4Sn	Ru cat. (**1**)
DMSO	–	–	–	–
DMF	–	±	±	±
acetone	–	±	±	±
CH_2Cl_2	+	+	+	+
THF	+	+	+	+
o-dichlorobenzene	+	+	+	+
chlorobenzene	+	+	+	+
$CHCl_3$	+	+	+	+
anisole	+	±	+	+
Et_2O	+	+	+	+
benzene	+	+	+	+
toluene	+	+	+	+
CCl_4	+	+	+	+
cyclohexane	+	+	+	+
hexane	–	±	+	+

+: soluble; ±: partly soluble; –: insoluble.

Solid-State ^{13}C NMR. The solid-state ^{13}C NMR spectra of a series of poly(**3**)s were measured in order to gain more detailed information about polymer structure. The spectra of poly(DPA)s synthesized with both $TaCl_5$/*n*-Bu_4Sn and Ru catalyst **1** were also studied for comparison because poly(DPA) is not accompanied by the problem of head-to-tail and head-to-head. Figure 7 exhibits the 110–160 ppm region of the ^{13}C CP/MAS spectra of poly(**3**)s and poly(DPA)s. The spectra of poly(**3**) and poly(DPA) obtained with the Ta catalyst resemble each other. The same

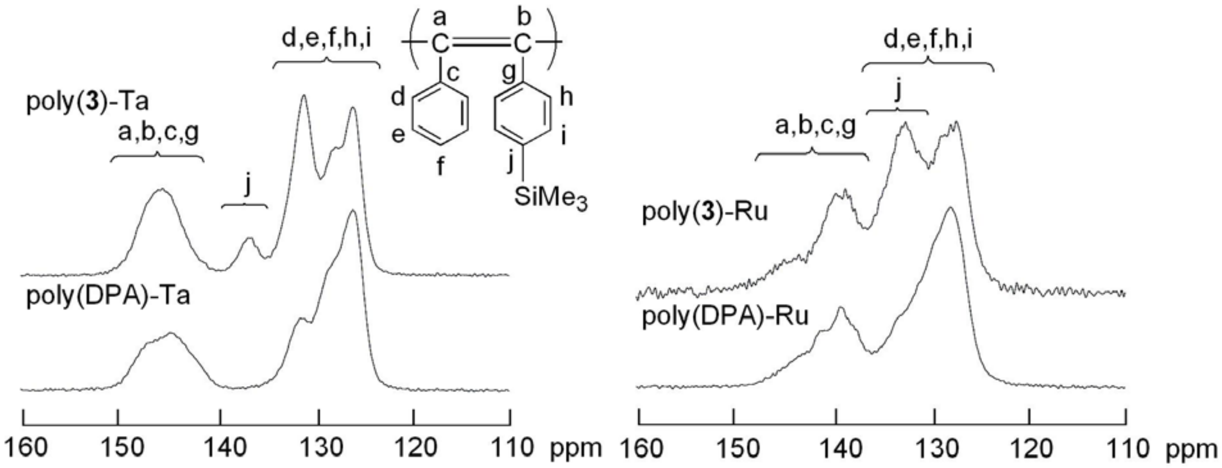


Figure 7. ^{13}C CP/MAS spectra of poly(**3**)s and poly(DPA)s.

thing can be said with poly(**3**) and poly(DPA) formed with Ru catalyst **1**. Since poly(DPA) does not involve the problem of regio-regularity, the difference in the spectra of the polymers with catalysts is attributable to the difference in the main-chain configuration.

The ^{13}C CP+DDPh (dipolar dephasing)/MAS experiments were performed to assign each peak in Figure 7. Dipolar dephasing spectra were observed by inserting a dephasing period between the CP period and detection. When the dephasing time was 100 μs, the Ta-based poly(**3**) displayed relatively strong peaks around 146 ppm, while the Ru-based poly(**3**) displayed a relatively broad peak around 140 ppm with a shoulder positioning at 145 ppm (Figure 8). These peaks are generally assigned to the carbons that do not have strong interaction with hydrogen atoms, and thus should be derived from main-chain carbon atoms of each polymer. By adopting a dephasing time of 60 μs, new peaks appeared at a higher magnetic field (Figure 9). Namely, two peaks were newly observed at 142 ppm as a shoulder and at 136 ppm in Ta-based poly(**3**), and at 138 and 134 ppm in Ru-based poly(**3**). These peaks can be assigned to the substituted carbons of the phenyl rings. Further, when compared with the spectra of poly(DPA), the peaks at 142 and 136 ppm in the Ta-based poly(**3**) are assigned to the benzene carbons attached to the main chain and the silyl group,

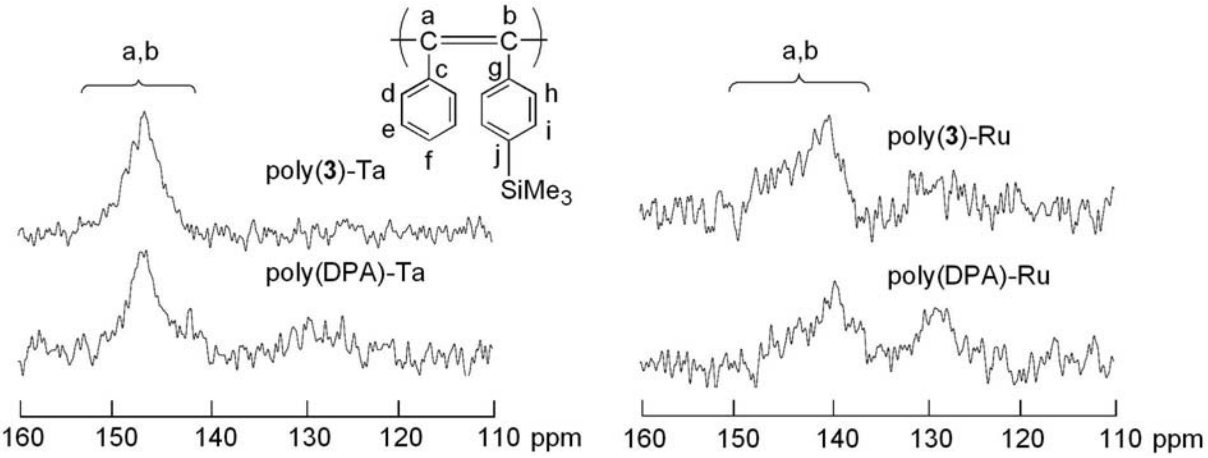


Figure 8. ^{13}C CP+DDPh/MAS spectra of poly(**3**)s and poly(DPA)s (the dephasing time 100 μs).

respectively; on the other hand, the peaks at 138 and 134 ppm in the Ru-based poly(**3**) are based on the benzene carbons attached to the main chain and the silyl group, respectively. From the above discussion, the signals of ^{13}C NMR spectra are assigned as shown in Figure 7. It is noteworthy that not only the main-chain carbons but also benzene carbons exhibit different chemical shifts depending on the kind of catalysts used. Further, it is noted that the Ru-based polymers have a broader distribution in the main-chain configuration according to the signals of the 146–140

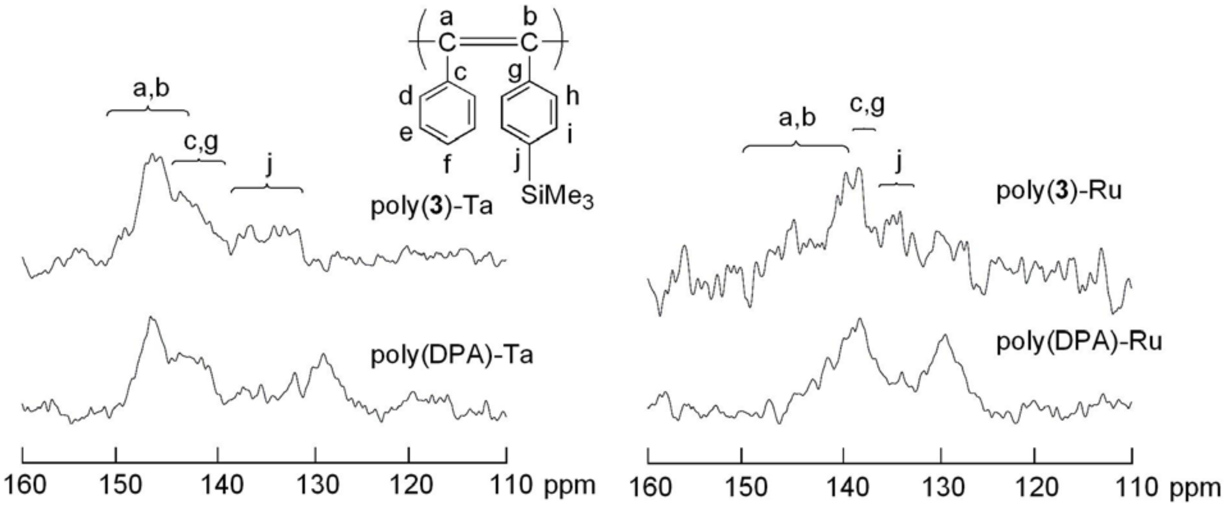


Figure 9. ^{13}C CP+DDPh/MAS spectra of poly(**3**)s and poly(DPA)s (the dephasing time 60 μs).

ppm region. At this moment, the author can say from the solid-state ^{13}C NMR spectra that the Ru- and Ta-based poly(**3**)s have clearly different geometric structures in the main chain to each other.

Conclusions

Hexyl propiolate (**2**) and 1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**3**) polymerized with Grubbs-Hoveyda catalyst. Monomer **2** gave polymers with M_n of ca. 20 000 in both toluene and bulk polymerization. The resulting poly(**2**) had high *cis* content, confirmed by ^{1}H NMR spectroscopy. The bulk polymerization of **3** provided a polymer in 42% at $[M]_0/[Ru] = 100$, 80 °C for 48 h. UV-vis spectra of poly(**3**)s indicate that the conjugation length of Ru-based polymer is much shorter than those of the polymers obtained with conventional catalysts including Ta, W, and Mo. It was revealed that the configuration of Ru-based poly(**3**) was different from those of polymers conducted with other catalysts according to the solid state ^{13}C NMR measurement.

Experimental Section

General. The molecular weights of polymers were estimated by gel permeation chromatography (THF as eluent, Showa Denko Shodex KF-805L × 3, polystyrene calibration). IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in $CDCl_3$ solution on a JEOL EX-400 spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and shown relative to tetramethylsilane. Thermogravimetric analyses (TGA) were conducted in air with a Perkin-Elmer TGA7 thermal analyzer. Ultraviolet-visible (UV-vis) and emission spectra were measured on Jasco V-550 and FP-750 spectrophotometers, respectively. Monomer conversions were determined by GC (Shimadzu GC-8A; Silicone SE30 (5% on Chromosorb W(AW-DMCS), 80–100 mesh); injection and column temperatures were 250 and 230 ºC, respectively) using cyclododecane as an internal standard.

Solid-State ^{13}C NMR Measurements (CP/MAS and CP+DDPh). The ^{13}C NMR spectra were recorded on a Bruker Avance DSX300 NMR (75.6 MHz) spectrometer at room temperature. A conventional 4 mm wide-bore CP/MAS probehead was used; the contact time was 2 ms and the $\pi/2$ pulse width was 3.2 μs for ^{1}H. The ^{13}C chemical shifts were calibrated by using adamantane (δ = 29.5 ppm) as an external standard relative to tetramethylsilane (δ = 0 ppm).

Materials. Grubbs-Hoveyda catalyst **1** was offered by Materia (USA). $TaCl_5$ (Strem Chemicals), WCl_6 (Aldrich), $MoCl_5$ (Aldrich), $MoOCl_4$ (Aldrich), and $WOCl_4$ (Aldrich) as main catalyst components and Ph_4Sn (Wako) as a cocatalyst were used without further purification. *n*-Bu_4Sn (Wako) as a cocatalyst, and 1-octyne (TCI) and phenylacetylene (Aldrich) as monomers were purified by distillation. Monomers **2**,[5b] **3**,[14] *N*-propargylhexanamide,[4g] and $[(nbd)RhCl]_2$[15] were prepared according to the literature methods. Toluene, THF, 1,2-dichloroethane, and acetonitrile as solvents for polymerization were purified by distillation, and DMSO and ethyl acetate were used as received (Wako).

Bulk Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under argon. Unless otherwise specified, the reactions were carried out for 24 h. The following procedure is exemplary: Momomer **2a** (0.15 g, 1.0 mmol) was added to a Schlenk tube that had been charged with catalyst **1** (6.3 mg, 10 μmol) beforehand. Polymerization was carried out at 80 °C for 24 h. The formed polymer was dissolved in toluene (2.0 mL) and isolated by precipitation into a large excess of methanol, filtered, and dried under vacuum to constant weight. Its yield was determined by gravimetry.

Solution Polymerization. Unless otherwise specified, polymerizations were carried out in an argon atmosphere for 24 h under the following conditions: $[M]_0$ = 0.50 M, [Ru] = 10 mM. A detailed procedure of polymerization is as follows: A monomer solution was prepared in a Schlenk tube with a three-way stopcock by mixing monomer **2a** (0.15 g, 1.0 mmol) and toluene (1.0 mL), and another Schlenk tube was charged with catalyst **1** (13 mg, 20 μmol) and toluene (1.0 mL). Polymerization was initiated by adding the monomer solution to the catalyst solution, and continued at 60 °C for 24 h. Then the reaction was quenched by adding a small amount of methanol. The formed polymer was isolated by precipitation into a large excess of methanol, filtered, and dried under vacuum to constant weight, whose yield was determined by gravimetry.

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Chapter 2

Polymerization of Diphenylacetylenes with Polar Functional Groups by the Grubbs-Hoveyda Catalyst

Abstract

Polymerization of various diphenylacetylene derivatives was investigated by using Grubbs-Hoveyda catalyst (**1**). Owing to excellent tolerance for polar functional groups, catalyst **1** polymerized diphenylacetylene (**2**) and diphenylacetylene derivatives bearing silyl (**3**), siloxy (**4** and **5**), ester (**6** and **7**), amide (**8**–**10**) and carbamate (**11**) groups. It is noteworthy that polymerization of monomers **6**–**11**, which have polar functional groups, has been impossible until now due to the deactivation of well-known Ta catalysts. Although monomers having ester groups (**6** and **7**) hardly polymerized, their copolymerization with trimethylsilyl group-containing diphenylacetylene (**3**) afforded copolymers, which incorporated ester moieties more than the monomer feed ratio. While polymers with relatively nonpolar groups (poly(**3**)–poly(**5**)) were soluble in hydrocarbon solvents such as cyclohexane and hexane, polar group-bearing homo- and copolymers (poly(**10**), poly(**11**), etc) dissolved in polar solvents (e.g., DMF and acetone). Polymerization of 1-(4-*tert*-butyldimethylsiloxy)phenyl-2-(4-fluorophenyl)acetylene (**5**) gave a high molecular weight polymer (M_n = 178 000) suitable for membrane fabrication, and the membrane of this polymer showed higher gas permeability and permselectivity than that of the Ta-based polymer.

Introduction

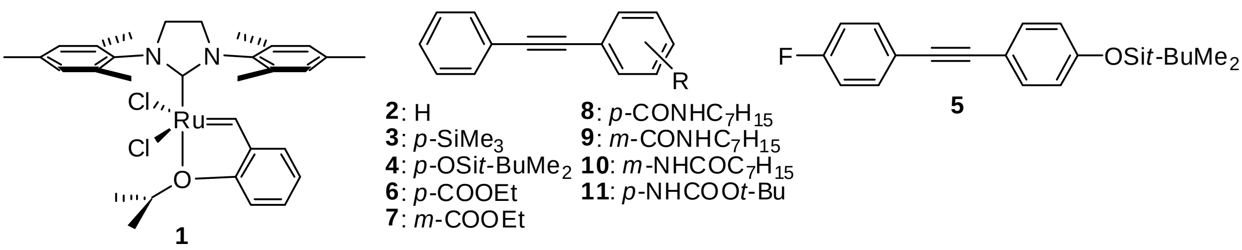
Substituted polyacetylenes have attracted considerable attention as functional polymeric materials owing to their unique properties such as electroluminescence, photoluminescence, energy transfer, energy migration, high gas permeability, formation of helical structure, etc.[1] In general, substituted polyacetylenes can be obtained by the polymerization of the corresponding acetylenic monomers with group 5 (Nb, Ta), 6 (Mo, W), and 9 (Rh) transition metal catalysts. Being sensitive to air and moisture, Nb, Ta, Mo, and W catalysts cannot be applied for the polymerization of substituted acetylenes bearing polar groups due to their deactivation. On the other hand, Rh catalysts display remarkable activity for the polymerization of monomers containing polar groups owing to their low oxophilicity. In addition, the Rh catalysts exhibit activity even in polar and protic solvents.[2] However, they suffer from a disadvantage of being effective only for monosubstituted acetylenes. Buchmeiser and coworkers developed living polymerization systems by using diethyl dipropargylmalonate as monomer and mainly Ru carbenes containing trifluoroacetate ligands as catalysts.[3] Recently, the author have reported that a highly active olefin metathesis Ru carbene catalyst (**1**)[4] mediates the polymerization of a monosubstituted acetylene (*n*-hexyl propiolate) and also disubstituted ones (diphenylacetylene (**2**) and 1-phenyl-2-(4-trimethylsilyl)phenylacetylene (**3**)).[5] However, polymerization of disubstituted acetylenes containing polar functional groups was not examined.

A wide variety of poly(diphenylacetylene) derivatives have been synthesized with $TaCl_5$–*n*-Bu_4Sn catalyst, and they feature high molecular weight ($M_n > 10^6$). The facile fabrication of these polymers into free-standing membranes allows to investigate their gas permeation properties in detail.[6] Poly(diphenylacetylenes) carrying hydroxy groups display excellent performance for CO_2 separation (P_{CO_2} = 100–300 barrers, P_{CO_2}/P_{N_2} = 35–45) thus fulfilling the criteria for industrial applications.[6a,c] It is anticipated that the membranes of polymers having polar groups will be highly permselective for CO_2, owing to its interaction with the polar groups.

It has been revealed that the geometric structure of the poly(**3**) obtained with the Ru catalyst (**1**) was different from that formed with the Ta catalyst.[5] The different geometrical structure of the polymer may affect its gas permeation properties.

This chapter discusses on the polymerization of diphenylacetylene derivatives bearing relatively nonpolar (**4**, **5**) and polar (**6**–**11**) functional groups using Grubbs-Hoveyda catalyst (**1**), and copolymerization of the ester group-containing monomers (**6** and **7**) with **3** (see the chart). The properties of poly(**5**), poly(**11**), and copolymers (poly(**6**-*co*-**3**) and poly(**7**-*co*-**3**)) were investigated by UV-vis spectrum and other methods, and properties of the Ru-based poly(**5**) were found to differ from those of Ta-based poly(**5**).

Chart. Structures of Catalyst (1) and Monomers (2-11).



Results and Discussion

Polymerization. Polymerization of various diphenylacetylenes (**2**–**11**) was examined by using Grubbs-Hoveyda catalyst (**1**) (Table 1). Diphenylacetylene (**2**) and its derivatives possessing trimethylsilyl (**3**), *tert*-butyldimethylsiloxy (**4** and **5**), carbethoxy (**6** and **7**), *n*-heptylcarbamoyl (**8** and **9**), *n*-octanamide (**10**), and *tert*-butoxycarbonylamino (**11**) groups were used as monomers.

It has been reported that an insoluble poly(**2**) and very high molecular weight poly(**3**)–poly(**5**) ($M_n > 10^6$) are obtained by the polymerization of the corresponding monomers **2**–**5**, which have no highly polar functional groups, with $TaCl_5$–*n*–Bu_4Sn.[6] Ru catalyst (**1**) also polymerized these monomers to provide poly(**2**)–poly(**5**) in

13–48% yields (M_n = 60 700–178 000, Table 1). Poly(**2**) was insoluble in common organic solvents (run 1), which is the same as the case of the Ta catalyst. The Ru-based poly(**2**) was a white polymer, while the Ta-based poly(**2**) is yellow, similar to the case of previously examined polymer of 1-phenyl-2-(trimethylsilylphenyl)acetylene (**3**).[5] In the polymerization of monomers **4** and **5** with the Ta catalyst, poly(**5**) bearing fluorine atoms has higher molecular weight ($M_w > 6.0\times10^6$) than dose poly(**4**) ($M_w = 4.0\times10^6$) without fluorine atoms.[6a,b] The same tendency was observed in the present case; i.e., the number-average molecular weights (M_n) of poly(**4**) and poly(**5**) were 93 000 and 178 000, respectively (runs 3 and 4).

Table 1. Polymerization of Monomers 2–11 by 1

		polymer[f]		
run	monomer	yield, %	M_n[g]	M_w/M_n[g]
1[a]	**2**	48	insoluble	insoluble
2[a]	**3**	42	60 700	2.22
3[a]	**4**	13	93 000	1.86
4[a]	**5**	19	178 000	1.87
5[b]	**6**	5	—	—
6[b]	**7**	4	13 000	1.55
7[c]	**8**	5	9 600	1.31
8[c]	**9**	trace	5 000	1.19
9[d]	**10**	20	33 900	1.52
10[e]	**11**	23	153 000	2.07

[a] Bulk polymerization, at 80 ºC, for 24 h, $[M]_0/[Ru] = 25$. [b] Bulk polymerization, at 80 ºC, for 7 days, $[M]_0/[Ru] = 100$. [c] In THF, at 80 ºC, for 7 days, $[M]_0$ = 1.0 M, [Ru] = 40 mM. [d] In THF, at 80 ºC, for 7 days, $[M]_0$ = 2.5 M, [Ru] = 0.10 M. [e] In THF, at 80 ºC, for 12 days, $[M]_0$ = 1.0 M, [Ru] = 40 mM. [f] Methanol insoluble part. [g] Measured by GPC (THF, PSt).

The results of the polymerization of diphenylacetylenes having polar functional groups (**6**–**11**) are also shown in Table 1 (runs 5–10). Monomers bearing ester (**6** and **7**) and amide (**8** and **9**) groups, whose carbonyl groups are directly connected with benzene rings, hardly polymerized (~5% yield, runs 5–8), whereas polymerization of monomer **10** possessing an amide group, with N atom directly attached with a benzene ring, afforded poly(**10**) in 20% yield (M_n = 33 900 and M_w/M_n = 1.52, run 9). Polymerization of monomer **11** possessing a carbamate group, whose N atom is also bonded with a benzene ring, resulted in 23% polymer yield (M_n = 153 000 and M_w/M_n = 2.07, run 10). Thus, catalyst **1** was more active for the polymerization of **10**, **11**, whose benzene rings were directly connected with the electron-donating groups (–NHCOn-C_7H_{15}, –NHCOOt-Bu), while the catalytic activity diminished in the cases of **6**–**9**, which contain electron-withdrawing groups (–COOEt, –CONHn-C_7H_{15}). It is noteworthy that monomers **6**–**11** do not polymerize with a classic metathesis catalyst, $TaCl_5$–n-Bu_4Sn, which is very active for diphenylacetylenes with nonpolar groups, due to deactivation of the catalyst by polar moieties in the monomers. By contrast, Ru carbene catalyst (**1**), on account of its high functional group tolerance, was capable of polymerizing the monomers (**6**–**11**) in moderate yields (~23%).

Copolymerization. Copolymerization was examined between the monomer bearing trimethylsilyl group (**3**) and the monomers possessing ester groups, **6** and **7**, which hardly underwent homopolymerization (Table 2). As the content of monomers **6** and **7** in the feed was raised, both polymer yield and molecular weight decreased. Homopolymerization of monomer **3** afforded poly(**3**) in a relatively high yield of 43% (M_n = 83 300 and M_w/M_n = 1.98, run 1). When the content of **6** in the feed was increased from 25 to 75 mol-%, the polymer yield decreased from 41wt.-% to 8wt.-%, and the molecular weight decreased from 97 300 to 19 900 (runs 2–4). A similar tendency was observed in the case of monomer **7**, i.e., as the content of **7** in the feed was increased, both polymer yield and M_n decreased from 41wt.-% and 87 000 to

Table 2. Copolymerization of Monomer 6 and 7 with 3 by 1[a]

run	monomer M_1 M_2	monomer feed M_1/M_2	polymer[b] yield, %	polymer[b] composition[c] M_1/M_2	polymer[b] M_n[d]	polymer[b] M_w/M_n[d]
1	**3**	0/100	43	0/100	83 300	1.98
2	**6** **3**	25/75	41	28/72	97 300	2.48
3		50/50	27	51/49	59 400	2.91
4		75/25	8	78/22	19 900	2.47
5		100/0	5	100/0	—	—
6	**7** **3**	25/75	41	54/46	87 000	1.89
7		50/50	28	29/71	46 600	2.03
8		75/25	18	15/85	23 400	1.97
9		100/0	4	100/0	13 000	1.55

[a] Bulk polymerization, at 80 ºC, for 7 days, $[M]_0/[Ru]$ = 100. [b] Methanol-insoluble part. [c] Determined by ^{1}H NMR. [d] Measured by GPC (THF, PSt).

18wt.-% and 23 400, respectively (runs 6–8). The content of ester groups in copolymers was larger than that in the feed, probably because of facile coordination of the oxygen atom of ester group of monomers **6** and **7** to the Ru metal center.

Solubility of Homo- and Copolymers. The solubility properties of the present homo- and copolymers are summarized in Table 3. Poly(**2**) is insoluble in any solvent. All the other polymers were soluble in $CHCl_3$, THF, and CH_2Cl_2, but insoluble in DMSO and methanol. Poly(**3**)–poly(**5**) showed good solubility in nonpolar solvents and dissolved even in hexane. Although poly(**10**) and poly(**11**) were soluble in DMF and acetone, they were insoluble in ether, benzene, toluene, cyclohexane, and hexane. Copolymers whose monomer feed ratios (**6**/**3** and **7**/**3**) were 75/25 and 50/50 were also soluble in polar solvents such as DMF and acetone.

Table 3. Solubility of Homo- and Copolymers[a]

solvent	poly(**2**)	poly(**3**)–poly(**5**)	poly(**6**-*co*-**3**), poly(**7**-*co*-**3**)[b]	poly(**10**), poly(**11**)
MeOH	–	–	–	–
DMSO	–	–	–	–
DMF	–	–	+	+
acetone	–	–	+	+
CH_2Cl_2	–	+	+	+
THF	–	+	+	+
$CHCl_3$	–	+	+	+
Et_2O	–	+	+	–
benzene	–	+	+	–
toluene	–	+	+	–
cyclohexane	–	+	–	–
hexane	–	+	–	–

[a] +: soluble; –: insoluble. [b] Copolymers obtained at the 25/75 and 50/50 (**6**/**3** or **7**/**3**) feed compositions.

These solubility properties can be well explained in terms of the polarity of pendant groups of these polymers.

UV-vis Spectra of Poly(3)–Poly(5) and Poly(11). As shown in Figure 1, the UV-vis spectra of Ru-based poly(**4**) and poly(**5**) were quite different from those of the Ta-based polymers. The wavelengths of absorption maxima of the Ru-based poly(**4**) and poly(**5**) were 290.5 and 293.0 nm, while the absorption maxima of the Ta-based polymers were 373.5, 431.0 and 375.0, 435.0 nm, respectively. These observations indicate that the Ru-based polymers have less conjugated main chain structure than that of the Ta-based polymers. In our previous work,[5] the same tendency was observed with Ru- and Ta-based poly(**3**)s. Thus, it seems that the Ru-catalyzed

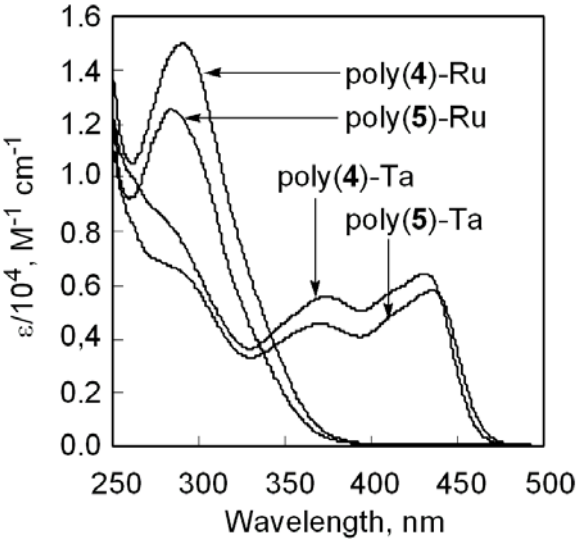


Figure 1. UV-vis spectra of poly(**4**) and poly(**5**) (measured in $CHCl_3$, $c = 1.0\times10^{-4}$ M).

polymerization produces poly(diphenylacetylenes) whose main chain is more twisted than that of Ta-based polymers.

UV-vis spectra of poly(**3**) and poly(**11**) were measured in $CHCl_3$. Both polymers showed strong absorptions around 300 nm, originating from the weakly conjugated main chain of these polymers. The λ_{max} of poly(**11**) was 298.5 nm, which was redshifted by 5.5 nm compared to the λ_{max} of poly(**3**). This finding can be explained by the idea that the –NHCOO*t*-Bu group functions as an auxochrome, while the trimethylsilyl group hardly does.

Gas Permeability of Poly(5). The Ru-based poly(**5**) had a high molecular weight (M_n = 178 000), and consequently its free-standing membrane could be prepared by casting its toluene solution. Fabrication of membrane by casting THF solution of poly(**11**), whose molecular weight was 153 000, was attempted but the resultant membrane was too brittle to measure the gas permeability. The gas permeability of the membrane of poly(**5**) was measured and compared with that of the Ta-based polymer (Table 4).[6a] The oxygen permeability of the Ru-based poly(**5**) (P_{O_2} = 180 barrers) was higher than that of the Ta-based poly(**5**) (P_{O_2} = 100 barrers), and

Table 4. Gas Permeability Coefficients of Polymer Membranes

	P^a								
membrane	He	H_2	O_2	N_2	CO_2	CH_4	P_{O_2}/P_{N_2}	density[b], g/cm^3	FFV[c]
poly(**5**)-Ta	140	230	100	46	590	110	2.2	1.03	0.176
poly(**5**)-Ru	220	400	180	64	1010	170	2.8	1.02	0.210

[a] At room temperature in the units of 1 × 10^{-10} cm^3 (STP) cm/(cm^2) (s) (cmHg) (= 1 barrer). [b] Determined by hydrostatic weighing. [c] FFV: fractional free volume. Calculated from membrane density.

the same tendency was observed with all other gases. Interestingly, the P_{O_2}/P_{N_2} of the Ru-based polymer (= 2.8) was higher than that of the Ta-based polymer (= 2.2). As mentioned above, the main chain of Ru-based polymer is twisted, thus preventing packing of its side chains more than in the Ta-based polymer, which may be responsible for higher gas permeability of the Ru-based polymer. This idea is further supported by the results of fractional free volume (FFV) measurements, which showed that the FFV value of membrane of the Ru-based poly(**5**) (FFV = 0.201) was larger than that of the Ta-based polymer (FFV = 0.176). Desilylation of the membrane of the Ru-based poly(**5**) according to the literature method[6a] rendered it non-uniform and brittle, making gas permeability measurements infeasible.

Thermal Stability of Homo- and Copolymers. The TGA curves of poly(**5**)s, poly(**10**) and poly(**11**) are shown in Figure 2. The onset temperatures of weight loss (T_0) of the Ta- and Ru-based poly(**5**)s were 350 ºC and 220 ºC, respectively, indicating a higher thermal stability of the Ta-based polymer. The residue around 700 ºC is attributable to SiO_2 whose weight is theoretically 19% of the polymer. The T_0 of Poly(**10**) was similar to that of poly(**5**), but poly(**10**) lost weight steeply with increasing temperature. Poly(**11**) started to decompose at 100 ºC and lost 36% of its

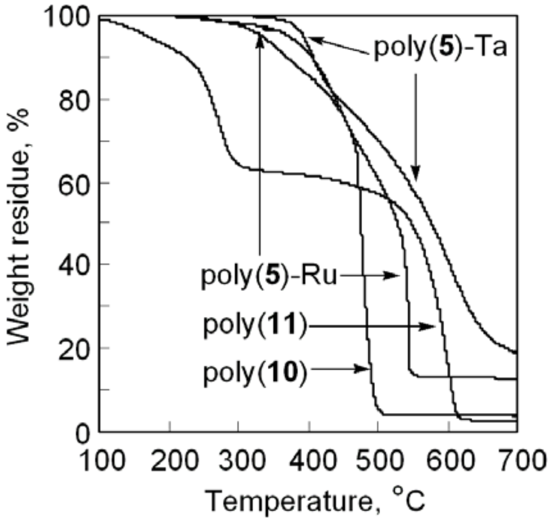


Figure 2. TGA curves of poly(**5**)s and poly(**11**) (measured in air; heating rate 10 °C/min).

weight at 290 ºC, due to removal of the *t*-BOC group as CO_2 and 2-methyl-1-propene (calculated value = 34%). Poly(**10**) and poly(**11**) appeared to completely decompose around 500 and 610 ºC, respectively; above these temperatures, a small amount of residue was observed, which is attributed to the remaining Ru catalyst (2%).

In Figure 3, all the copolymers of poly(**6**-*co*-**3**) and poly(**7**-*co*-**3**) showed almost the same T_0 values (300 ºC), and residual SiO_2 was observed at high temperature above 500 ºC in every case. It is noted that the amount of the residue

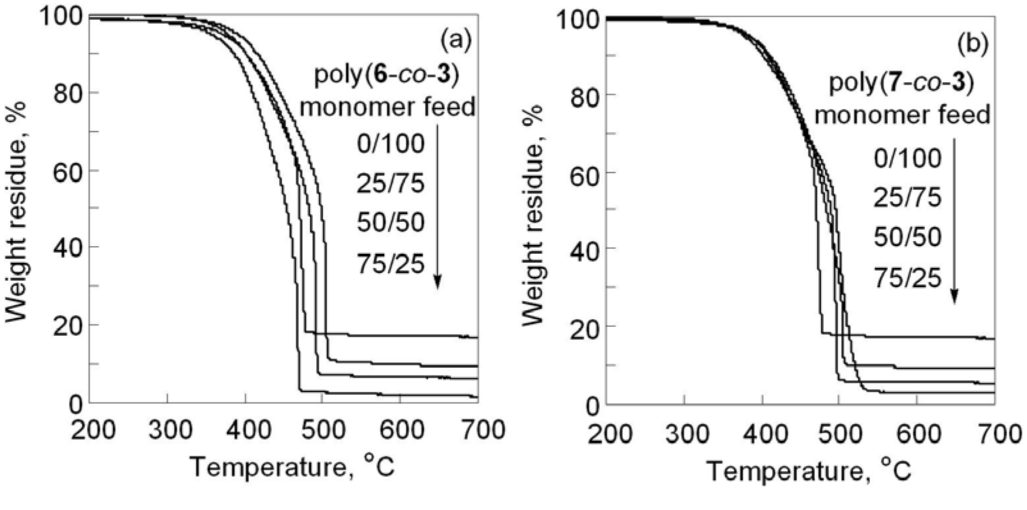


Figure 3. TGA curves of (a) poly(**6**-*co*-**3**) and (b) poly(**7**-*co*-**3**) (measured in air; heating rate 10 °C/min).

decreases with increasing ester content in the copolymer. The thermal stability of the copolymers was not very different from those of Ru-based poly(**3**). Hence it is assumed that the stability of poly(**6**) and poly(**7**) is comparable to that of poly(**3**).

Conclusions

In this study, it was revealed that the Grubbs-Hoveyda catalyst (**1**) was capable of polymerizing not only disubstituted acetylenes bearing nonpolar groups (**2**–**5**) but also those having polar groups such as ester (**6** and **7**), amide (**8**–**10**), and carbamate (**11**) groups. To the best of our knowledge, this is the first example of the polymerization of the diphenylacetylene derivatives carrying polar functional groups. The polymerization of the diphenylacetylene having a carbamate group (**11**) provided the corresponding polymer possessing the highest molecular weight (M_n = 153 000) among the present polymers with polar functional groups (poly(**6**)–poly(**11**)). The properties of poly(**5**) obtained with the Ru catalyst (**1**) were different from those of Ta-based poly(**5**). The gas permeability of the Ru-based poly(**5**) was twice as large as that of the Ta-based poly(**5**).

Experimental Section

General. The molecular weights of polymers were estimated by gel permeation chromatography (THF as eluent, Showa Denko Shodex KF-805L × 3, polystyrene calibration). IR spectra were recorded on a Shimadzu FT/IR-4100 spectrophotometer. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in $CDCl_3$ by a JEOL EX-400 spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C NMR are referenced to internal solvent resonances and shown relative to tetramethylsilane (TMS). Thermogravimetric analyses (TGA) were conducted in air with a Perkin-Elmer TGA7 thermal analyzer. Ultraviolet-visible (UV-vis) spectra were measured with a Jasco V-550 spectrophotometer.

Materials. Hoveyda-Grubbs catalyst **1** was donated by Materia (USA).

Ethyl *p*-iodobenzoate (TCI), ethyl *m*-iodobenzoate (TCI), *n*-heptylamine (TCI), *p*-iodoaniline (Aldrich), *m*-iodoaniline (Aldrich), *n*-octanoic acid (Aldrich), *N*-methylmorpholine (Wako), isobutyl chloroformate (Wako), *N*-*t*-BOC-iodoaniline (*t*-BOC = *tert*-butoxycarbonyl, Wako), phenylacetylene (Aldrich), triphenylphosphine (Wako), copper(I) iodide (Wako), triethylamine (Wako) were used as received. 1-Phenyl-2-(4-trimethylsilyl)phenylacetylene (**3**),[7] 1-(4-*tert*-butyldimethylsiloxy)phenyl-2-phenylacetylene (**4**),[6c] and 1-(4-*tert*-butyldimethylsiloxy)phenyl-2-(4-fluorophenyl)acetylene (**5**)[6a] were prepared according to the literature methods. Monomers **6**–**11** were synthesized as shown in Scheme according to the methods reported in the literature.[8] Diphenylacetylene (**2**) was commercially obtained (TCI) and purified by sublimation. THF as a solvent for polymerization was purified by distillation under nitrogen.

***N*-*n*-Heptyl-4-iodobenzylamide (12).** *N*-Methylmorpholine (10.2 g, 101 mmol) was added to a solution of 4-iodobenzoic acid (25.0 g, 101 mmol) in THF (700 mL) at room temperature. Isobutyl chloroformate (13.8 g, 101 mmol) was added to the above solution to give white precipitate of *N*-methylmorpholine hydrochloride. Then, *n*-heptylamine (11.6 g, 101 mmol) was added, and the resulting mixture was stirred at room temperature overnight. The precipitate was removed by filtration, and the filtrate was concentrated by rotary evaporation. The resulting residue was dissolved in ethyl acetate (500 mL), washed three times with water (500 mL), and dried over anhydrous sodium sulfate. After filtration, the solvent was removed to obtain the crude product. It was purified by recrystallization from ethyl acetate/hexane (1/2 volume ratio). Yield 74%, white solid; IR (KBr): 3326, 2952, 2923, 2873, 2851, 1628, 1587, 1537, 1469, 1391, 1303, 1151, 1059, 1010, 843, 755, 620 $\mathrm{cm^{-1}}$. ^{1}H NMR ($CDCl_3$, ppm): 7.90–7.70 (m, 2H, Ar), 7.55–7.40 (m, 2H, Ar), 6.27 (s, 1H, CON*H*), 3.41 (q, 2H, $CONHCH_2(CH_2)_5CH_3$), 1.68–1.50 (m, 2H, $CONHCH_2CH_2(CH_2)_4CH_3$), 1.50–1.20 (m, 8H, $CONH(CH_2)_2(CH_2)_4CH_3$), 0.90 (t, 3H, $CONH(CH_2)_6CH_3$). ^{13}C NMR ($CDCl_3$, ppm):166.7, 137.6, 134.1, 128.4, 98.1, 40.2, 31.7, 29.6, 29.0, 27.0, 22.6, 14.1.

***N*-*n*-Heptyl-3-iodobenzylamide (13).** This compound was synthesized from 3-iodobenzoic acid in a manner similar to **12**. It was purified by recrystallization from ethyl acetate/hexane (1/5 volume ratio). Yield 69%, white solid; IR (KBr): 3243, 3065, 2956, 2923, 2850, 1633, 1544 1467, 1313, 1292, 1150, 1060, 995, 902, 808, 723, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): 8.08 (s, 1H, Ar), 7.80 (d, 1H, Ar), 7.71 (d, 1H, Ar), 7.15 (t, 1H, Ar), 6.20 (s, 1H, CON*H*), 3.42 (q, 2H, $CONHCH_2(CH_2)_5CH_3$), 1.70–1.55 (m, 2H, $CONHCH_2CH_2(CH_2)_4CH_3$), 1.55–1.20 (m, 8H, $CONH(CH_2)_2(CH_2)_4CH_3$), 0.89 (t, 3H, $CONH(CH_2)_6CH_3$). ^{13}C NMR ($CDCl_3$, ppm):165.9, 140.1, 136.8, 135.8, 130.1, 126.0, 94.2, 40.3, 31.7, 29.6, 29.0, 27.0, 22.6, 14.1.

***N*-(3-Iodophenyl)-*n*-octanamide (14).** This compound was synthesized from 3-iodoaniline and *n*-octanoic acid in a manner similar to **12**, and was purified by recrystallization from ethyl acetate/hexane (1/3 volume ratio). Yield 80%, white solid; IR (KBr): 3313, 2946, 2919, 2865, 2849, 1665, 1519, 1486, 1391, 1304, 1247, 1180, 1006, 817, 692, 504 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): 7.70–7.50 (m, 2H, Ar), 7.4–7.20 (m, 2H, Ar), 7.19 (s, 1H, N*H*CO), 2.32 (t, 2H, $NHCOCH_2(CH_2)_5CH_3$), 1.80–1.60 (m, 2H, $NHCOCH_2CH_2(CH_2)_4CH_3$), 1.40–1.18 (m, 8H, $NHCO(CH_2)_2(CH_2)_4CH_3$), 0.90 (t, 3H, $NHCO(CH_2)_6CH_3$). ^{13}C NMR ($CDCl_3$, ppm):171.4, 137.8, 137.7, 121.5, 87.2, 37.8, 31.7, 29.2, 29.0, 25.5, 22.6, 14.1.

1-(4-Ethoxycarbonyl)phenyl-2-phenylacetylene (6). A 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar, and was flushed with dry argon. Ethyl *p*-iodobenzoate (20.0 g, 72.4 mmol), bis(triphenylphosphine)palladium(II) dichloride (225 mg, 0.320 mmol), copper(I) iodide (366 mg, 1.92 mmol), triphenylphosphine (336 mg, 1.28 mmol), and triethylamine (300 mL) were placed in the flask. Then, phenylacetylene (8.20 g, 80.0 mmol) in triethylamine (10.0 mL) was added, and the reaction mixture was stirred overnight. After the triethylamine in the reaction mixture was evaporated, ether (150 mL) was added, and the insoluble part was filtered off. The solution was washed with 1 N hydrochloric acid and then with water. The ethereal solution was dried over anhydrous sodium sulfate followed by rotary evaporation of ether. Purification of the crude product by flash column chromatography (eluent: ethyl acetate/hexane = 1/9) afforded the desired product **6**. Yield 98%, white solid; mp 75.0–76.0 °C; IR (KBr): 3094, 3062, 2987, 2957, 2940, 2901, 2214, 1703, 1605, 1552, 1484, 1473, 1441, 1406, 1366, 1308, 1278, 1173, 1140, 1105, 1023, 862, 773, 758, 690, 514, 458, 406 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 8.02–8.00 (m, 2H, Ar), 7.70–7.50 (m, 4H, Ar), 7.49–7.31 (m, 3H, Ar), 4.38 (q, 2H, $COOCH_2CH_3$), 1.40 (t, 3H, $COOCH_2CH_3$). ^{13}C NMR ($CDCl_3$, ppm):166.0, 131.6, 131.4, 129.7, 129.4, 128.7, 128.4, 127.8, 122.6, 92.2, 88.6, 61.1, 14.3. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.80; H, 5.64.

1-(3-Ethoxycarbonyl)phenyl-2-phenylacetylene (7). This compound was synthesized from ethyl *m*-iodobenzoate in a manner similar to **6**, and was purified by flash column chromatography (eluent: ethyl acetate/hexane = 1/9). Yield 98%, colorless liquid; IR (KBr): 3063, 2981, 2214, 1721, 1603, 1578, 1493, 1442, 1429, 1367, 1318, 1281, 1254, 1147, 1102, 1081, 1026, 916, 865, 817, 754, 689, 540, 521 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 8.02 (s, 1H, Ar), 7.98 (d, 1H, Ar), 7.66, (d, 1H, Ar), 7.62–7.45 (m, 2H, Ar), 7.45–7.25 (m, 4H, Ar), 4.36(q, 2H, $COOCH_2CH_3$), 1.38 (t, 3H, $COOCH_2CH_3$). ^{13}C NMR ($CDCl_3$, ppm): 165.6, 135.4, 132.5, 131.5, 130.6, 129.0, 128.4, 128.3, 128.2, 123.5, 122.7, 90.1, 88.3, 61.0, 14.2. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.52; H, 5.72.

1-(4-*N*-*n*-Heptylcarbamoyl)phenyl-2-phenylacetylene (8). This compound was synthesized from **12** in a manner similar to **6** and purification was carried out by flash column chromatography (eluent: ethyl acetate/hexane = 1/9). Yield 50%, white solid; mp 137.8–138.8 °C; IR (KBr): 3338, 3053, 2953, 2922, 2850, 1949, 1631, 1536, 1503, 1469, 1441, 1298, 1281, 1187, 1153, 1104, 1070, 1027, 915, 853, 766, 751, 689, 613, 505 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 7.78–7.70 (m, 2H, Ar), 7.62–7.49 (m, 4H, Ar), 7.40–7.31 (m, 3H, Ar), 6.27 (s, 1H, CONH), 3.44 (dt, 2H, $CONHCH_2(CH_2)_5CH_3$), 1.61 (*v*t, 2H, CONHCH$_2$C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.53–1.20 (m, 8H, CONH(CH$_2$)$_2$(C*H*$_2$)$_4$CH$_3$), 0.89 (t, 3H, CONH(CH$_2$)$_6$C*H*$_3$). ^{13}C NMR (CDCl$_3$, ppm):166.7, 134.1, 131.6, 131.6, 128.6, 128.3, 126.8, 126.3. Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.52; H, 7.79; N, 4.44.

1-(3-*N*-*n*-Heptylcarbamoyl)phenyl-2-phenylacetylene (9). This compound was synthesized from **13** in a manner similar to **6**, and was purified by flash column chromatography (eluent: ethyl acetate/hexane = 1/9). Yield 53%, white solid; mp 117.8–118.8 °C; IR (KBr): 3302, 3050, 2951, 2925, 2854, 1635, 1601, 1577, 1532, 1495, 1467, 1337, 1297, 1264, 1170, 1134, 1073, 1028, 899, 815, 754, 686, 660, 526 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.89 (s, 1H, Ar), 7.74 (d, 1H, Ar), 7.62 (d, 1H, Ar), 7.56–7.49 (m, 2H, Ar), 7.42–7.32 (m, 4H, Ar), 6.32 (s, 1H, CON*H*), 3.43 (dt, 2H, CONHC*H*$_2$(CH$_2$)$_5$CH$_3$), 1.61 (*v*t, 2H, CONHCH$_2$C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.51–1.21 (m, 8H, CONH(CH$_2$)$_2$(C*H*$_2$)$_4$CH$_3$), 0.88 (t, 3H, CONH(CH$_2$)$_6$C*H*$_3$). ^{13}C NMR (CDCl$_3$, ppm): 166.7, 135.1, 134.0, 131.6, 129.8, 128.6, 128.5, 128.3, 126.8, 123.6, 122.8, 90.2, 88.4, 40.2, 31.7, 29.6, 29.0, 27.0, 22.6, 14.1. Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.54; H, 7.61; N, 4.28.

1-(3-*n*-Octanamido)phenyl-2-phenylacetylene (10). This compound was synthesized from **14** in a manner similar to **6**, and flash column chromatography (eluent: ethyl acetate/hexane = 1/9) was used to purify it. Yield 22%, white solid; mp 92.3–93.0 °C; IR (KBr): 3272, 3195, 3134, 3049, 2952, 2926, 2849, 1658, 1605, 1583, 1535, 1495, 1426, 1273, 1243, 1188, 1111, 1072, 1028, 970, 912, 898, 887, 790, 752, 707, 688, 537 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.71 (s, 1H, N*H*CO), 7.60–7.20 (m, 9H, Ar), 2.35 (t, 2H, NHCOC*H*$_2$(CH$_2$)$_5$CH$_3$), 1.72 (*v*t, 2H, NHCOCH$_2$C*H*$_2$(CH$_2$)$_4$CH$_3$), 1.48–1.20 (m, 8H, NHCO(CH$_2$)$_2$(C*H*$_2$)$_4$CH$_3$), 0.88 (t, 3H, NHCO(CH$_2$)$_6$C*H*$_3$). ^{13}C NMR (CDCl$_3$, ppm): 171.5, 137.9, 131.5, 128.9, 128.3, 127.3, 123.9, 123.0, 122.6, 119.7, 89.5, 88.9, 37.8, 31.7, 29.2, 29.0, 25.6, 22.6, 14.1. Anal. Calcd for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.94; H, 8.03; N, 4.47.

1-(4-*tert*-Butoxycarbonylamino)phenyl-2-phenylacetylene (11). A 500 mL three-necked flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar, and was flushed with dry argon. *N*-*t*-BOC-iodoaniline (37.0 g, 116 mmol), bis(triphenylphosphine)palladium(II) dichloride (326 mg, 0.464 mmol), copper(I) iodide (357 mg, 1.86 mmol), triphenylphosphine (369 mg, 1.39 mmol), triethylamine (300 mL), and piperidine (30 mL) were placed in the flask. Then, phenylacetylene (14.2 g, 139.0 mmol) in triethylamine (10.0 mL) was added, and the reaction mixture was heated at 40 ºC for 4 h. After the triethylamine and piperidine in the reaction mixture were evaporated, ethyl acetate (500mL) was added, and the insoluble part was filtered off. The solution was washed with 1 N hydrochloric acid and then with water. The ethyl acetate solution was dried over anhydrous sodium sulfate followed by rotary evaporation of ethyl acetate. Purification of the crude product by flash column chromatography (eluent: ethyl acetate/hexane = 1/19) and recrystallization from hexane/chloroform = 1/2 (volume ratio) afforded the desired product **11**. Yield 56%, white solid; mp 170.0–171.0 °C; IR (KBr): 3303, 3096, 3004, 2985, 2930, 2221, 1696, 1587, 1521, 1452, 1406, 1392, 1369, 1314, 1243, 1154, 1061, 1027, 904, 840, 755, 691, 542 cm^{-1}. ^1H NMR ($CDCl_3$, ppm):7.28–7.60 (m, 9H, Ar), 6.59 (s, 1H, N*H*COO), 1.52 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm):152.3, 138.4, 132.4, 131.4, 128.2, 128.0, 123.4, 118.0, 117.4, 89.3, 88.6, 80.8, 28.3. Anal. Calcd for $C_{11}H_{14}INO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.56; H, 6.67; N, 4.77.

Bulk Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under argon. Unless otherwise specified, polymerizations were carried out at 80 °C for 24 h. The following procedure is exemplary: Momomer **2** (0.13 g, 0.50 mmol) was added to a Schlenk tube that had been charged with Ru catalyst **1** (13 mg, 0.020 mmol) beforehand. Polymerization was carried out at 80 °C for 24 h. The formed polymer was dissolved in toluene (0.5 mL), and ethyl vinyl ether (0.10 mL) was added to quench the polymerization. Then, polymer was isolated by precipitation into a large excess of methanol, filtered by a membrane filter, and dried to a constant weight.

Solution Polymerization. Unless otherwise specified, polymerizations were carried out in an argon atmosphere at 80 °C. A detailed procedure of polymerization is as follows: A Schlenk tube with a three-way stopcock was charged with monomer **11** (0.15 g, 0.50 mmol) and Ru catalyst **1** (13 mg, 0.020 mmol). Polymerization was started by adding THF as a solvent, and continued at 80 °C for 7 days. Then THF (0.2 mL) was added to the reaction solution for dilution, and ethyl vinyl ether (0.10 mL) was added to quench the polymerization. The formed polymer was isolated by precipitation into a large excess of methanol, filtered by a membrane filter, and dried to a constant weight.

Membrane Fabrication. Membrane (thickness: 120 μm) of Ru-based poly(**5**) was fabricated by casting toluene solution of the polymer (concentration ca. 1.5 wt-%) onto a flat-bottomed Petri dish. The dish was covered with a glass vessel to reduce the rate of solvent evaporation (ca. 4 days).

Membrane Density. Membrane density was determined by hydrostatic weighing using a Mettler Toledo balance (model AG204, Switzerland) and a density determination kit.[9] In this method, a liquid with known density (ρ_0) is needed, and the membrane density (ρ) is given by the following equations:

$$\rho = \frac{M_A}{M_A - M_L} \times \rho_0$$

where M_A is membrane weight in air and M_L is membrane weight in the auxiliary liquid. Aqueous $NaNO_3$ solution was used as the auxiliary liquid.

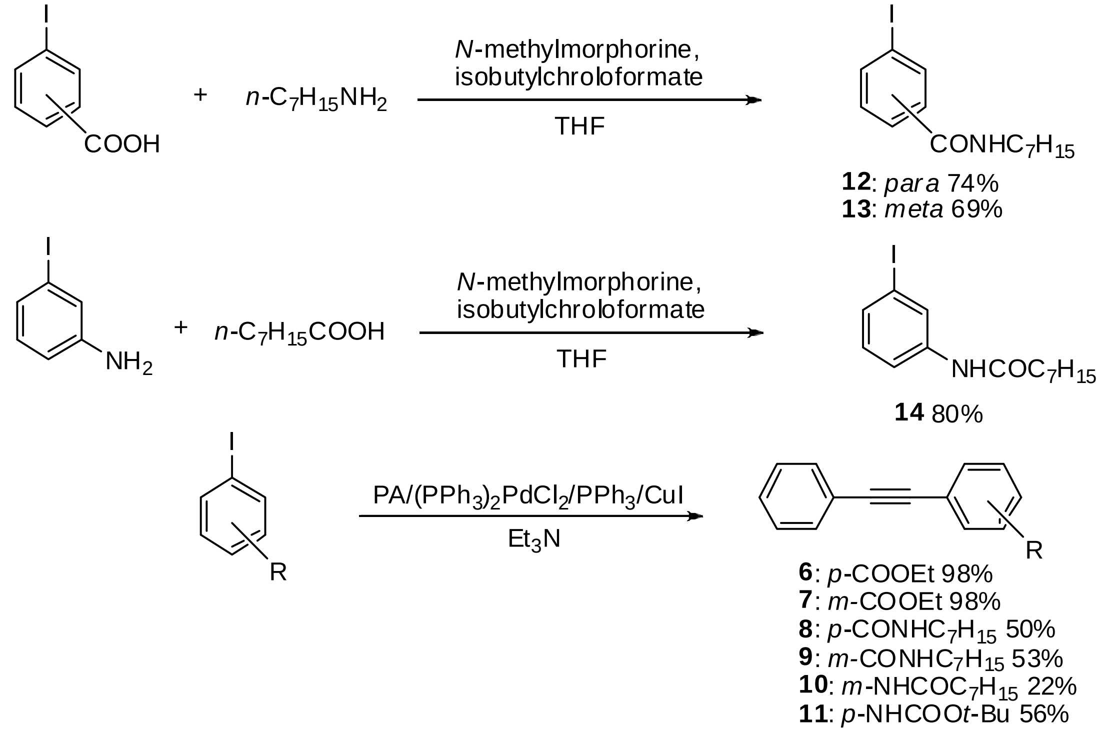
Density and Fractional Free Volume (FFV) of Polymer Membranes. FFV (cm^3 of free volume/cm^3 of polymer) is commonly used to estimate the efficiency of chain packing and the amount of space (free volume) available for gas permeation in a polymer matrix. It is defined as[10]

$$FFV = \frac{v_{SP} - v_O}{v_{SP}} \approx \frac{v_{SP} - 1.3 v_W}{v_{SP}}$$

where v_{SP} and v_O are the specific volume and occupied volume (or zero-point volume at 0 K) of the polymer, respectively. Typically, v_O is 1.3 times larger than the van der

Waals volume (v_W), which is calculated by the group contribution methods.[11]

Scheme. Preparation of Monomers 6–11



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Chapter 3

Polymerization of *ortho*-Substituted Phenylacetylenes with Ru Carbene Catalysts

Abstract

The polymerization of various phenylacetylene derivatives was carried out with ruthenium (Ru) carbene catalysts, and the properties of the formed polymers were studied. Ru catalysts were active only for the polymerization of phenylacetylenes *ortho*-substituted with alkoxy, ester, fluoro, and silyl groups, to give polymers with moderate molecular weights. The Ru-based polymers possessed high *trans* contents according to ^{1}H NMR spectroscopy. Chiral group-carrying polymers obtained with a Ru catalyst took a helical conformation with predominantly one-handed screw sense.

Introduction

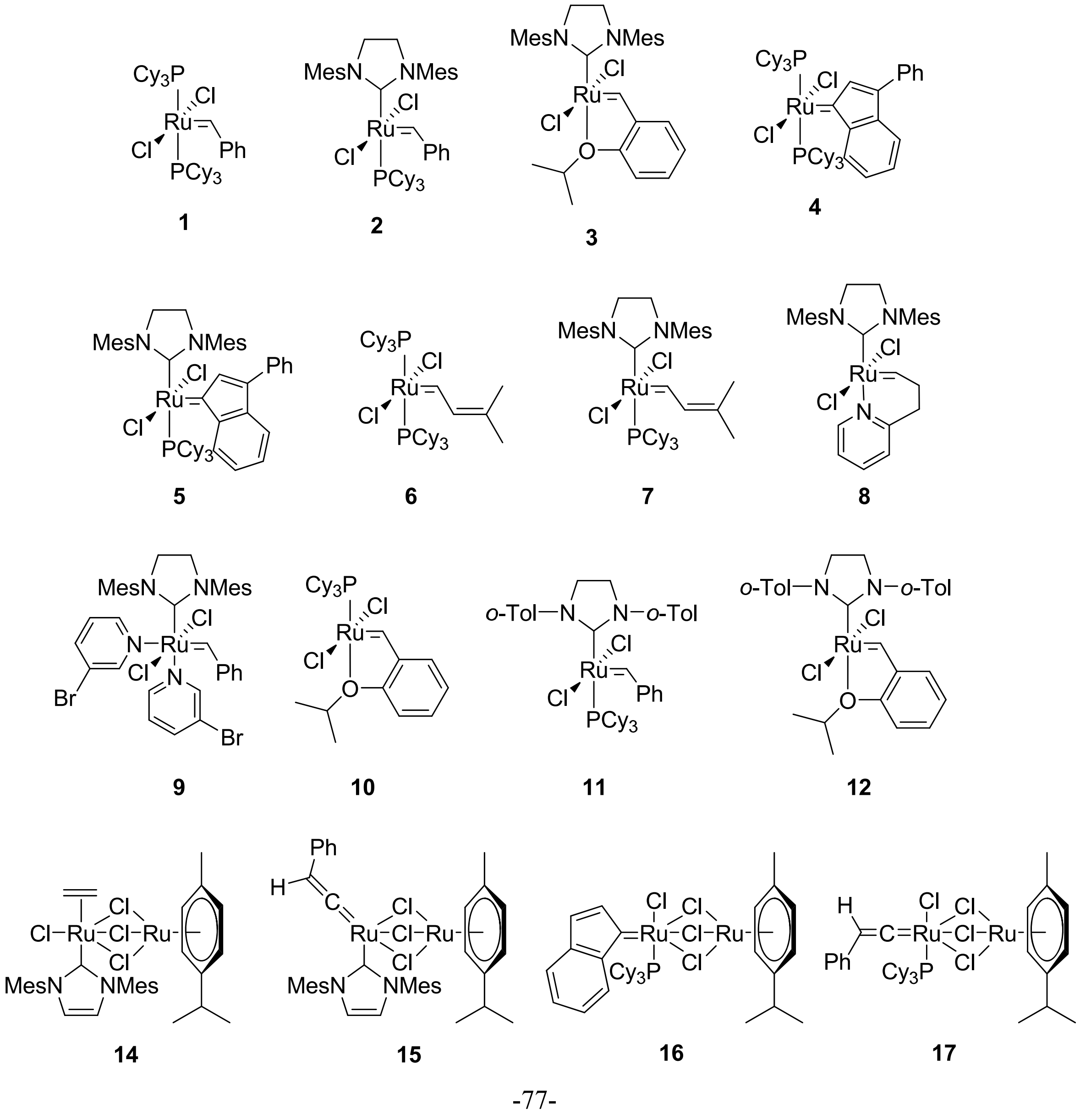
Substituted polyacetylenes have attracted attention for their interesting properties and functions; e.g. energy transfer, energy migration, high gas permeability, and formation of helical conformation.[1] Transition metal catalysts for synthesizing substituted polyacetylenes have also been studied extensively so far.[2] Though early transition metal catalysts including tantalum (Ta), niobium (Nb), tungsten (W), and molybdenum (Mo) induce the metathesis polymerization of both mono- and disubstituted acetylenes, they are sensitive to air and moisture , and therefore ineffective to polar functional group-containing monomers. On the other hand, complexes of rhodium (Rh), a late transition metal of group 9, catalyze the polymerization of alkynes bearing amide, carboxy, amino, and hydroxy groups even in water as well as in organic solvents due to their excellent tolerance to polar functional groups. However, Rh catalysts commonly do not polymerize disubstituted acetylenes.

Substituted polyacetylenes ideally take four geometrical structures (*trans*-transoidal, *trans*-cisoidal, *cis*-transoidal, and *cis*-cisoidal), and stereoregular *cis*-polyacetylenes are obtained by the polymerization with Rh catalysts, which can form helical structures with predominantly one-handed screw sense by introducing chiral substituents into the side chains. There are two methodologies to stabilize helicity in polymers: One is repulsion between bulky pendant groups, and the other is attractive interaction between the side chains such as intramolecular hydrogen bonding. The former examples include poly(propiolates),[3] poly(phenylacetylenes),[4] and poly(1-methylpropargyl alcohol) and its ester derivatives,[5] and the latter ones include poly(*N*-propargylamides),[6] poly(*N*-propargylcarbamates),[7] and poly(phenylacetylenes) bearing amide groups.[8] On the other hand, there have been few examples of helical *trans*-rich polyacetylenes produced with metathesis catalysts. To the best of our knowledge, poly(propiolates) obtained with a Mo catalyst take a helical conformation, although they contain fair amounts of *trans* structure.[3c]

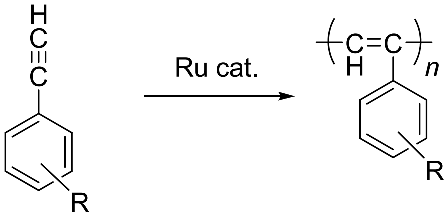
Recently, the author have developed a novel synthetic method of substituted polyacetylenes using Ru carbene complexes.[9] Diphenylacetylene bearing polar groups such as ester, amide, and carbamate have proved to be polymerized with Ru catalysts. Ru carbene catalysts are useful for the polymer synthesis from disubstituted acetylenes bearing polar groups, because no such conventional catalysts had been reported previously.

This chapter deals with the polymerization of phenylacetylene derivatives especially those bearing *ortho*-substituents (Scheme 1). The author has elucidated

Chart 1. Ru Carbene Catalysts 1–16 (Mes = 2,4,6-trimethylphenyl, *o*-tol = 2-methylphenyl).



Scheme 1. Polymerization of Phenylacetylene Derivatives with Ru Carbene Catalysts.



the relationship between the activity of Ru carbenes and monomer structures, along with the properties of the resulting polymers. The author also demonstrates the formation of helical structures of Ru-based poly(phenylacetylenes) carrying chiral groups at the *ortho* position.

Results and Discussion

Polymerization of 17 with Various Ruthenium Carbene Complexes. Bulk polymerization of (2-isopropoxyphenyl)acetylene **17** with various Ru carbene catalysts was examined at $[M]_0/[Ru] = 100$, 80 °C for 48 h. Although all the catalysts polymerized **17**, some catalysts provided only a trace amount of polymer. As seen from the results of runs 1–12 in Table 1, chelated catalysts **3** and **12** having no phosphine ligands were highly active (runs 3 and 12). This is due to their good stability in the monomer liquid at 80 °C. Phosphine-containing catalysts (**1**, **2**, **4**–**7**, and **11**) were all less active in this polymerization presumably because the phosphine ligand has a strong coordinative ability to prevent the monomers from coordination. Highly stable bimetallic complexes **14**–**16** displayed good activity to provide poly(**17**) with M_n = 9 500–13 800 in 17–42% yields (runs 13–16).

Polymerization of 17 with 3. Polymerization of **17** with the most active catalyst **3** in this study was examined in detail at 80 °C for 48 h (Table 2). Catalyst **3** showed activity in either bulk or toluene solution. Bulk polymerization of **17** at $[M]_0/[Ru] = 100$ gave poly(**17**) with M_n = 10 600 in 55% yield (run 3). Increase of

Table 1. Polymerization of **17** with Various Ru Carbenes[a]

run	catalyst	polymer[b] yield, %	M_n[c]	M_w/M_n[c]
1	**1**	7	2 600	3.13
2	**2**	trace	9 200	1.11
3	**3**	55	10 600	1.59
4	**4**	trace	9 200	1.23
5	**5**	trace	3 100	1.15
6	**6**	trace	—	—
7	**7**	trace	—	—
8	**8**	trace	—	—
9	**9**	trace	—	—
10	**10**	trace	—	—
11	**11**	trace	—	—
12	**12**	22	8 500	1.42
13	**13**	32	9 500	1.55
14	**14**	42	11 500	1.40
15	**15**	17	11 900	1.33
16	**16**	22	13 800	1.32

[a] Bulk polymerization, 48 h, 80 °C; $[M]_0/[Ru] = 100$. [b] MeOH-insoluble part. [c] Determined by GPC (THF, PSt).

monomer-to-catalyst ratio to 200 resulted in molecular weight increase (M_n = 12 000), whereas the polymer yield decreased to 23% (run 4). On the other hand, the polymer yield improved when the $[M]_0/[Ru]$ decreased to 50 (run 2). Solution polymerization in toluene also provided polymers whose molecular weight increased with decreasing monomer-to-catalyst ratio (runs 5–8). At $[M]_0/[Ru] = 25$, poly(**17**) was obtained in the highest yield (72%, run 5). The polydispersities of the formed polymers were

Table 2. Polymerization of 17 with 3[a]

			polymer[c]		
run	solvent	$[M]_0/[Ru]$	yield, %	M_n[d]	M_w/M_n[d]
1	—	25	45	7 000	1.51
2	—	50	60	9 700	1.60
3	—	100	55	10 600	1.59
4	—	200	23	12 000	1.66
5[b]	toluene	25	72	9 600	1.43
6[b]	toluene	50	28	9 600	1.45
7[b]	toluene	100	26	12 600	1.58
8[b]	toluene	200	7	9 700	1.56

[a] Bulk polymerization, 48 h, 80 °C. [b] $[M]_0$ = 0.50 M, [Ru] = 5.0 mM. [c] $[M]_0/[Ru]$ = 100. [d] MeOH-insoluble part. [e] Determined by GPC (THF, PSt).

relatively narrow (1.43–1.66).

Polymerization of Various Monomers with 3. Table 3 shows the result of the polymerization of various phenylacetylenes with catalyst **3**. Neither phenylacetylene **18** nor (2-methoxyphenyl)acetylene **19** gave any MeOH-insoluble part under the conditions (runs 1 and 2); They gave no polymer at 30, 60, and 90 °C both in bulk and solution polymerizations as well. Although monomer **17** bearing isopropoxy group at *ortho* position polymerized as described above, *meta*- and *para*-substituted ones (**26** and **27**) did not (runs 9 and 10). These results indicate that the presence of *ortho*-substituents is important for the polymerization of phenylacetylene derivatives. Other phenylacetylenes *ortho*-substituted with ethoxycarbonyl (**20**), fluoro (**21**), trifluoromethyl (**22**), and trimethylsilyl (**23**) groups were also polymerized with catalyst **3** (runs 3–6). In the cases of monomers **17** and **20**, it is likely that the oxygen atoms of alkoxy and ester groups at *ortho* position stabilize the active species during the polymerization reaction, which would be one

Table 3. Polymerization of 18–24 with 3[a]

		polymer[b]		
run	monomer	yield, %	M_n[c]	M_w/M_n[c]
1	**18**	0	—	—
2	**19**	0	—	—
3	**20**	34	5 900	1.69
4	**21**	17	1 300	1.63
5	**22**	35	38 600	4.78
6	**23**	10	15 000	1.56
7	**24**	16	4 000	2.62
8	**25**	0	—	—
9	**26**	0	—	—
10	**27**	0	—	—

[a] Bulk polymerization, 48 h, 80 °C; $[M]_0/[Ru] = 100$. [b] MeOH-insoluble part. [c] Determined by GPC (THF, PSt).

reason for the finding that only *ortho*-substituted monomers polymerized. Although the effect was weak, even a fluorine atom can interact with Ru to prevent the catalyst from decomposing.[16] Poly(**22**) bearing strong electron-withdrawing trifluoromethyl group had a broad polydispersity with a shoulder peak in a GPC curve. In our previous study,[9a] a propiolate, an electron-poor alkyne, provided a polymer exhibiting a bimodal GPC peak. The electron-poor acetylene moiety of monomer **22** might cause this trend, which could possibly be due to the presence of two mechanisms such as metathesis and insertion. The trimethylsilyl group in monomer **23** might suppress the side reaction which deactivates the catalyst due to its bulkiness, as is observed in the case of W and Mo catalysts. Nitro group-containing (2-isopropoxyphenyl)acetylene **24** provided a polymer with a lower molecular weight in a lower yield than those of poly(**17**) obtained under the same conditions (run 7). This is presumably because the electron-withdrawing nitro group decreases the electron density on the oxygen atom of alkoxy group to diminish the stability of active species. Diisopropoxy-substituted monomer **27** did not polymerize, which is attributable to the steric hindrance of two substituents at *ortho* positions.

Structure and Properties of Poly(17) and Poly(24). In order to investigate the dependence of the polymer properties on the catalysts used in the polymerization, **17** and **24** were polymerized with Rh and W catalysts. As shown in Table 4, poly(**17**) possessing M_n = 17 700 was obtained with (nbd)$Rh^+[\eta^6-(C_6H_5)B^-(C_6H_5)_3]$ in a high yield (90%, run 1), and that obtained with WCl_6/Ph_4Sn had a low molecular weight (M_n = 4 000, run 2). The incorporation of nitro group resulted in the insolubility of the polymer obtained with the Rh catalyst (run 3). In contrast, the W catalyst did not provide poly(**24**) presumably because of the low tolerance of the catalyst to functional groups (run 4).

Table 5 summarizes the solubility properties of poly(**17**)s and poly(**24**)s obtained with Ru and Rh catalysts. Both Ru- and Rh-based poly(**17**)s were well soluble in relatively low polar solvents including CH_2Cl_2, $CHCl_3$, benzene, and toluene.

Table 4. Polymerization of Monomers 17 and 24 with Rh and W Catalysts

			polymer[c]		
run	monomer	catalyst	yield, %	M_n[d]	M_w/M_n[d]
1[a]	**17**	(nbd)$Rh^+[\eta^6-(C_6H_5)B^-(C_6H_5)_3]$	90	17 700	2.74
2[b]	**17**	WCl_6/Ph_4Sn	24	4 000	1.79
3[a]	**24**	(nbd)$Rh^+[\eta^6-(C_6H_5)B^-(C_6H_5)_3]$	100	—[e]	—[e]
4[b]	**24**	WCl_6/Ph_4Sn	0	—	—

[a] In THF, 30 °C, 24 h; $[M]_0$ = 0.30 M, [Rh] = 6.0 mM. [b] In toluene, 30 °C, 24 h; $[M]_0$ = 1.0 M, [W] = 10 mM, [Sn] = 20 mM. [c] MeOH-insoluble part. [d] Measured by GPC (THF, PSt). [e] Insoluble in any common organic solvents.

Table 5. Solubility of Poly(17)s and Poly(24)s Obtained with Ru and Rh Catalysts

solvent	poly(**17**)-Ru	poly(**17**)-Rh	poly(**24**)-Ru	poly(**24**)-Rh
MeOH	–	–	–	–
DMSO	–	–	+	–
DMF	+	±	+	–
acetone	±	±	+	–
CH_2Cl_2	+	+	+	–
THF	+	+	+	–
$CHCl_3$	+	+	+	–
Et_2O	+	±	+	–
benzene	+	+	±	–
toluene	+	+	±	–
cyclohexane	+	±	–	–
hexane	±	–	–	–

+: soluble, ±: partly soluble, –: insoluble.

Ru-based poly(**17**) was soluble in hexane as well. On the other hand, the solubility of poly(**24**)s was quite different from one another; Rh-based poly(**24**) was insoluble in any common organic solvents, while the Ru-based one was soluble in DMSO, DMF, acetone, CH_2Cl_2, THF, $CHCl_3$, and Et_2O. This suggests that the Ru-based polymer has a differently configurated main chain from that of the Rh-based one.

The ^1H NMR spectra of poly(**17**)s obtained with Rh, Ru, and W catalysts are shown in Figure 1. The spectrum of poly(**17**) obtained with Rh catalyst shows sharp peaks, and a *cis* vinyl proton is clearly observed at 5.5 ppm, indicating that this polymer has a *cis*-stereoregular main chain.. Meanwhile, the spectrum of Ru-based poly(**17**) is quite different from that of the Rh-based one and very similar to that of the W-based one. This suggests that the Ru-based polymer has a very low *cis* content.

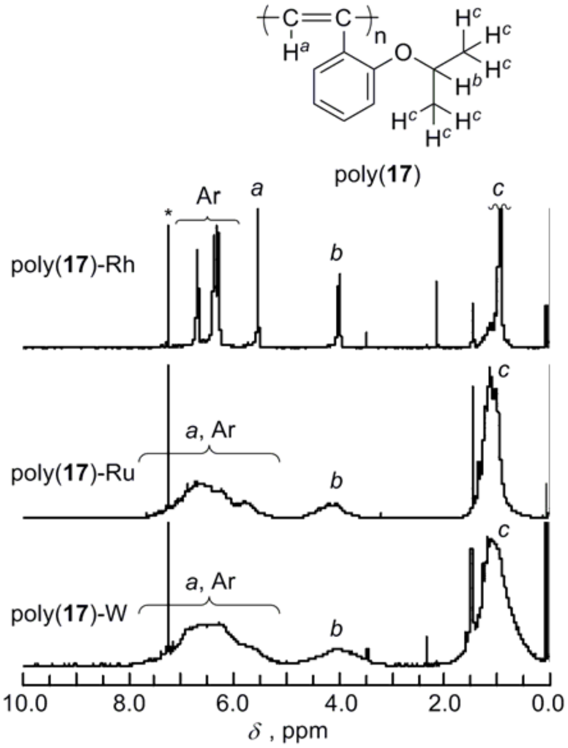


Figure 1. ^{1}H NMR spectra of poly(**17**)s obtained with Ru and Rh catalysts measured in $CDCl_3$ at 50 °C. Asterisk is $CHCl_3$.

The thermal stability of poly(**17**)s and poly(**24**)s was examined by TGA in air (Figure 2). The onset temperatures (T_0) of weight loss of Ru- and Rh-based poly(**17**)s and Rh-based poly(**24**) were 200 °C. Ru-based poly(**24**) started to decompose around 100 °C presumably due to its low molecular weight.

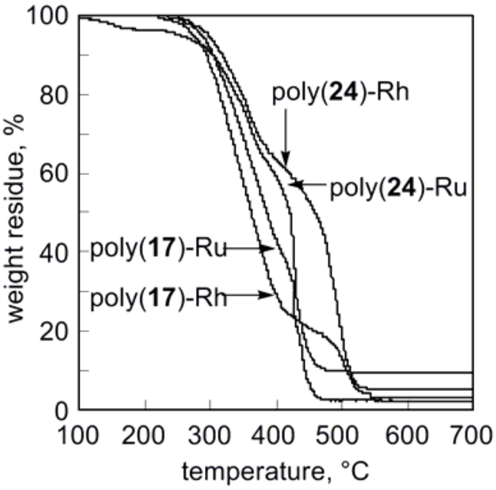


Figure 2. TGA curves of poly(**17**)s and poly(**24**)s obtained with Ru and Rh catalysts measured in air at 10 °C/min.

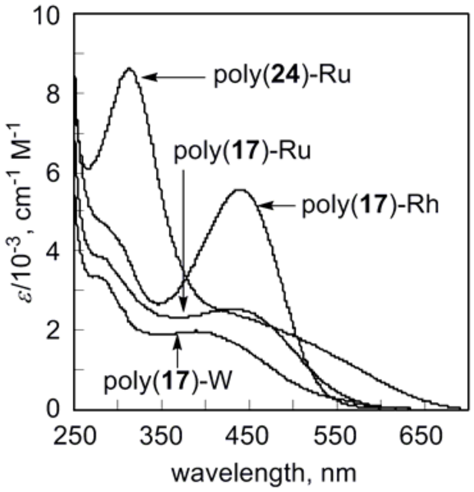


Figure 3. UV-vis spectra of poly(**17**)s and poly(**24**) obtained with Ru, Rh, and W catalysts measured in $CHCl_3$ ($c = 0.936–1.47 \times 10^{-4}$ M).

Figure 3 depicts the UV-vis spectra of poly(**17**)s and poly(**24**) measured in $CHCl_3$. Although the spectrum pattern of Ru-based poly(**17**) was similar to that of the W-based one, the wavelength of absorption maximum (λ_{max}) of the Ru-based polymer (450 nm) was longer than that of the W-based one (410 nm), which is attributable to the difference of molecular weight. The Rh-based polymer also showed the λ_{max} at 450 nm, whereas its molar absorptivity was much higher than that of the Ru-based one. The λ_{max} of nitro group containing-poly(**24**) was 260 nm, while the band edge was longer than that of poly(**17**).

Helical Conformation of Poly(28) and Poly(29). The polymerization of chiral group carrying-monomers **28**–**30** was examined with Ru catalyst **3** and Rh catalyst (Table 6). Alkoxy and ester derivatives **28** and **29** were polymerized with **3** to give the polymers in moderate yields (runs 1 and 3) and gave polymers with (nbd)$Rh^+[\eta^6\text{-}(C_6H_5)B^-(C_6H_5)_3]$ in high yields (runs 2 and 4). However, catalyst **3** did not polymerize monomer **30** bearing an amide group.

Figure 4 shows the ^1H NMR spectra of poly(**28**)s and poly(**29**)s measured in $CDCl_3$ at 50 °C. The spectra of the Ru-based polymers showed broad peaks, and no *cis* vinyl protons, suggesting that these polymers possess a *trans*-rich configuration.

Table 6. Polymerization of 28–30 with Ru and Rh Catalysts

			polymer[c]		
run	monomer	catalyst	yield, %	M_n[d]	M_w/M_n[d]
1[a]	**28**	**3**	38	12 400	1.63
2[b]	**28**	(nbd)$Rh^+[\eta^6-(C_6H_5)B^-(C_6H_5)_3]$	94	21 400	1.59
3[a]	**29**	**3**	54	17 900	1.31
4[b]	**29**	(nbd)$Rh^+[\eta^6-(C_6H_5)B^-(C_6H_5)_3]$	79	29 900	1.51
5[a]	**30**	**3**	0	—	—

[a] Bulk polymerization, 48 h, 80 °C; $[M]_0/[Ru] = 100$. [b] In THF, 30 °C, 24 h; $[M]_0 = 0.30$ M, [Rh] = 6.0 mM. [c] MeOH-insoluble part. [d] Measured by GPC (THF, PSt).

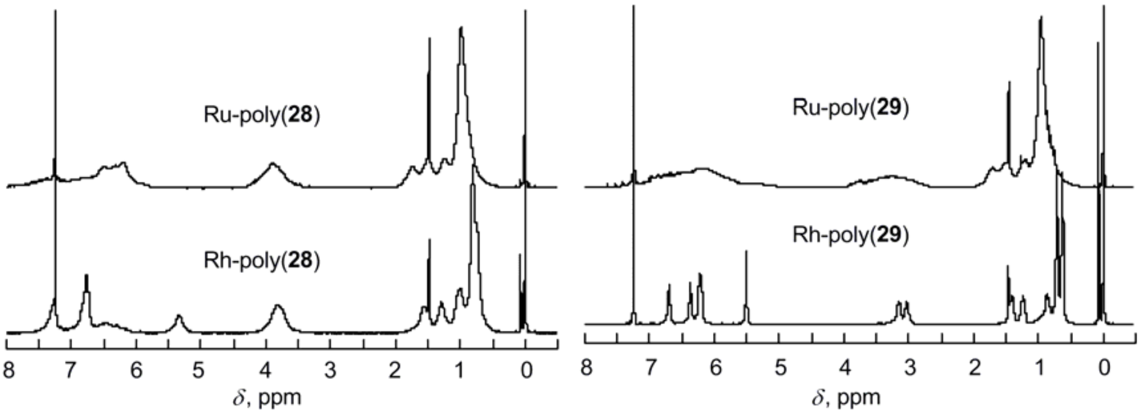


Figure 4. ^{1}H NMR spectra of poly(**28**)s and poly(**29**)s obtained with Ru and Rh catalysts measured in $CDCl_3$ at 50 °C.

In contrast, the high *cis* content of the polymers obtained with a Rh catalyst was confirmed by the presence of a sharp peak at 5.3–5.5 ppm.

The CD and UV-vis spectra were measured to investigate the secondary structures of the formed polymers (Figure 5). Both poly(**28**) and poly(**29**) showed intense CD signals in the absorption region of the main-chain chromophore, which is attributable to the helical polyacetylene main chains with predominantly one-handed

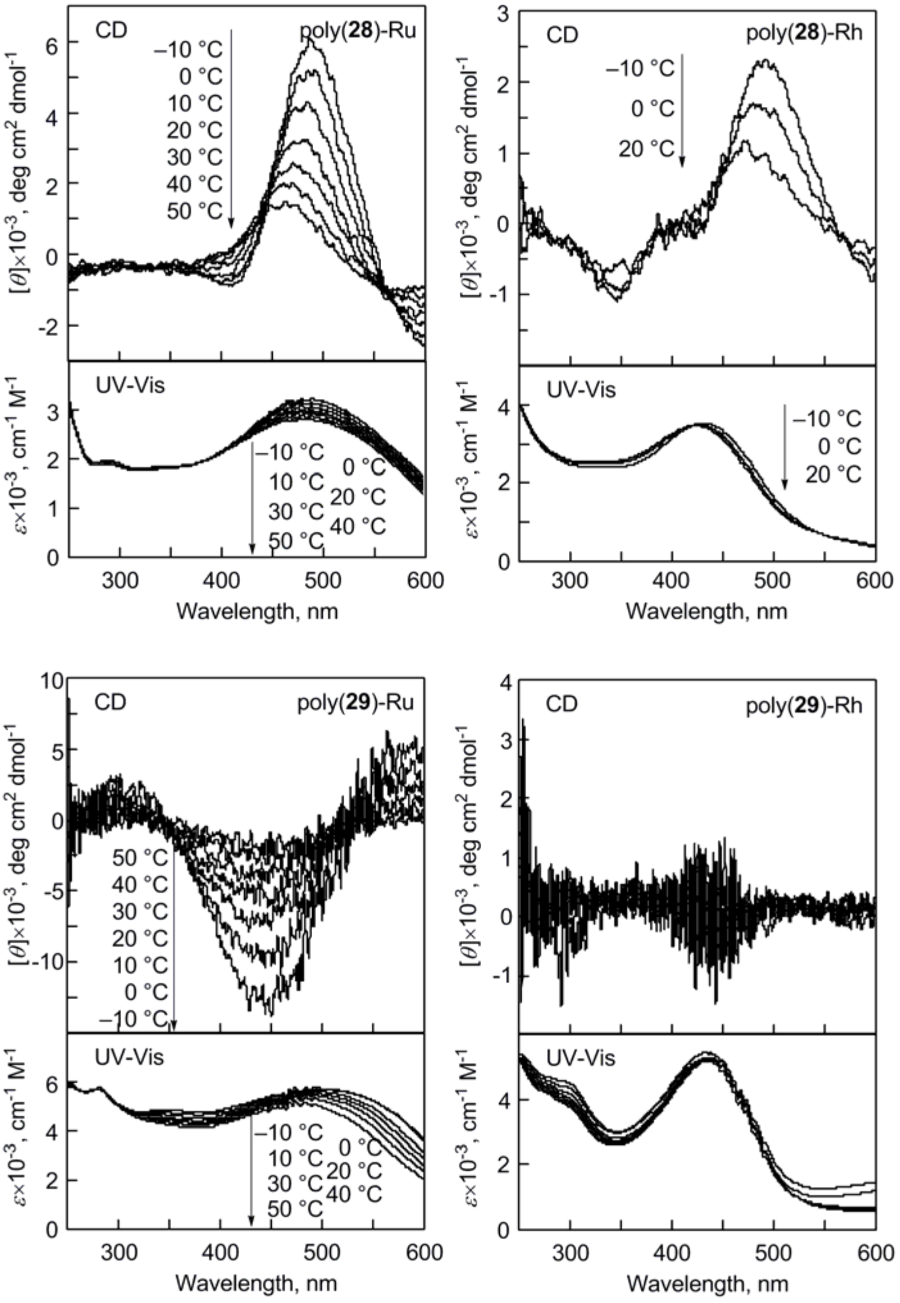
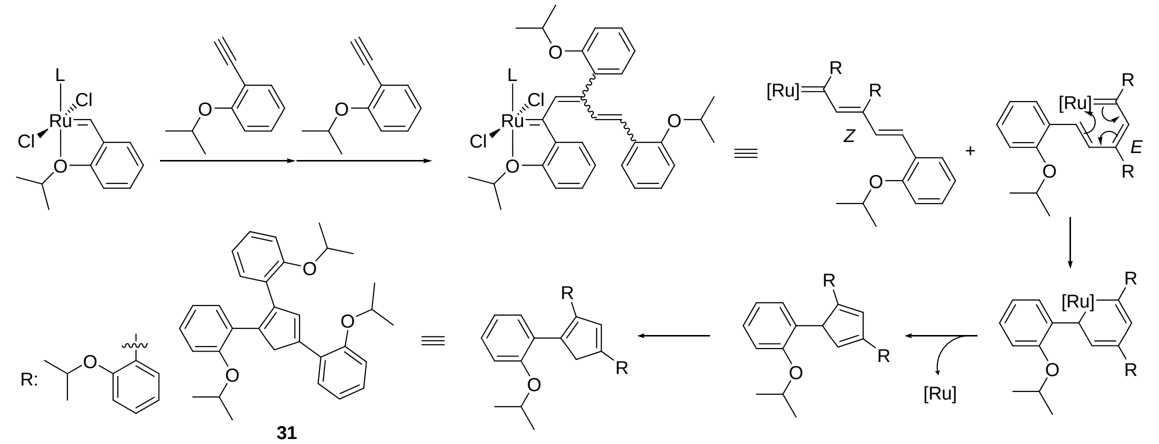


Figure 5. CD and UV-vis spectra of poly(**28**)s and poly(**29**)s obtained with Ru and Rh catalysts (in $CHCl_3$, c = 0.50 mM).

screw sense. In order to examine the thermal stability of helical conformation of the polymers, the CD spectra were measured upon raising temperature from –10 to 50 °C. The molar ellipticity [θ] gradually decreased, but the wavelength of absorption maxima hardly changed with increasing temperature, indicating that the bias of the helical sense is reduced. Rh-based poly(**28**) also showed the Cotton effect in its CD spectrum, whereas its intensity was lower than that of Ru-based poly(**28**). Furthermore, no peak was observed in the CD spectrum of Rh-based poly(**29**), suggesting that it forms no helix or have no bias of helix sense. These results show that the *trans*-rich polymer takes a helical conformation with one-handed screw sense more easily than the *cis*-rich one in the case of *ortho*-substituted poly(phenylacetylenes). This is the first example that the metathesis-based poly(phenylacetylenes) form a helical structure.

Proposed Termination Reaction. Although the polymerization of phenylacetylene derivatives was achieved by using Ru carbene complexes, the polymer yields were low and the molecular weight control was impossible. These results suggest that the termination and/or side reactions proceeded. Recently, Diver and coworkers have reported that the Ru carbene complexes react with two equivalents of alkyne compounds to convert the carbene moiety into cyclopentadienes.[11] When this reaction occurs, the Ru complexes no longer have a carbene moiety to become inactive for olefin metathesis reactions. The filtrate obtained during the isolation process of poly(**17**) (MeOH-soluble part) was examined in detail. Cyclopentadiene compound **31** was detected by ^{1}H NMR spectroscopy and FAB-MS. Cyclotrimers

Scheme 2. Proposed Mechanism of the Decomposition of Ru Carbene Catalysts



31

HRMS (FAB) $C_{32}H_{36}O_3$
found 468.2673
requires 468.2664

were also present according to mass spectrometry. The formation of these compounds supports the decomposition mechanism shown in Scheme 2, which presumed in accordance with Diver's report.

Conclusions

The polymerization of phenylacetylene derivatives was investigated with various Ru catalysts. Phenylacetylene did not polymerize, whereas (2-isopropoxyphenyl)acetylene **17** provided the corresponding polymer in moderate to good yields. Interestingly, 3- and (4-isopropoxyphenyl)acetylene (**26** and **27**) did not polymerize, indicating that the substituent at *ortho* position is important to accomplish polymerization. Other phenylacetylenes *ortho*-substituted with ethoxycarbonyl, fluoro, trifluoromethyl, and trimethylsilyl groups gave polymers with M_n = 1 300–38 600 in 10–34%. Poly(**17**) obtained with Ru catalyst **3** possessed a high *trans* content according to ^{1}H NMR spectroscopy. The CD spectroscopic analysis revealed that the Ru-based *trans*-rich poly(phenylacetylenes) bearing chiral groups, poly(**28**) and poly(**29**), took a helical conformation with predominantly one-handed screw sense.

Experimental Section

Measurements. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX-400 spectrometer using tetramethylsilane as an internal standard. IR, UV–vis and CD spectra were measured on JASCO FT/IR-4100, V-550 spectrophotometers and JASCO J-820 spectropolarimeter, respectively. Thermogravimetric analyses (TGA) were conducted in air with a Shimadzu TGA-50 thermogravimetric analyzer and TGA-60WS thermal analyzer. Melting points (Mp) were measured on a Yanaco micromelting point apparatus. Elemental analysis was carried out at the Microanalytical Center of Kyoto University. Number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a JASCO GULLIVER system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns KF-805L × 3), using THF as an eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standards at 40 °C.

Materials. Unless otherwise stated, reagents were commercially obtained, and used without further purification. 2-Iodo-1,3-dihydroxybenzene,[12] (2-isopropoxyphenyl)acetylene,[13] [2-(trifluoromethyl)phenyl]acetylene,[14] [2-(trimethylsilyl)phenyl]acetylene,[15] (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$,[16] and complexes **14**–**17**[17] were synthesized according to the literatures. Solvents for polymerization were purified before use by the standard methods.

2-Isopropoxy-5-nitroiodobenzene. A solution of $NaNO_2$ (11.2 g, 162 mmol) in water (40 mL) was added dropwise at 0 °C to a stirred solution of 2-hydroxy-5-nitroaniline (25.0 g, 162 mmol) in H_2SO_4/H_2O/DMSO (30 mL/200 mL/100 mL) over a period of 2 hours. After stirring for an additional 30 min, a solution of KI (33 g, 199 mmol) in water (35 mL) was added dropwise for 30 min. The reaction mixture was stirred at 40 °C for 4 hours and then heated at 60 °C overnight. It was extracted with $CHCl_3$ (300 mL × 3), and the organic phase was washed with water (300 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product of 2-hydroxy-5-nitroiodobenzene.

Isopropyl iodide (2.04 g, 12.0 mmol) and K_2CO_3 (5.53 g, 40.0 mmol) were added to a stirred solution of crude 2-hydroxy-5-nitroiodobenzene (2.65 g, 10.0 mmol) in dry DMF (20 mL) under dry argon, and the resulting suspension was stirred at 65 °C overnight. The mixture was then diluted with water (100 mL) and extracted with hexane (150 mL × 3). The combined organic extracts were washed with water (150 mL × 3) before being dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford the crude product. It was purified by silica gel column chromatography eluted with hexane and crystallization from hexane. Yield 55% (pale yellow solid). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 8.65 (d, $J = 2.4$ Hz, 1H, Ar), 8.21 (dd, *J* = 9.0 and 2.2, 1H, Ar), 6.83 (d, *J* = 9.2, 1H, Ar), 4.72 (sept, *J* = 6.0 Hz, 1H, OCH(CH$_3$)$_2$), 1.45 (d, *J* = 6.0 Hz, 6H, CH_3). ^{13}C NMR (400 MHz, CDCl$_3$, δ in ppm) 161.8, 141.3, 135.3, 125.5, 111.2, 86.7, 73.0, 21.8.

2,6-Diisopropoxyiodobenzene. Isopropyl iodide (10.2 g, 60.0 mmol) and K$_2$CO$_3$ (24.9 g, 180 mmol) were added to a stirring solution of 2,6-dihydroxyiodophenol (4.70 g, 20.0 mmol) in dry DMF (50 mL) under dry argon, and the resulting suspension was stirred at 65 °C for 12 h. The mixture was then diluted with water (200 mL) and extracted three times with hexane (200 mL portions). The combined organic extracts were washed three times with water (150 mL portions) before being dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure to afford the pure desired product. Yield quantitative (colorless oil). ^{1}H NMR (400 MHz, CDCl$_3$, δ in ppm) 7.16 (t, *J* = 8.2 Hz, 1H, Ar), 6.46 (d, *J* = 8.0 Hz, 2H, Ar), 4.55 (sept, *J* = 6.0 Hz, 2H, OCH(CH$_3$)$_2$), 1.38 (d, *J* = 6.1 Hz, 12H, CH_3). ^{13}C NMR (400 MHz, CDCl$_3$, δ in ppm) 158.4, 129.2, 107.1, 83.0, 72.1, 22.2.

3-Isopropoxyiodobenzene. This compound was synthesized from 3-iodophenol in a manner similar to 2,6-diisopropoxyiodobenzene. Yield 96% (colorless oil). ^{1}H NMR (400 MHz, CDCl$_3$, δ in ppm) 7.30–7.20 (m, 2H, Ar), 6.96 (vt, *J* = 8.0 1H, Ar), 6.83 (d, *J* = 8.0, 1H, Ar), 4.48 (sept, *J* = 6.0 Hz, 1H, OCH(CH$_3$)$_2$), 1.30 (d, *J* = 6.0 Hz, 6H, CH_3). ^{13}C NMR (400 MHz, CDCl$_3$, δ in ppm) 158.4, 130.7, 129.4, 124.9, 115.2, 94.3, 70.1, 21.8.

4-Isopropoxyiodobenzene. This compound was synthesized from 4-iodophenol in a manner similar to 2,6-diisopropoxyiodobenzene. Yield 97% (colorless oil). ^{1}H NMR (400 MHz, CDCl$_3$, δ in ppm) 7.52 (d, *J* = 8.4 Hz, 2H, Ar), 6.65 (d, *J* = 8.8 Hz, 2H, Ar), 4.48 (sept, *J* = 6.0 Hz, 1H, OCH(CH$_3$)$_2$), 1.30 (d, *J* = 6.0 Hz, 6H, CH_3). ^{13}C NMR (400 MHz, CDCl$_3$, δ in ppm) 157.7, 138.1, 118.2, 82.3, 70.0, 21.8.

(*S*)-2-Methylbutyl 2-iodobenzoate. (*S*)-2-Methylbutanol (3.31 g, 37.5 mmol) in pyridine (10 mL) was added dropwise to a stirred solution of 2-iodobenzoyl chloride (10.0 g, 37.5 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C for 10 min under dry argon, and the resulting mixture was stirred for 1 h. After stirring at room temperature for an additional 2 h, the solution was washed with 1 M aqueous HCl (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and then concentrated at reduced pressure to provide the desired product. Yield 100% (colorless oil). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.98 (d, J = 7.8 Hz, 1H, Ar), 7.78 (d, J = 7.4 Hz, 1H, Ar), 7.39 (vt, J = 7.6 Hz, 1H, Ar), 7.14 (vt, J = 7.7 Hz, 1H, Ar), 4.27–4.08 (m, 2H, $COOCH_2$), 1.93–1.80 (m, 1H, $CH(CH_3)(CH_2CH_3)$), 1.60–1.45 and 1.35–1.21 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 1.02 (d, J = 6.6 Hz, 3H, $CH(CH_3)(CH_2CH_3)$), 0.95 (t, J = 7.4 Hz, 3H, $CH(CH_3)(CH_2CH_3)$). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 166.6, 141.2, 135.4, 132.4, 130.8, 127.8, 93.9, 70.2, 34.1, 26.1, 16.5, 11.2.

(*S*)-2-(2-Methylbutyloxy)iodobenzene. This compound was synthesized from 2-iodophenol and *(S)*-1-bromo-2-methylbutane in a manner similar to 2,6-diisopropoxyiodobenzene. Yield 52% (colorless oil). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.75 (dd, J = 7.8 and 1.5 Hz, 1H, Ar), 7.31–7.20 (m, 1H, Ar), 6.77 (dd, J = 7.8 and 1.0 Hz, 1H, Ar), 6.67 (doublet of virtual triplet, J = 7.5 and 1.2 Hz, 1H, Ar), 3.90–3.73 (m, 2H, OCH_2), 1.99–1.86 (m, 1H, $CH(CH_3)(CH_2CH_3)$), 1.68–1.55 and 1.40–1.28 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 1.08 (d, J = 6.6 Hz, 3H, $CH(CH_3)(CH_2CH_3)$), 0.96 (t, J = 7.6 Hz, 3H, $CH(CH_3)CH_2CH_3)$). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 157.6, 139.3, 129.3, 122.1, 111.8, 86.6, 73.7, 34.7, 26.1, 16.7, 11.4.

(*S*)-(2-Methylbutyl)-2-iodophenylamide. This compound was synthesized from 2-iodobenzoyl chloride and *(S)*-1-amino-2-methylbutane in a manner similar to (*S*)-2-methylbutyl 2-iodobenzoate. Yield 72% (pale yellow solid). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.84 (d, J = 8.0 Hz, 1H, Ar), 7.43–7.33 (m, 2H, Ar), 7.14–7.02 (m, 1H, Ar), 5.91 (s, 1H, NHCO), 3.42–3.20 (m, 2H, $CONHCH_2$), 1.77–1.64 (m, 1H, $CH(CH_3)(CH_2CH_3)$), 1.57–1.44 and 1.30–1.17 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 1.02–0.86 (m, 6H, $CH(CH_3)(CH_2CH_3)$). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 169.4, 142.6, 139.7, 130.9, 128.2, 128.1, 92.3, 45.6, 34.7, 27.0, 17.3, 11.2.

(2-Methoxyphenyl)acetylene (19). A 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and was flushed with argon. 2-Methoxyiodobenzene (6.0 g, 25.6 mmol), bis(triphenylphosphine)palladium dichloride (90.0 mg, 0.128 mmol), copper iodide (146 mg, 0.769 mmol), triphenylphosphine (134 mg, 0.513 mmol), and triethylamine (200 mL) were placed in the flask. Then, (trimethylsilyl)acetylene (3.02 g, 30.8 mmol) was added and the reaction mixture was stirred overnight. After the triethylamine in the reaction mixture was evaporated, ether (150 mL) was added, and then the insoluble salt was filtered off. The solution was washed with 1 M HCl (100 mL × 2) and then with water (100 mL). The ethereal solution was dried over anhydrous $MgSO_4$ followed by the rotary evaporation of ether. The crude product of 1-(2-methoxyphenyl)-2-(trimethylsilyl)acetylene was dissolved in THF (200 mL), and 1 M TBAF (tetrabutylammonium fluoride) in THF (27 mL) was added to the solution. The resulting mixture was stirred overnight. THF was removed by evaporation, and the residue was dissolved in ether (150 mL) and washed with water (100 mL × 3). The organic layer was dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation to give pale yellow liquid. It was purified by silica gel column chromatography eluted with hexane/*tert*-butyl methyl ether (97/3 v/v). Yield 45% (colorless oil). IR (KBr): 3284, 3006, 2944, 2837, 2106, 1596, 1491, 1465, 1435, 1254, 1112, 1024, 753, 655 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.61 (dd, J = 7.2 and 1.6 Hz, 1H, Ar), 7.45 (doublet of virtual triplet, J = 7.2 and 1.6 Hz, 1H, Ar), 7.12–6.98 (m, 2H, Ar), 4.02 (s, 3H, OCH_3), 3.47 (s, 1H, $HC{\equiv}C$). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 160.4, 134.0, 130.1, 120.3, 111.0, 110.5, 81.0, 80.0, 55.6. Anal. Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.99; H, 6.36.

[2-(Ethoxycarbonyl)phenyl]acetylene (20). This compound was synthesized from ethyl 2-iodobenzoate in a manner similar to **19**. Yield 95% (white solid). IR (KBr): 3262, 2983, 2953, 2903, 2218, 1927, 1720, 1594, 1563, 1476, 1365, 1289, 1250, 1133, 1102, 1075, 850, 762, 698, 532 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$,

δ in ppm) 7.94 (d, J = 7.6 Hz, 1H, Ar), 7.62 (d, J = 7.6 Hz, 1H, Ar), 7.47 (vt, J = 7.4 Hz, 1H, Ar), 7.40 (vt, J = 7.6 Hz, 1H, Ar), 4.40 (q, J = 7.1 Hz, 2H, $COOCH_2CH_3$), 1.40 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 165.9, 134.8, 132.7, 131.5, 130.2, 128.4, 122.5, 82.2, 82.0, 61.2, 14.1. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 76.04; H, 6.05.

[(2-Isopropoxy-5-nitro)phenyl]acetylene (24). This compound was synthesized from 2-isopropoxy-5-nitroiodobenzene in a manner similar to **19**. Yield 86% (pale yellow solid). IR (KBr): 3294, 2985, 2935, 2125, 1906, 1811, 1602, 1579, 1509, 1489, 1345, 1284, 1104, 1082, 949, 907, 747, 684, 635 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 8.32 (d, J = 2.4 Hz, 1H, Ar), 8.18 (dd, J = 8.8, 2.4 Hz, 1H, Ar), 6.95 (d, J = 9.6 Hz, 1H, Ar), 4.73 (sept, J = 6.0 Hz, 1H, $OCH(CH_3)_2$), 3.35 (s, 1H, $HC{\equiv}C$), 1.44 (d, J = 6.0 Hz, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 163.9, 140.3, 129.8, 125.8, 113.1, 112.2, 82.9, 77.8, 72.3, 21.7. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 65.22; H, 5.60; N, 6.43.

(2,6-Diisopropoxyphenyl)acetylene (25). This compound was synthesized from 2,6-diisopropoxyiodobenzene in a manner similar to **19**. Yield 22% (pale yellow oil). IR (KBr): 3280, 2979, 2933, 2874, 2106, 1587, 1462, 1385, 1373, 1254, 1116, 1068, 902, 777, 733, 634 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.15 (t, J = 8.3 Hz, 1H, Ar), 6.50 (d, J = 8.5 Hz, 2H, Ar), 4.56 (sept, J = 6.0 Hz, 2H, $OCH(CH_3)_2$), 3.43 (s, 1H, $HC{\equiv}C$), 1,36 (d, J = 6.1 Hz, 12H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 160.9, 129.5, 107.0, 104.1, 84.8, 71.7, 71.6, 22.1. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.3. Found: C, 77.08; H, 8.32.

(3-Isopropoxyphenyl)acetylene (26). This compound was synthesized from 3-isopropoxyiodophenybenzene in a manner similar to **19**. Yield 67% (colorless oil). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.20 (vt, J = 8.0 Hz, 1H, Ar), 7.05 (d, J = 7.6 Hz, 1H, Ar), 7.00 (s, 1H, Ar), 6.88 (d, J = 8.0 Hz, 1H, Ar), 4.52 (sept, J = 6.0 Hz, 1H, $OCH(CH_3)_2$), 3.04 (s, 1H $HC{\equiv}C$), 1.32 (d, J = 6.4 Hz, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 157.6, 129.4, 124.4, 123.0, 119.0, 117.2, 114.7, 83.6, 76.8, 70.0, 21.9.

(4-Isopropoxyphenyl)acetylene (27). This compound was synthesized from 4-isopropoxyiodophenybenzene in a manner similar to **19**. Yield 72% (colorless oil). IR (KBr): 3289, 2979, 2935, 2106, 1604, 1504, 1385, 1374, 1286, 1249, 1178, 1119, 953, 834, 657, 541 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.40 (d, J = 8.8 Hz, 2H, Ar), 6.80 (d, J = 8.7 Hz, 2H, Ar), 4.53 (sept, J = 6.0 Hz, 1H, $OCH(CH_3)_2$), 2.98 (s, 1H, $HC{\equiv}C$), 1.32 (d, J= 6.1 Hz, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 158.3, 133.5, 115.5, 113.7, 83.7, 75.6, 69.8, 21.9. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.72; H, 7.64.

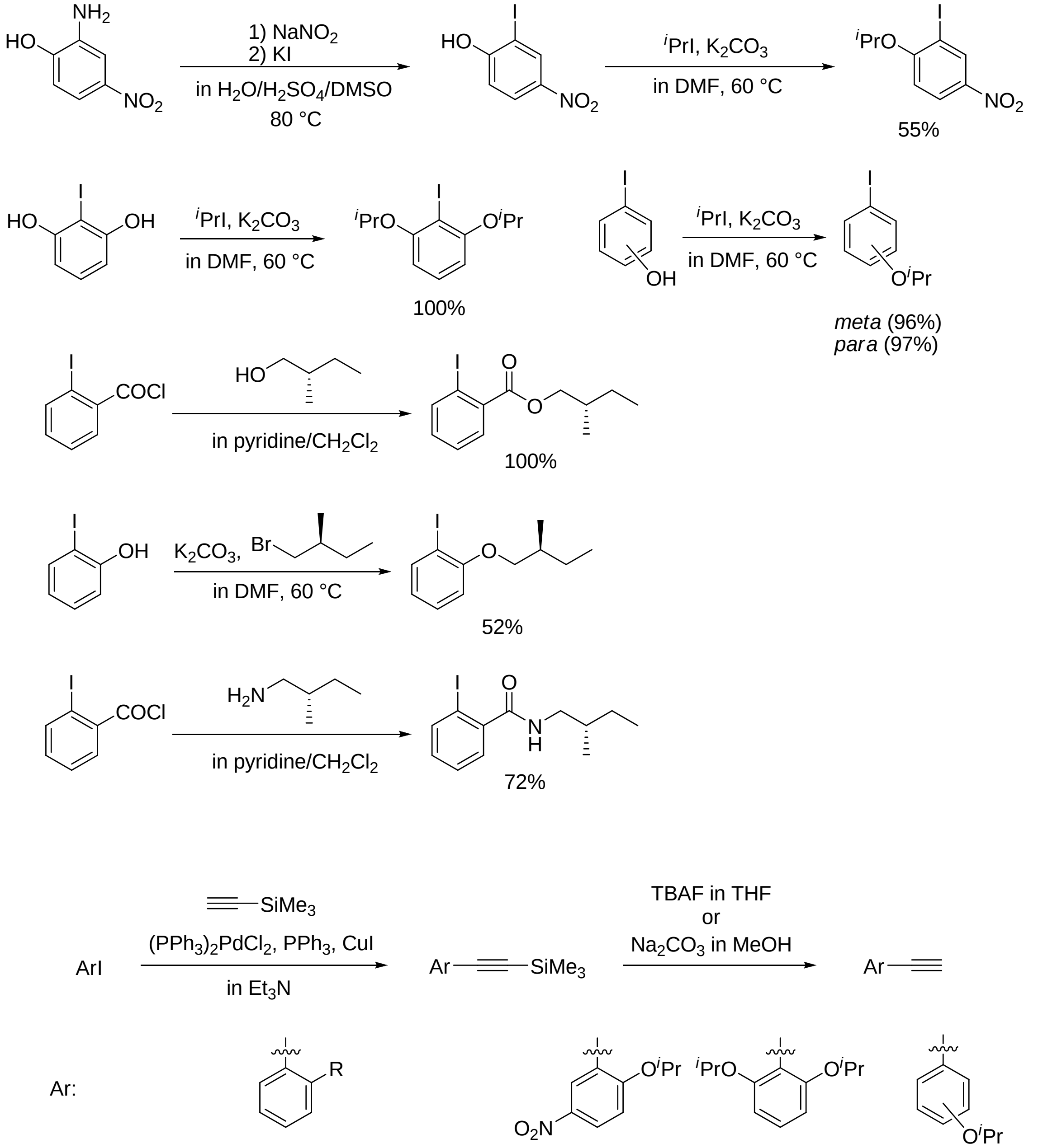
(*S*)-[2-(2-Methylbutyloxycarbonyl)phenyl]acetylene (28). This compound was synthesized from (*S*)-2-methylbutyl 2-iodobenzoate in a manner similar to **19**. Yield 52% (colorless oil). IR (KBr): 3264, 2963, 2935, 2877, 2107, 1726, 1597, 1569, 1464, 1387, 1290, 1254, 1131, 1077, 1041, 964, 759, 700, 660 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.95 (d, J = 7.8 Hz, 1H, Ar), 7.61 (d, J = 7.5 Hz, 1H, Ar), 7.46 (vt, J = 7.0 Hz, 1H, Ar), 7.39 (vt, J = 7.5 Hz, 1H, Ar), 4.29–4.08 (m, 2H, $COOCH_2$), 3.39 (s, 1H, $HC{\equiv}C$), 1.95–1.80 (m, 1H, $CH(CH_3)(CH_2CH_3)$), 1.61–1.48 and 1.35–1.21 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 1.02 (d, J = 3.4 Hz, 3H, $CH(CH_3)(CH_2CH_3)$), 0.95 (t, J = 7.6 Hz, 3H, $CH(CH_3)(CH_2CH_3)$). ^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm) 165.9, 134.9, 132.7, 131.4, 130.2, 128.3, 122.5, 82.2, 82.1, 69.8, 34.1, 26.0, 16.5, 11.1. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.48; H, 7.40.

(*S*)-[2-(2-Methylbutyloxy)phenyl]acetylene (29). This compound was synthesized from (*S*)-2-(2-methylbutyloxy)iodobenzene in a manner similar to **19**. Yield 29% (colorless oil). IR (KBr): 3314, 2962, 2933, 2876, 2108, 1716, 1698, 1596, 1577, 1490, 1457, 1446, 1288, 1254, 1113, 1044, 751, 669 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.43 (d, J = 7.2 Hz, 1H, Ar), 7.25 (vt, J = 8.1 Hz, 1H, Ar), 6.93–6.79 (m, 2H, Ar), 3.92–3.74 (m, 1H, OCH_2CH), 3.23 (s, 1H, $HC{\equiv}C$), 2.00–1.86 (m, 1H, $CH(CH_3)(CH_2CH_3)$), 1.68–1.53 and 1.36–1.22 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 1.04 (d, *J* = 3.4, 3H, CH(C*H*$_3$)(CH$_2$CH$_3$), 0.94 (t, *J* = 7.4 Hz, CH(CH$_3$)(CH$_2$C*H*$_3$)). ^{13}C NMR (400 MHz, CDCl$_3$, δ in ppm) 160.3, 133.9, 130.0, 120.0, 111.8, 111.6, 80.4, 80.0, 73.3, 34.6, 26.0, 16.4, 11.3. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.65; H, 8.67.

(*S*)-[2-(2-Methylbutylcarbamoyl)phenyl]acetylene (30). The crude product of (*S*)-1-[2-(2-Methylbutylcarbamoyl)phenyl]-2-(trimethylsilyl)acetylene (2.36 g, 8.21 mmol), which was synthesized from (*S*)-(2-methylbutyl)-2-iodophenylamide in a manner similar to 1-(2-methoxyphenyl)-2-(trimethylsilyl)acetylene, was dissolved in MeOH (100 mL), and Na_2CO_3 (2.65 g, 25 mmol) was added to the solution. After the resulting mixture was stirred overnight, the solution was concentrated to about 20 mL. Hexane (150 mL) and water (100 mL) were added, and the organic layer was washed with water (100 mL × 2). The organic part was dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation to give pale yellow liquid. It was purified by silica gel column chromatography eluted with hexane/ethyl acetate (9/1 v/v). Yield 49% (white solid). ^{1}H NMR (400 MHz, CDCl$_3$, δ in ppm) 7.97 (d, *J* = 7.5 Hz, 1H, Ar), 7.55 (d, *J* = 7.1 Hz, 1H, Ar), 7.50–7.36 (m, 2H, Ar), 7.29 (s, 1H, CON*H*), 3.49 (s, 1H, *H*C≡C), 3.48–3.25 (m, 2H, CONHC*H*$_2$), 1.80–1.62 (m, 1H, C*H*(CH$_3$)(CH$_2$CH$_3$)), 1.60–1.42 and 1.36–1.18 (m, 2H, CH(CH$_3$)(C*H*$_2$CH$_3$)), 0.98 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)(CH$_2$CH$_3$)), 0.94 (t, *J* = 7.4 Hz, 3H, CH(CH$_3$)(CH$_2$C*H*$_3$)). ^{13}C NMR (400 MHz, CDCl$_3$, δ in ppm) 166.1, 136.8, 134.0, 130.1, 129.7, 129.2, 118.1, 83.3, 82.3, 45.6, 34.7, 27.0, 17.4, 17.4, 11.2.

Bulk Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under argon. Unless otherwise specified, the reactions were carried out for 48 h. The following procedure is exemplary: Monomer **17** (0.16 g, 1.0 mmol) was added to a Schlenk tube that had been charged with catalyst **3** (6.3 mg, 10 μmol) beforehand. Polymerization was carried out at 80 °C for 48 h. The formed mass was dissolved in toluene (0.5 mL) and ethyl vinyl ether (0.1 mL)

Scheme 3. Synthesis of Monomers.



19: R = OMe (45%)
20: R = COOEt (95%)
28: R = COO-(*S*)-$CH_2CH(CH_3)CH_2CH_3$ (52%)
29: R = O-(*S*)-$CH_2CH(CH_3)CH_2CH_3$ (29%)
30: R = CONH-(*S*)-$CH_2CH(CH_3)CH_2CH_3$ (49%)

24 86%

25 22%

26: *meta* (67%)
27: *para* (72%)

was added to the solution to quench the polymerization. Then a polymer was precipitated by pouring the solution into a large excess of MeOH, filtered, and dried under vacuum to constant weight. Its yield was determined by gravimetry.

Solution Polymerization. Unless otherwise specified, polymerizations were carried out in an argon atmosphere for 48 h under the following conditions: $[M]_0$ = 0.50 M, [Ru] = 5.0 mM. A detailed procedure of polymerization is as follows: A monomer solution was prepared in a Schlenk tube with a three-way stopcock by mixing monomer **17** (0.16 g, 1.0 mmol) and toluene (1.0 mL), and another Schlenk tube was charged with catalyst **1** (6.3 mg, 10 μmol) and toluene (1.0 mL). Polymerization was initiated by adding the monomer solution to the catalyst solution, and continued at 80 °C for 48 h. Ethyl vinyl ether (0.1 mL) was added to the solution to quench the polymerization. After stirring for 15 min, the solvent was concentrated to about 0.5 mL. Then, the formed polymer was isolated by precipitation into a large excess of MeOH, filtered, and dried under vacuum to constant weight, whose yield was determined by gravimetry.

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Chapter 4

Synthesis and Properties of Various Poly(diphenylacetylenes) Containing *tert*-Amine Moieties

Abstract

The polymerization of diphenylacetylene derivatives possessing *tert*-amine moieties, such as triphenylamine, *N*-substituted carbazole and indole, was examined in the presence of $TaCl_5$–*n*-Bu_4Sn (1:2) catalyst. A polymer with high molecular weight (M_w = 570 × 10^3) was obtained in good yield by the polymerization of diphenylamine-containing monomer **1b,** whereas the isopropylphenylamine derivative (**1c**) gave a polymer with relatively low molecular weight (M_w = 2.4 × 10^3). The polymerization of monomer **1d** containing cyclohexylphenylamine group did not proceed; however, carbazolyl- and indolyl-containing monomers also produced polymers. Poly(**1b**), poly(**2f**) and poly(**4b**) could be fabricated into free-standing membranes by casting toluene solutions of these polymers. The gas permeability of poly(**1b**) was too low to be evaluated accurately whereas poly(**4b**) possessing two chlorine atoms in the repeating unit showed higher gas permeability than that of poly(**1b**); furthermore, poly(**2f**) having trimethylsilyl and 3-methylindolyl groups exhibited relatively high gas permeability (P_{O_2} = 49 barrers). In the cyclic voltammograms of diphenylamino group-containing polymers, poly(**1b**) and poly(**2b**), the intensities of oxidation and reduction peaks decreased more than those of carbazolyl-containing poly(**2a**). The molar absorptivity (ε) of poly(**1b**) at ~ 700 nm increased with increasing applied voltage in the UV-Vis spectrum.

Introduction

Substituted polyacetylenes having a variety of pendants and stiff main chain composed of alternating double bonds are one of the most attractive classes of functionalized polymers, which exhibit interesting properties such as energy transfer, energy migration, gas permeability, and formation of helical conformation.[1] Unsubstituted polyacetylene is insoluble in common organic solvents and easily decomposes in air. On the other hand, substituted polyacetylenes feature excellent solubility, high thermal stability, facile fabrication of membranes, and high gas permeability.[2]

The past few decades have witnessed extensive research activity for the synthesis and exploration of various properties of poly(diphenylacetylenes).[3] For example, the free-standing membrane of poly(diphenylacetylene) bearing *p*-trimethylsilyl group shows remarkably high gas permeability (P_{O_2} = 1500 barrers) and high thermal stability.[2c,e] Although tantalum catalysts are commonly used for the polymerization of diphenylacetylene derivatives, hydroxy-containing diphenylacetylenes do not polymerize with any of early transition metal catalysts including tantalum, molybdenum, and tungsten due to their low tolerance against polar functional groups. However, the protection of hydroxy groups by sterically bulky silyl moieties such as *tert*-$BuMe_2Si$ enables polymerization of oxygen-containing monomers, and deprotection of silyl groups after polymerization provides hydroxy-containing poly(diphenylacetylene)s.[4] The resultant polymers possessing hydroxy groups exhibit excellent CO_2 permselectivity due to high affinity of the hydroxy group for CO_2 molecules (P_{CO_2} = 100–300, P_{CO_2}/P_{N_2} = 35–45), thus are expected to serve as interesting candidates for CO_2 separation membranes.

Although the gas permeation properties of polyimides, a well-known class of polymers possessing nitrogen in the form of imide, have been extensively investigated, their gas permeability is relatively low.[5] On the other hand, there have been few reports regarding the gas permeability of substituted polyacetylenes bearing amino groups till today. Amino group-containing polymers are expected to show high CO_2 permselectivity as amino groups, due to their polar nature, have been reported to interact with the carbon dioxide molecules. Although introduction of nitrogen functionalities to poly(diphenylacetylene) may lead to novel membrane materials featuring both high gas permeability and remarkable permselectivity, proper selection of amino groups is a prerequisite to avoid the possible deactivation of $TaCl_5$ which otherwise shows high activity in the polymerization of diphenylacetylene derivatives. The only one example of poly(diphenylacetylenes) bearing nitrogen-containing pendants/substituents is poly[1-(*p*-*N*-carbazolylphenyl)-2-phenylacetylene], whose oxygen permeability is too low to measure accurately.[6]

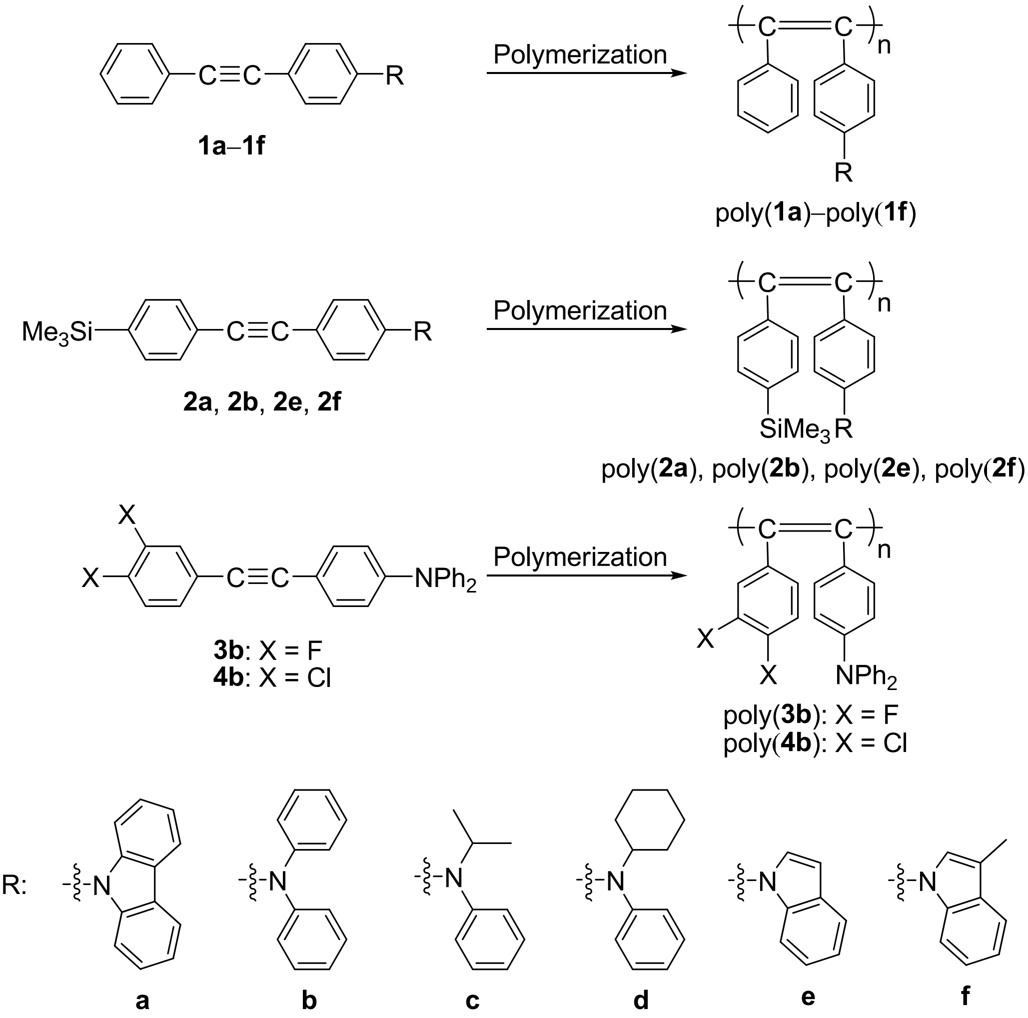
Furthermore, conjugated aromatic amines such as carbazole and triphenylamine carry a lone-pair of electrons on nitrogen atom which undergoes a redox reaction to generate cation radical, hence they have been widely studied in the domains of electrochemistry, magnetism, etc.[7] Polymers with these moieties are also well known to show interesting properties including hole transfer,[8] electroluminescence,[9] photoluminescence,[10] and electrochromism.[11]

This chapter deals with the polymerization of several diphenylacetylenes carrying tertiary amine moieties as shown in Scheme 1. The author prepared free-standing membranes of the resulting polymers and elucidated their general properties, gas permeability, and electrochromism. In general, tantalum-based metathesis catalysts are more or less sensitive to nitrogen-containing monomers, hence bulky substituent- and/or conjugated amine-bearing monomers were chosen to avoid the coordination of nitrogen atom with the metal center of catalyst.

Results and Discussion

Polymerization. The polymerization of diphenylacetylenes **1** and **2** having amine moiety was carried out in toluene with $TaCl_5$–*n*-Bu_4Sn (Table 1). Monomer **1b** bearing diphenylamino group polymerized in 73% yield with a weight-average

Scheme 1. Polymerization of Diphenylacetylenes 1–4



molecular weight of 570 × 10^3 (run 1). The polymerization of monomer **1c**, substituted with isopropylphenylamino group, also proceeded successfully and a polymer with $M_w = 2.4 \times 10^3$ was obtained (run 2). In contrast, cyclohexylphenylamine-substituted monomer **1d** did not polymerize (run 3). Monomer **1b** provided the corresponding polymer with a very high molecular weight probably because the three conjugated phenyl groups decrease the electron density on the nitrogen atom to avoid the complexation and deactivation of the active species. On the other hand, monomer **1c** has two conjugated phenyl groups and moreover an electron-donating isopropyl group, which caused increase of the electron density on the nitrogen atom. This seems to have led to the lower yield and molecular weight of

Table 1. Polymerization of Monomers 1–4[a]

		polymer[c]		
run	monomer	yield, %	$M_w \times 10^{-3d}$	$M_w/M_n{}^d$
1	**1b**	73	570	3.6
2	**1c**	59	2.4	2.5
3	**1d**	0	—	—
4	**1e**	94	insoluble	
5	**1f**	93	insoluble	
6	**2a**	55	1500	4.2
7	**2b**	61	520	4.1
8	**2e**	73	insoluble	
9	**2f**	65	> 6000	—
10[b]	**3b**	50	1100	1.5
11	**4b**	67	570	1.3

[a] In toluene, 80 °C, 48 h; $[M]_0$ = 0.20 M, $[TaCl_5]$ = 20 mM, $[n\text{-}Bu_4Sn]$ = 40 mM. [b] For 120 h. [c] Methanol-insoluble part. [d] Estimated by GPC (THF, PSt).

poly(**1c**) than those of poly(**1b**). Furthermore, cyclohexyl group of monomer **1d**, which is a stronger electron-donating group than isopropyl group, completely suppressed the polymerizability. Diphenylacetylenes carrying conjugated indole and 3-methylindole moieties (**1e** and **1f**) did polymerize but the obtained polymers were insoluble in common organic solvents (runs 4 and 5). Monomers **2a**, **2b**, **2e**, and **2f**, which have a trimethylsilyl group on one phenyl ring and an aromatic amino group on the other, were also examined. Monomer **2b** polymerized in a slightly lower yield than that of **1b**, and poly(**2b**) possessed a somewhat lower molecular weight, which are probably due to the steric bulk of trimethylsilyl substituent (run 7). Poly(**2e**) and poly(**2f**) were obtained in high yield, and poly(**2f**) was soluble in toluene and $CHCl_3$, whereas poly(**2e**) was insoluble in these solvents due to the absence of methyl group in the indolyl substituent (runs 8 and 9). Monomer **3b** bearing two fluorine atoms gave a polymer in 19% yield after 48 hours, and the polymer yield was improved (50%) by extending the polymerization time to 120 hours (run 10). Monomer **4b** having two chlorine atoms polymerized in 67% yield after 48 hours (run 11).

To examine the relationship of the monomer structure and polymerizability, the electron densities on nitrogen atoms of monomers **1a**–**1f** were calculated by the semiempirical molecular orbital method, MOPAC, AM1 Hamiltonian, running on Spartan '06, Windows. The order of the electron density on nitrogen atoms of monomers is: **1e** (0.29 e) < **1f** (0.30 e) < **1a** (0.47 e) < **1b** (0.52 e) < **1c** (0.78 e) < **1d** (0.83 e). It terms out that the electron density has a direct bearing on the polymer yield of poly(**1b**)–poly(**1f**); namely, the lower the electron density on the nitrogen atom, the higher the polymer yield. For instance, monomers **1c** and **1d** differ only slightly in terms of the steric bulk but their polymerizability is quite different from each other (Table 1), most probably being strongly affected by the electron density on the nitrogen atom.

Gas Permeation Properties of Polymers. The fabrication of free-standing membranes of high molecular weight polymers, poly(**1b**), poly(**2a**), poly(**2b**), poly(**2f**), poly(**3b**), and poly(**4b**), was attempted by casting their toluene solution, and gas permeation properties of the membranes were elucidated (Table 2). The free-standing membranes fabricated from poly(**1b**), poly(**2f**), and poly(**4b**) had adequate strength to render gas permeability measurements possible but unfortunately those from poly(**2a**), poly(**2b**), and poly(**3a**) were too brittle. Poly(**1b**) showed low gas permeability (e.g., P_{O_2} = 3.6 barrers) and permeability coefficients for nitrogen, carbon dioxide, and methane could not be determined. Poly(**1a**) also exhibited small gas permeability coefficients, which is probably due to the favored packing of polymer chains ensuing from the high planarity of the carbazolyl group. Poly(**4b**) possessing two chlorine atoms on the phenyl ring without the amine moiety in poly(**1b**), exhibited improved gas permeability which can be attributed to the increase of the number/size

Table 2. Gas Permeability Coefficients (P) of Polymer Membranes[a]

	P (barrer)							
membrane	He	H_2	O_2	N_2	CO_2	CH_4	P_{O_2}/P_{N_2}	P_{CO_2}/P_{N_2}
poly(**1b**)	23	37	3.6	—[b]	—[b]	—[b]	—[b]	—[b]
poly(**2f**)	108	185	49	14	255	32	3.5	18
poly(**4b**)	29	45	8.6	1.9	55	3.4	4.5	29

[a] At room temperature in the units of 1×10^{-10} cm^3 (STP) cm/(cm^2) (s) (cmHg) (= 1 barrer). [b] Could not be determined due to low gas permeability.

of molecular voids caused by electron repulsion between halogen atoms, as reported for poly[*p*-(trimethylsilyl)diphenylacetylene] derivatives.[3d] Poly(**2f**) bearing 3-methylindolyl and trimethylsilyl groups exhibited higher gas permeability than poly(**1b**) and poly(**4b**), presumably originating from the high local mobility of trimethylsilyl group. The P_{N_2} and P_{CO_2} values of poly(*p*-adamantyldiphenylacetylene) are 16 and 29 barrers (P_{CO_2}/P_{N_2} = 1.8), respectively,[12] and those of poly[1-(*n*-hexylthio)-1-propyne] are 14 and 150 barrers (P_{CO_2}/P_{N_2} = 11), respectively.[13] Meanwhile, those of nitrogen-containing poly(**4b**) synthesized in this chapter were 14 and 255 barrers (P_{CO_2}/P_{N_2} = 18), respectively, where high CO_2 separation performance should have emanated from high affinity of CO_2 for polar amine moiety.

Thermal Properties of Polymers. TGA curves of the polymers measured in air are shown in Figure 1. All the polymers exhibited excellent thermal stability and the onset temperatures of weight loss (T_0) were in a range of 200–500 °C. Upon heating the polymers, substituted with trimethylsilyl group, above 600 °C about 15% of residue remained, which is attributable to SiO_2 resulting from the oxidation of the silyl group.

UV-Vis and Fluorescence Spectra of Polymers. The UV-Vis spectra of

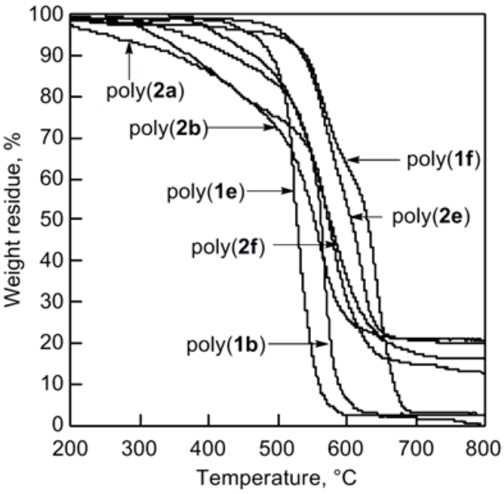


Figure 1. TGA curves of polymers (measured in air, heating rate 10 °C/min).

triphenylamine- or carbazole-containing polymers were measured in chloroform (Figure 2). All the polymers exhibited absorption maxima around 300 nm due to the nitrogen-containing aromatic groups and weaker absorptions or shoulders in a range of 350–500 nm assignable to the main chain conjugation.

On the other hand, the fluorescence spectra of the polymers varied largely, depending on the substituents (Figure 3). This suggests that vibrational relaxation is

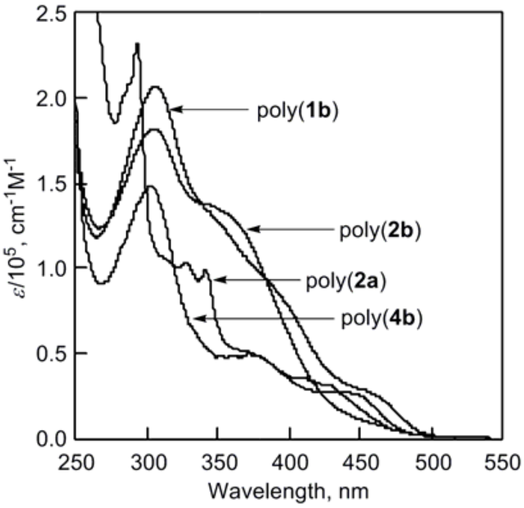


Figure 2. UV-Vis spectra of poly(**1b**), poly(**2a**), poly(**2b**), and poly(**4b**) (measured in $CHCl_3$, concentrations; poly(**1b**): 5.8×10^{-5} M, poly(**2a**): 4.8×10^{-5} M, poly(**2b**): 2.4×10^{-5} M, poly(**4b**): 2.4×10^{-5} M).

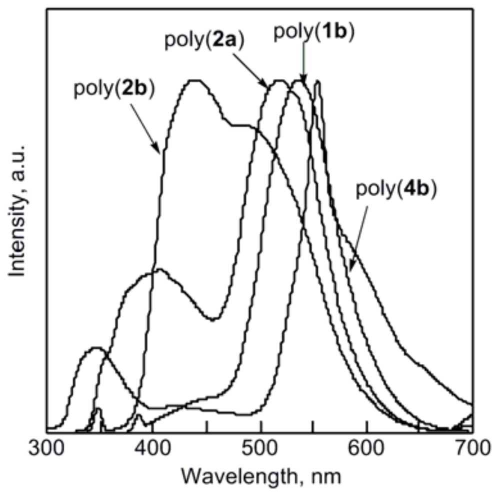


Figure 3. Fluorescence spectra of polymers (measured in $CHCl_3$, exited at 389 nm for poly(**1b**), 274 nm for poly(**2a**), 350 nm for poly(**2b**), 281 nm for poly(**4b**), concentrations; poly(**1b**): 5.8×10^{-5} M, poly(**2a**): 4.8×10^{-5} M, poly(**2b**): 2.4×10^{-5} M, poly(**4b**): 2.4×10^{-5} M).

different from polymer to polymer. However, no solvatochromism was observed in the UV-Vis and fluorescence spectra of poly(**1b**) measured in THF, toluene, and 1,4-dioxane.

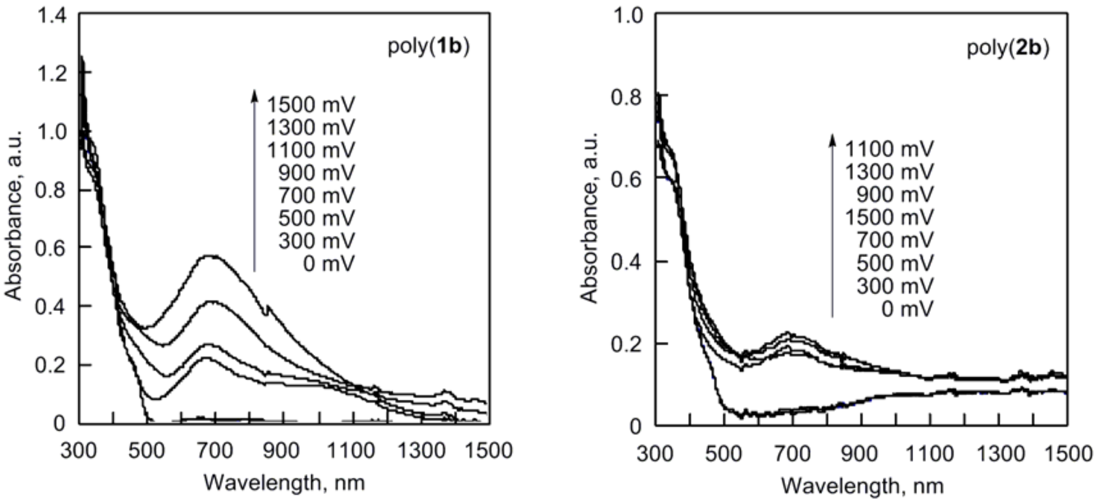


Figure 4. UV-Vis spectra of poly(**1b**) and poly(**2b**) films under application of voltage.

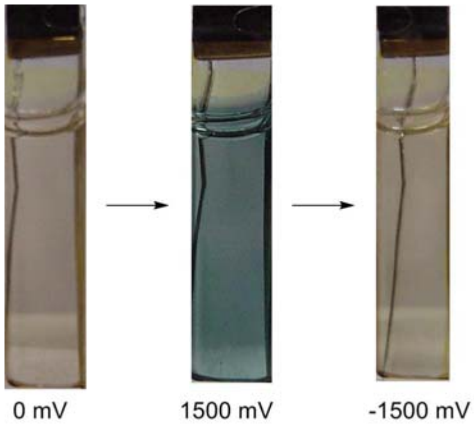


Figure 5. Images of the ITO electrode coated with poly(**1b**) under application of 0 mV, 1500 mV, and –1500 mV.

Electrochromism of Polymers. Figure 4 depicts the UV-Vis spectra of voltage-applied poly(**1a**) and poly(**2b**) films. The films were fabricated by spin coating on ITO glass. The absorption maxima appeared around 700 nm by applying voltages higher than 900 mV, especially in poly(**1b**). This is attributed to the generation of a low energy level due to the formation of charged polaron at the triphenylamine moiety. The polymer films were yellow-colored before the application of electric potential, while they turned blue by applying a voltage of 1500 mV. Furthermore, the films regained the original yellow color when a negative voltage of –1500 mV was employed (Figure 5). However, the poly[*p*-(trimethylsilyl)diphenylacetylene] film did not display electrochromism thus suggesting the significance of amino group to endow the polymers with electrochromism.

Cyclic Voltammograms of Polymers. The cyclic voltammograms of poly(**1b**), poly(**2a**), and poly(**2b**) were measured, and results are shown in Figure 6. The intensity of the oxidation and reduction peaks decreased with the scan time of measurement. This might be due to the formation of thin films of polymers on the surface of the electrode. The redox reaction of poly(**2a**) possessing carbazole moieties did not change very much with scan time as those of poly(**1b**) and poly(**2b**)

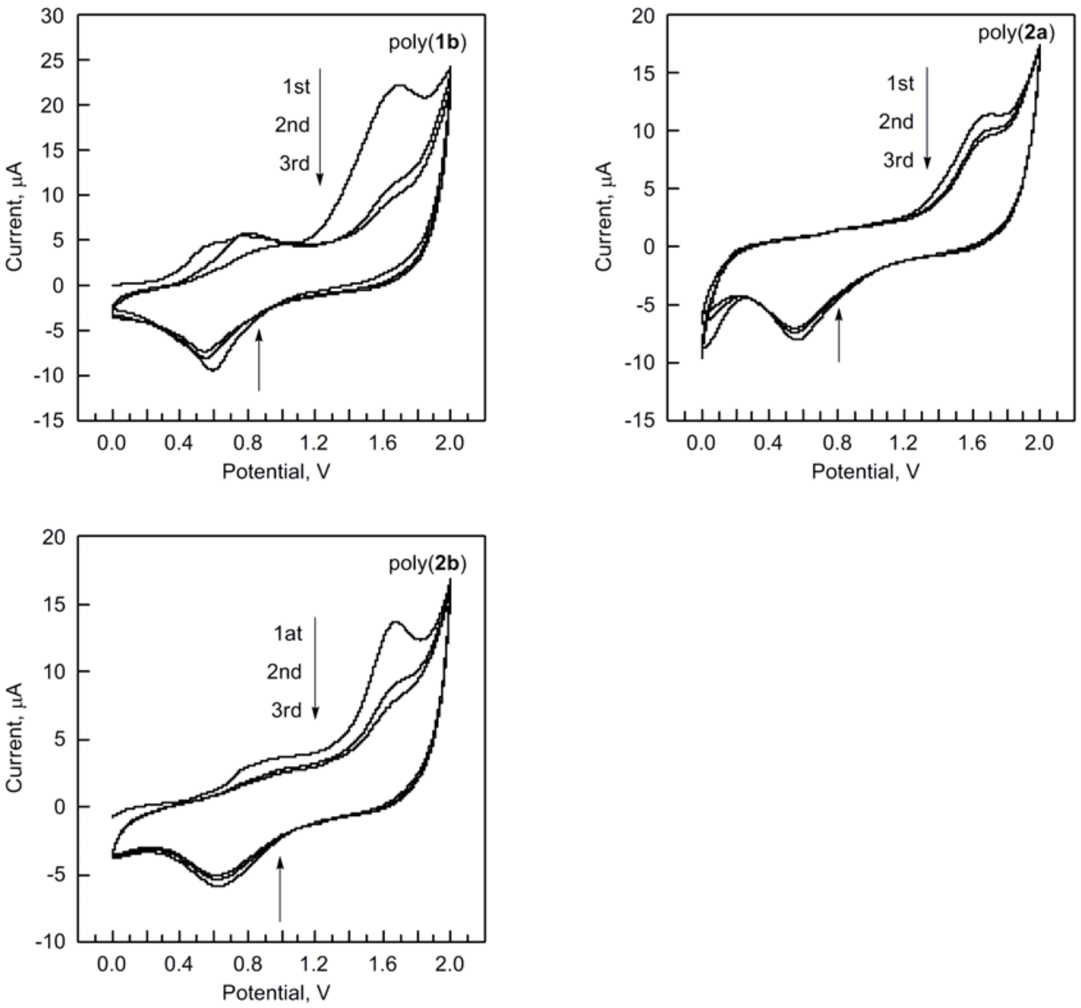


Figure 6. Cyclic voltammograms of poly(**1b**), poly(**2a**), and poly(**2b**) (1.0 mM) measured in CH_2Cl_2 solution in the presence of TBAP (tetrabutylammonium perchlorate) (0.10 M) with consecutive scans at 0.1 V/s.

having triphenylamine moieties. The reduction peaks of poly(**2a**) did not increase, indicating that the dimerization at 3- or 6-position of carbazole did not occur.

Conclusions

This chapter has revealed that some of diphenylacetylenes bearing tertiary amine moieties, such as diphenylamine, carbazole, and indole, polymerize with tantalum catalyst system. This is the first example of polymerization of diphenylacetylenes having triphenylamine and indole moieties. The monomer with cyclohexylphenylamine substituent, having high electron density on the nitrogen atom, could not polymerize indicating that the polymerizability is largely affected by the electron density on the nitrogen atom. A few of the present series of polymers could be fabricated into free-standing membranes and poly(**2f**) and poly(**4b**) exhibited good CO_2 separation performance, owing to the affinity of polar amine groups for carbon dioxide. Some polymers displayed absorption maxima around 700 nm in UV-Vis spectra by applying voltage, which is explained by the formation of low energy-level excited states of radical cations.

Experimental Section

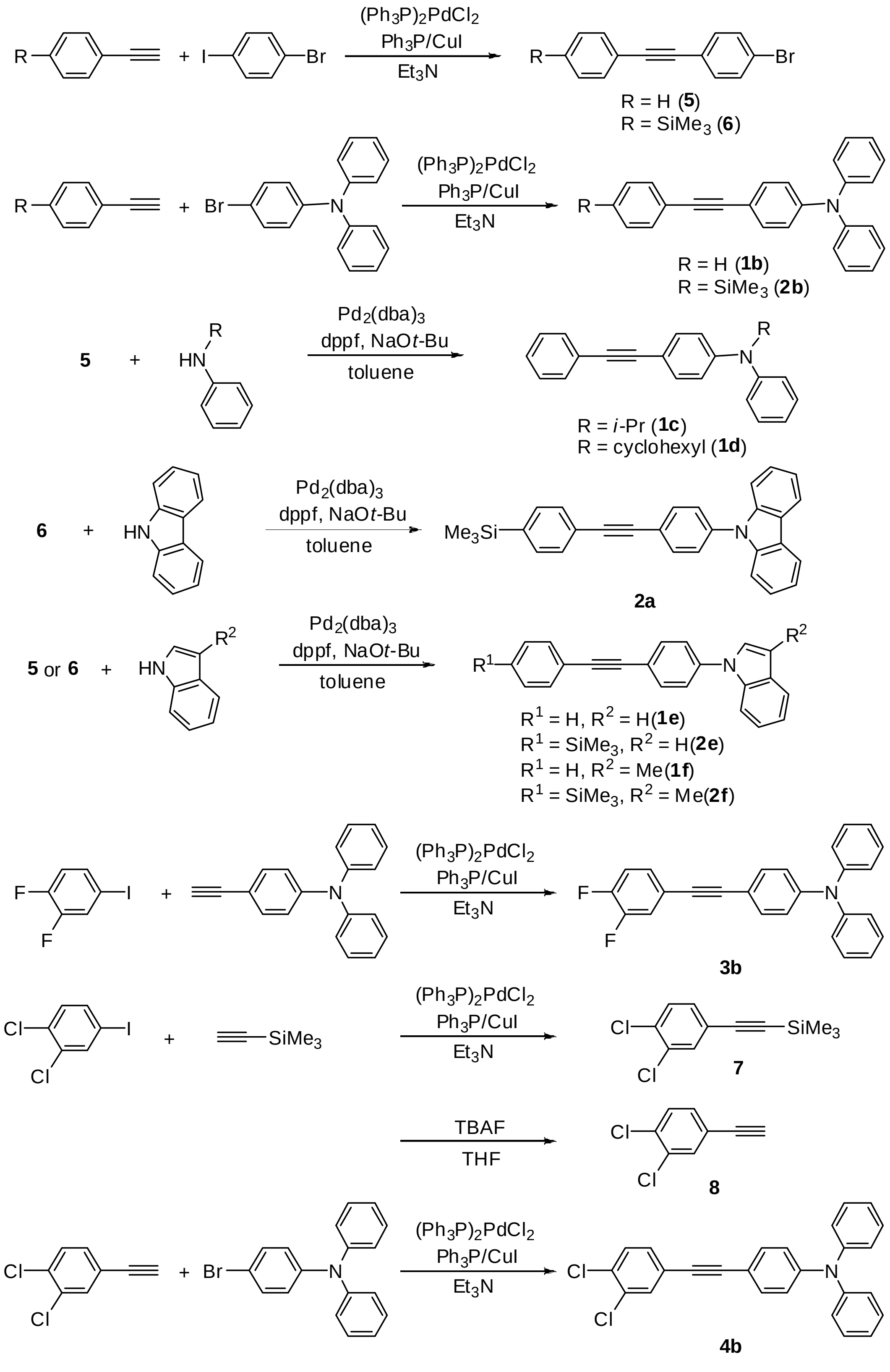
Measurements. The molecular weights of polymers were estimated by gel permeation chromatography ($CHCl_3$ as eluent, Showa Denko Shodex K-805, K-806, and K-807, polystyrene calibration). IR spectra were recorded on a Shimadzu FT/IR-4100 spectrophotometer. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in $CDCl_3$ on a JEOL EX-400 spectrometer. Chemical shifts (δ) for ^1H and ^{13}C are referenced to the resonances of the internal solvent and shown relative to tetramethylsilane (TMS). Thermogravimetric analyses (TGA) were conducted in air with a Perkin-Elmer TGA7 thermal analyzer. Ultraviolet-Visible (UV-Vis) and emission spectra were measured on Jasco V-550 and FP-750 spectrophotometers, respectively. Melting points (mp) were determined on a Yanaco micro melting point apparatus. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center. Cyclic voltammograms were measured on an HCH Instruments electrochemical analyzer ALS600A-n. The measurements were carried out with a modified ITO substrate as the working electrode coupled with a Pt plate counter and Ag/AgCl reference electrode, with a solution of a polymer (1 mM) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in CH_2Cl_2. UV-Vis spectra of polymer films under application of voltage were measured as follows. A polymer solution (0.2 M in $CHCl_3$) was spin coated on an ITO electrode at a spin rate of 1000 rpm, and the electrode was dried under vacuum at 50 °C for 16 h. It was immersed in a solution of TBAP (0.2 M) in acetonitrile in a quartz cell. UV-Vis absorption spectra of the cell were recorded under application of voltage from 0 to 2500 mV with respect to an Ag/AgCl (saturated) reference electrode. The voltage was scanned anodically, and 5-min equilibration time was taken before each spectral scan to minimize the transient effect. The applied voltages reported herein were calibrated using ferrocene as a standard.

Materials and Methods. $TaCl_5$ (Strem) as catalyst was used as received, while *n*-Bu_4Sn (Wako) as cocatalyst was purified by distillation before using. Phenylacetylene (Aldrich), triphenylamine (Aldrich), triethylamine (Wako), triphenylphosphine (Wako), copper iodide (Wako), Pd_2(dibenzylideneacetone)$_3$ ($Pd_2(dba)_3$, Aldrich), 1,4-bis(diphenylphosphino)ferrocene (dppf, Aldrich), carbazole (Aldrich), indole (Wako), 3-methylindole (Wako), sodium *tert*-butoxide (Wako), *N*-cyclohexyaniline (Wako), *N*-isopropylaniline (Wako), 1 M tetrabutylammonium fluoride (TBAF) solution in THF (Wako), 3,4-difluoroiodobenzene (Wako), 3,3-dichloroiodobenzene (Wako) and 4-bromoiodobenzene (Wako) were used without further purification. Toluene and cyclohexane as polymerization solvents were purified by distillation. 4-(Trimethylsilyl)phenylacetylene[14] and 4-bromophenyldiphenylamine[15] were prepared according to the literature procedures.

Synthesis of Monomers. Monomers were synthesized according to Scheme 2 referring to the literature.[16] The details of the synthetic procedure and analytical data are as follows.

1-(4-Bromophenyl)-2-phenylacetylene (5). A 1 L three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and flushed with nitrogen. 4-Bromoiodobenzene (25.0 g, 88.4 mmol), bis(triphenylphosphine)palladium dichloride (620 mg, 0.884 mmol), copper iodide (1.01 g, 5.30 mmol), triphenylphosphine (925 mg, 3.54 mmol), and triethylamine (500 mL) were placed in the flask. Then, phenylacetylene (9.03 g, 88.4 mmol) in

Scheme 2. Synthesis of Monomers 1–4.



triethylamine (20.0 mL) was added and the reaction mixture was stirred overnight at room temperature. After the triethylamine in the reaction mixture was evaporated, diethyl ether (500 mL) was added, and then the insoluble salt was filtered off. The solution was washed with 1 M hydrochloric acid (500 mL) and then with water (500 mL). The ethereal solution was dried over anhydrous sodium sulfate followed by the rotary evaporation of ether. The purification of the crude product by flash column chromatography (eluent: hexane) provided the desired product. Yield 96%, white solid; ^{1}H NMR ($CDCl_3$, ppm): 7.58–7.42 (m, 5H, Ar), 7.42–7.28 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, ppm): 133.0, 131.6, 131.5, 128.5, 128.3, 122.9, 122.4, 122.2, 90.5, 88.3.

1-(4-Bromophenyl)-2-(4-trimethylsilyl)phenylacetylene (6). The compound was synthesized from 4-(trimethylsilyl)phenylacetylene in a manner similar to **5**. Yield 95%, white solid; ^{1}H NMR ($CDCl_3$, ppm): 7.55–7.42 (m, 6H, Ar), 7.37 (d, 2H, Ar), 0.27 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, ppm): 141.4, 133.2, 133.0, 131.6, 130.6, 123.1, 122.4, 122.3, 90.7, 88.7, –1.3.

1-(4-*N,N*-Diphenylamino)phenyl-2-phenylacetylene (1b). A 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and was flushed with hydrogen. 4-bromophenyldiphenylamine (13.0 g, 40.0 mmol), bis(triphenylphosphine)palladium dichloride (140 mg, 0.200 mmol), copper iodide (229 mg, 1.20 mmol), triphenylphosphine (210 mg, 0.800 mmol), and triethylamine (300 mL) were placed in the flask. Then, phenylacetylene (4.09 g, 40.0 mmol) in triethylamine (20.0 mL) was added and the reaction mixture was stirred overnight. After the triethylamine in the reaction mixture was evaporated, ether (300 mL) was added, and then the insoluble salt was filtered off. The solution was washed with 1 N hydrochloric acid and then with water. The ethereal solution was dried over anhydrous sodium sulfate followed by the rotary evaporation of ether. The purification of the crude product by flash column chromatography (eluent: hexane) provided the desired product. Yield 46%, white solid; mp 103.5–104.5 °C; IR (KBr): 3052, 3036, 2202, 1586, 1488, 1321, 1279, 1176, 1071, 833, 755, 689 cm^{-1}. ^{1}H NMR

($CDCl_3$, ppm): 7.47 (d, 2H, Ar), 7.34 (d, 2H, Ar), 7.28–7.16 (m, 7H, Ar), 7.10–7.04 (m, 4H, Ar), 7.04–6.93 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, ppm): 147.7, 147.0, 132.4, 131.9, 129.3, 128.2, 127.8, 124.8, 123.5, 122.3, 122.1, 116.0, 89.7, 88.6. Anal. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.39; H, 5.64; N, 4.02.

1-(4-*N*,*N*-Diphenylamino)phenyl-2-(4-trimethylsilyl)phenylacetylene (2b). The compound was synthesized from 4-(trimethylsilyl)phenylacetylene in a manner similar to **1a**. Yield 40%, pale yellow solid; mp 46.1–47.1 °C; IR (KBr): 3061, 3034, 2952, 2893, 2211, 1588, 1509, 1494, 1279, 1248, 1100, 838, 753, 695 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 7.26–7.18 (m, 4H, Ar), 7.15 (d, 2H, Ar), 7.05–6.91 (m, 4H, Ar), 6.90–6.80 (m, 4H, Ar), 6.80–6.68 (m, 4H, Ar), 0.28 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, ppm): 147.7, 147.1, 140.3, 133.1, 132.5, 130.5, 129.3, 124.8, 123.9, 123.4, 122.2, 116.1, 90.1, 88.9, –1.2. Anal. Calcd for $C_{29}H_{27}NSi$: C, 83.40; H, 6.52; N, 3.35. Found: C, 83.15; H, 6.78; N, 3.20.

1-(4-*N*-Isopropyl-*N*-phenylamino)phenyl-2-phenylacetylene (1c). A 300 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar and was flushed with nitrogen. 1-(4-bromophenyl)-2-phenylacetylene (2.57 g, 10.0 mmol), $Pd_2(dba)_3$ (183 mg, 0.200 mmol), potassium *tert*-butoxide (1.92 g, 20.0 mmol), dppf (166 mg, 0.300 mmol) and toluene (100 mL) were placed in the flask. Then, *N*-isopropylaniline (1.35 g, 10.0 mmol) was added with a syringe and the reaction mixture was heated to reflux for 24 h. After cooling, the reaction solution was filtered off and the solid was washed with ether (50 mL). The solution was washed with water (200 mL) and the organic layer was dried over anhydrous sodium sulfate followed by the rotary evaporation of ether. Purification of the crude product by flash column chromatography (eluent: hexane) provided the desired product. Yield 41%, white solid; mp 152.9–153.4 °C; IR (KBr): 2988, 2973, 2207, 1587, 1513, 1493, 1320, 1228, 1198, 1106, 821, 754, 707, 689 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 7.57–7.19 (m, 10H, Ar), 7.05 (d, 2H, Ar), 6.59 (d, 2H, Ar), 4.33 (sep, 1H, $NCHMe_2$), 1.16 (d, 6H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): 148.2, 143.0, 132.4, 131.2, 129.4, 128.9, 128.2, 127.4, 125.4, 120.5, 116.1, 111.9, 90.2, 87.6, 50.0, 20.9. Anal. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50. Found: C, 88.52; H, 7.01; N, 4.51.

1-(4-*N*-Cyclohexyl-*N*-phenylamino)phenyl-2-phenylacetylene (1d). The compound was synthesized from *N*-isopropylaniline in a manner similar to **1c**. Yield 28%, white solid; mp 107.8–108.6 °C; IR (KBr): 3056, 3034, 2930, 2853, 2206, 1882, 1586, 1512, 1491, 1383, 1338, 1299, 1136, 1075, 818, 753, 706 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 7.47 (m, 2H, Ar), 7.42–7.17 (m, 8H, Ar), 7.02 (m, 2H, Ar), 6.54 (m, 2H, Ar), 3.85–3.78 (m, 1H, NCH<), 2.05–0.85 (m, 10H, CH_2). ^{13}C NMR ($CDCl_3$, ppm): 148.3, 143.4, 132.4, 131.2, 129.4, 129.0, 128.1, 127.4, 125.5, 123.9, 115.8, 111.8, 90.4, 87.6, 56.8, 31.7, 26.1, 25.7. Anal. Calcd for $C_{26}H_{25}N$: C, 88.85; H, 7.17; N, 3.99. Found: C, 88.61; H, 7.25; N, 3.96.

1-{4-(9-Carbazolyl)}phenyl-2-(4-trimethylsilyl)phenylacetylene (2a). The compound was synthesized from carbazole and **6** in a manner similar to **1c**. Yield 37%, pale brown solid; mp 169.0–170.0 °C; IR (KBr): 3419, 3049, 2952, 2893, 2216, 1924, 1592, 1515, 1452, 1314, 1232, 1099, 854, 838, 823, 750, 724 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 8.13 (d, 2H, Ar), 7.74 (d, 2H, Ar), 7.67–7.17 (m, 14H, Ar), 0.29 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, ppm): 142.3, 141.4, 134.2, 134.0, 131.6, 127.7, 126.9, 126.7, 124.4, 121.2, 121.1, 120.3, 111.4, 110.6, 91.4, 89.9, –0.3. Anal. Calcd for $C_{29}H_{25}NSi$: C, 83.81; H, 6.06; N, 3.37. Found: C, 83.43; H, 6.09; N, 3.65.

1-{4-(1-Indolyl)}phenyl-2-phenylacetylene (1e). The compound was synthesized from indole in a manner similar to **1c**. Yield 68%, white solid; mp 95.5–96.2 °C; IR (KBr): 3131, 3044, 2335, 1717, 1593, 1521, 1455, 1335, 1213, 1137, 840, 760, 744, 725, 688 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 7.75–7.00 (m, 14H, Ar), 6.57 (d, 1H, Ar). ^{13}C NMR ($CDCl_3$, ppm): 139.4, 135.5, 132.8, 131.6, 129.5, 128.4, 127.5, 123.8, 123.0, 122.6, 121.2, 121.1, 120.6, 110.5, 104.2, 90.1, 88.7. Anal. Calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77. Found: C, 90.33; H, 5.26; N, 4.84.

1-{4-(1-Indolyl)}phenyl-2-(4-trimethylsilyl)phenylacetylene (2e). The compound was synthesized from indole and **6** in a manner similar to **1c**. Yield 93%, pale yellow solid; mp 125.0–126.0 °C; IR (KBr): 3062, 3025, 2950, 2893, 2216, 1922, 1592, 1518, 1454, 1335, 1248, 1210, 1132, 1102, 839, 741 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.70–7.38 (m, 10H, Ar), 7.35–7.10 (m, 3H, Ar), 6.68 (d, 1H, Ar), 0.31 (s, 9H, SiCH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 141.3, 139.5, 135.6, 133.3, 132.9, 130.7, 129.5, 127.6, 123.8, 123.3, 122.6, 121.2, 121.2, 120.6, 110.5, 104.2, 90.3, 89.0, –1.2. Anal. Calcd for $C_{25}H_{23}NSi$: C, 82.14; H, 6.34; N, 3.83. Found: C, 82.38; H, 6.49; N, 3.86.

1-{4-(3-Methyl-1-indolyl)}phenyl-2-phenylacetylene (1f). The compound was synthesized from 3-methylindole in a manner similar to **1c**. Yield 83%, white solid; mp 94.8–95.6 °C; IR (KBr): 3057, 3029, 2914, 2857, 2216, 1918, 1594, 1518, 1455, 1356, 1217, 1104, 840, 754, 736, 690 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.72–7.60 (m, 3H, Ar), 7.60–7.52 (m, 3H, Ar), 7.52–7.44 (m, 2H, Ar), 7.44–7.30 (m, 3H, Ar), 7.30–7.15 (m, 3H, Ar), 2.38 (s, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 139.7, 135.7, 132.8, 131.6, 130.0, 128.4, 128.3, 125.0, 123.4, 123.1, 122.6, 120.5, 120.1, 119.3, 113.5, 110.4, 89.9, 88.8, 9.6. Anal. Calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56. Found: C, 90.03; H, 5.69; N, 4.63.

1-{4-(3-Methyl-1-indolyl)}phenyl-2-(4-trimethylsilyl)phenylacetylene (2f). The compound was synthesized from 3-methylindole and **6** in a manner similar to **1c**. Yield 52%, pale yellow solid; mp 134.2–135.2 °C; IR (KBr): 3062, 3012, 2958, 2913, 2856, 2212, 1912, 1592, 1515, 1456, 1388, 1241, 1101, 839, 739 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 7.70–7.41 (m, 10H, Ar), 7.27–7.10 (m, 3H, Ar), 2.38 (s, 3H, CH$_3$), 0.28 (s, 9H, SiCH$_3$). ^{13}C NMR (CDCl$_3$, ppm): 141.2, 139.7, 135.7, 133.2, 132.9, 130.6, 130.0, 125.1, 123.4, 122.6, 120.6, 120.1, 119.3, 113.5, 110.4, 90.1, 89.2, 9.6. Anal. Calcd for $C_{26}H_{25}NSi$: C, 82.27; H, 6.64; N, 3.69. Found: C, 82.12; H, 6.92; N, 3.60.

1-(4-*N*,*N*-Diphenylamino)phenyl-2-(3,4-difluorophenyl)acetylene (3b). The compound was synthesized from 3,4-difluoroiodobenzene and 4-(*N*,*N*-diphenylamino)phenylacetylene in a manner similar to **1b**. Yield 50%, pale yellow solid; mp 106.2–107.2 °C; IR (KBr): 3064, 3037, 1893, 1592, 1516, 1489, 1416, 1265, 1102, 948, 872, 749, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): 7.36–7.15 (m, 8H, Ar), 7.15–7.01 (m, 7H, Ar), 7.01–6.94 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, ppm): 151.3 (dd), 148.6 (dd), 148.2, 147.0, 132.5, 129.4, 127.9 (dd), 125.1, 123.7, 122.0, 120.5 (dd), 120.2 (d), 117.4 (d), 115.1, 90.2, 86.4. Anal. Calcd for $C_{26}H_{17}F_2N$: C, 81.87; H, 4.49; N, 3.67. Found: C, 81.62; H, 4.77; N, 3.64.

1-(3,4-Dichlorophenyl)-2-trimethylsilylacetylene (7). The compound was synthesized from 3,4-dichloroiodobenzene and trimethylsilylacetylene in a manner similar to **1b**. Yield 96%, pale yellow solid; ^{1}H NMR ($CDCl_3$, ppm): 7.54 (s, 1H, Ar), 7.35 (d, 1H, Ar), 7.26, (d, 1H, Ar), 0.25 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$, ppm): 133.5, 132.8, 132.4, 131.0, 130.2, 123.1, 102.4, 96.7, –0.2.

3,4-Dichlorophenylacetylene (8). The compound **7** (16 g, 66 mmol) was dissolved in THF (400 mL), and aq. 1 M TBAF in THF (66 mL) was added to the solution. The resulting mixture was stirred overnight. THF was removed by evaporation, and the residue was dissolved in ether (250 mL) and washed with water (250 mL × 3). The organic layer was dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation to give pale yellow liquid. It was purified by silica gel column chromatography eluted with hexane. Yield 42%, colorless liquid; ^{1}H NMR ($CDCl_3$, ppm): 7.57 (s, 1H, Ar), 7.39 (d, 1H, Ar), 7.27, (d, 1H, Ar), 3.14 (s, 1H, ≡CH). ^{13}C NMR ($CDCl_3$, ppm): 133.8, 133.4, 132.6, 131.2, 130.4, 122.0, 81.3, 79.2.

1-(4-*N*,*N*-Diphenylamino)phenyl-2-(3,4-dichlorophenyl)acetylene (4b). The compound was synthesized from **8** and 4-bromo-*N*.*N*-diphenylaniline in a manner similar to **1b**. Yield 26%, pale yellow solid; mp 152.8–153.8 °C; IR (KBr): 3035, 2222, 2193, 1584, 1508, 1486, 1281, 1179, 1121, 1028, 877, 841, 819, 755, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): 7.63–7.50 (d, 1H, Ar), 7.44–7.15 (m, 9H, Ar), 7.15–7.12 (m, 5H, Ar), 7.12–6.88 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, ppm): 148.3, 147.0, 132.9, 132.5, 132.4, 130.5, 130.3, 129.4, 125.1, 124.1, 123.7, 123.6, 121.9, 114.9, 91.8, 86.3. Anal. Calcd for $C_{26}H_{17}Cl_2N$: C, 75.37; H, 4.14; N, 3.38. Found: C, 75.17; H, 4.27; N, 3.20.

Polymerization. Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen at 80 °C for 24 h under the following conditions: $[M]_0 = 0.20$ M, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM. The detailed procedure of polymerization is as follows: A monomer solution was prepared in a Schlenk tube by mixing monomer **1b** (138 mg) and toluene (1.0 mL). Another Schlenk tube was charged with $TaCl_5$ (14 mg), n-Bu_4Sn (26 μL), and toluene (1.0 mL); this catalyst solution was aged at 80 °C for 10 min. Then the monomer solution was added to the catalyst solution. Polymerization was carried out at 80 °C for 24 h, which was quenched with a small amount of methanol. The resulting polymer was isolated by precipitation into a large excess of methanol and its yield was determined by gravimetry.

Membrane Fabrication. Membranes (thickness ca. 100 μm) of poly(**1b**), poly(**2a**), poly(**2b**), poly(**2f**), poly(**3b**), and poly(**4b**) were fabricated by casting toluene solution of the polymers (concentration ca. 1.0 wt %) onto a flat-bottomed Petri dish. The dish was covered with a glass vessel to retard the rate of solvent evaporation (ca. 3–5 days).

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Chapter 5

Synthesis and Properties of Polynorbornenes Bearing Oligomeric Siloxane Pendant Groups

Abstract

The ring-opening metathesis polymerization (ROMP) of norbornene derivatives **1–5** bearing oligomeric siloxane pendant groups was carried out with Grubbs 1st and 2nd generation, and Grubbs-Hoveyda ruthenium (Ru) catalysts. Monomer 1 gave high-molecular-weight polymers (M_n ca. 27 000–180 000) in high yields (80–100%). Monomers **2–5** also polymerized with Ru carbene catalysts to give high-molecular-weight polymers (M_n ca. 34 000–240 000) in high yields (66–100%). The onset temperatures of weight loss (T_0) of the polymers were 180–250 °C. The glass transition temperatures (T_g) of poly(**1**) and poly(**2**) bearing branched siloxane linkages were near or higher than room temperature (27 and 101 °C). Meanwhile, the T_g's of poly(**3**)–poly(**5**) bearing linear siloxane linkages were much lower (–115 ~ –23 °C), and decreased with increasing length of the siloxane linkages. Poly(**1**) and poly(**2**) were hydrogenated completely, which was confirmed by ^{1}H NMR spectroscopy. The free-standing membranes of poly(**1**) and poly(**2**) showed high gas permeability; especially poly(**2**) is the most permeable to various gases among ROMP-polynorbornene derivatives reported so far.

Introduction

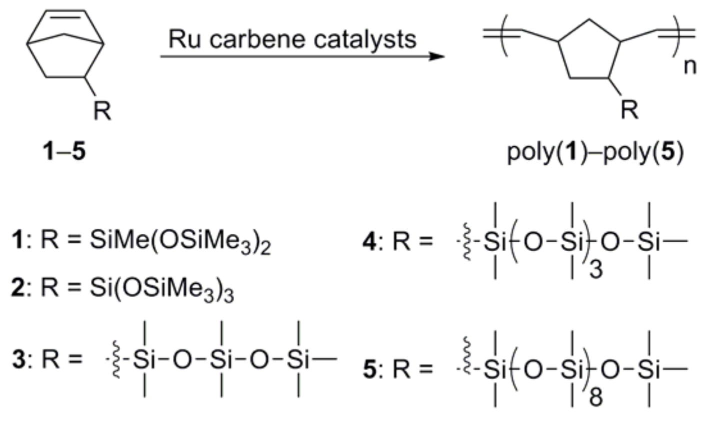
Olefin metathesis reaction is one of the most useful and efficient methods in organic and polymer syntheses due to the formation of new carbon–carbon double bonds. Titanium, tantalum, molybdenum, tungsten, and ruthenium catalysts are well-known for olefin metathesis reactions.[1] However, transition metal catalysts of groups 4–6 are readily deactivated under air and moisture and by polar functional groups in substrates and solvents. On the other hand, catalysts based on ruthenium (Ru), a late transition metal of group 8, can be handled in air and used for substrates having polar functional groups and/or in polar and protic solvents including water.[2] These advantages allow a wide variety of applications of Ru catalysts.

Ru carbene catalysts show high activity for olefin metathesis, and they are widely applied not only to organic reactions such as ring-closing metathesis (RCM), cross metathesis (CM), and ring-opening cross metathesis (ROCM) but also to polymer syntheses including ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization.[3] In particular, cycloolefins with large ring strain readily polymerize with Ru carbene catalysts, and their living polymerization has been achieved by using suitable Ru catalysts.[4] There are few limitations about the kind of substituents in the monomer in the Ru-catalyzed polymerization of norbornenes due to excellent functional group tolerance of the catalysts.

The siloxane (Si–O–Si) linkage is characterized by unique properties such as high flexibility and high thermal stability. Thus, siloxane-containing polymers have been gathering attentions as interesting functional and high-performance polymers, especially with respect to their excellent thermal properties and applications to gas and liquid separation membranes.[5] Poly(dimethylsiloxane) is a rubbery polymer whose glass transition temperature (T_g) is about –125 °C, and it displays high gas permeability (P_{O_2} = 800 barrers).[6] Various polymers carrying dimethylsiloxane polymeric and/or oligomeric moieties have also been developed.[7] Polystyrenes with several trimethylsiloxy groups are more gas-permeable than are polystyrene and poly{(*p*-trimethylsilyl)styrene} because gas molecules easily diffuse in the former membranes due to the high local mobility of siloxane linkage (e.g., poly[*p*-{bis(trimethylsiloxy)methylsilyl}styrene]: $P_{\mathrm{O_2}}$ = 72 barrers, $P_{\mathrm{O_2}}/P_{\mathrm{N_2}}$ = 2.8; polystyrene: $P_{\mathrm{O_2}}$ = 1 barrer, $P_{\mathrm{O_2}}/P_{\mathrm{N_2}}$ = 5.5; poly{*p*-(trimethylsilyl)styrene}: $P_{\mathrm{O_2}}$ = 14 barrers, $P_{\mathrm{O_2}}/P_{\mathrm{N_2}}$ = 3.4).[8] The gas permeation properties of polynorbornene derivatives have been studied.[9] Polynorbornenes bearing trimethylsilyl or trifluoromethyl groups are more gas-permeable than the unsubstituted counterparts, but their permeability coefficients are not very large compared to those of the other gas-permeable polymers.[10] Although several examples of polynorbornene carrying siloxane pendant groups have been reported,[11] gas permeation properties of theses polymers have not been investigated so far.

This chapter deals with the synthesis of polynorbornene derivatives poly(**1**)–poly(**5**) bearing dimethylsiloxane oligomeric pendant groups via ROMP (Scheme 1), along with the hydrogenation of poly(**1**) and poly(**2**). Thermal properties and gas permeation properties of the formed polymers have also been investigated.

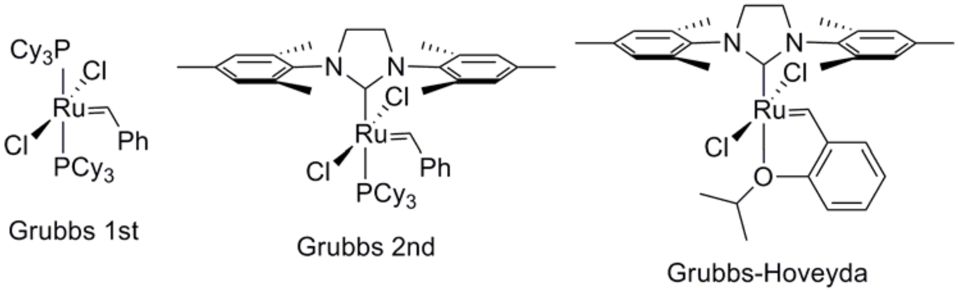
Scheme 1. Polymerization of 1–5



Results and Discussion

Polymerization. The polymerization of monomer **1** with Grubbs 1st generation, 2nd generation, and Grubbs-Hoveyda catalysts shown in Chart 1 was examined in toluene and THF (Table 1). Polymers were obtained almost quantitatively under all the conditions examined. The polymers formed by the polymerization with Grubbs 2nd generation (runs 3 and 4) and Grubbs-Hoveyda catalysts (runs 5 and 6) possessed rather broad molecular weight distributions (MWD), suggesting the proceeding of intra- and intermacromolecular metathesis reactions. The number-average molecular weight (M_n) of the polymer obtained by the

Chart 1. Ruthenium Catalysts



Grubbs 1st

Grubbs 2nd

Grubbs-Hoveyda

Table 1. Polymerization of Monomer 1 with Various Ru Carbene Catalysts[a]

			polymer[b]		
run	catalyst	solvent	yield, %	M_n[c]	M_w/M_n[c]
1	Grubbs 1st	toluene	96	114 300	2.74
2	Grubbs 1st	THF	92	126 900	2.40
3	Grubbs 2nd	toluene	96	123 300	3.96
4	Grubbs 2nd	THF	91	146 600	5.09
5	Grubbs-Hoveyda	toluene	100	27 400	7.32
6	Grubbs-Hoveyda	THF	99	183 200	5.46

[a] At 40 °C for 2.5 h; $[M]_0 = 0.20$ M, [Ru] = 1.0 mM. [b] Methanol-insoluble part. [c] Measured by GPC (THF, PSt).

polymerization with Grubbs-Hoveyda catalyst in toluene (run 5) was the lowest and the MWD was the broadest.

The effects of monomer and catalyst concentrations on the polymerization were examined at 40 °C (Table 2). Poly(**1**) formed by the polymerization at $[M]_0$ = 0.10 M was insoluble in common organic solvents (runs 1–3), presumably because the M_n was very high. The decrease of $[M]_0$ to 0.050 M resulted in the formation of soluble polymers when [Ru] was 0.20 mM and lower. The monomer/catalyst ratio hardly affected the M_n of the formed polymers, while the MWD was broad, indicating that the polymerization of monomer **1** did not proceed in a living fashion. In general, the living polymerization of norbornene derivatives can be achieved at low temperature (e.g., –20 ºC) due to their high polymerizability based on large ring strains, and the Grubbs-Hoveyda catalyst does not show high initiation efficiency. These facts seem to be responsible for the non-living character of the present polymerization.

Table 3 shows the results of polymerization of monomers **2**–**5** using Grubbs 1st and 2nd generation catalysts. Monomer **2** gave a polymer insoluble in common

Table 2. Polymerization of Monomer 1 with Grubbs 2nd Generation Catalyst[a]

			polymer[b]		
run	$[M]_0$, M	[Ru], mM	yield, %	M_n[c]	M_w/M_n[c]
1	0.10	0.50	100	—[d]	—[d]
2	0.10	0.20	100	—[d]	—[d]
3	0.10	0.10	100	—[d]	—[d]
4	0.050	0.50	80	—[d]	—[d]
5	0.050	0.20	95	124 300	4.99
6	0.050	0.10	99	110 800	6.54
7	0.050	0.050	100	169 000	5.76

[a] In toluene at 40 °C for 20 min. [b] Methanol-insoluble part. [c] Measured by GPC (THF, PSt). [d] Insoluble in common organic solvents.

Table 3. Polymerization of Monomers 2–5[a]

		polymer[b]		
monomer	catalyst	yield, %	M_n[c]	M_w/M_n[c]
2	Grubbs 1st	95	240 000	2.51
3	Grubbs 1st	99	—[d]	—[d]
4	Grubbs 2nd	100	142 000	4.00
5	Grubbs 2nd	66	33 600	1.64

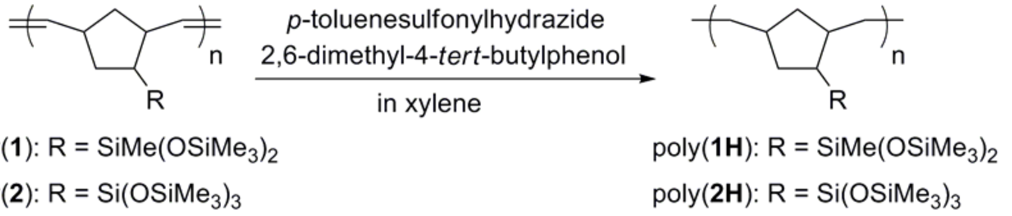
[a] In toluene at 30 °C for 15 min; $[M]_0$ = 0.050 M, [Ru] = 0.50 mM. [b] Methanol-insoluble part. [c] Measured by GPC (THF, PSt). [d] Insoluble in common organic solvents.

organic solvents with Grubbs 2nd generation and Grubbs-Hoveyda catalysts. On the other hand, Grubbs 1st generation catalyst provided poly(**2**) with a high molecular weight (M_n = 240 000) and good solubility in $CHCl_3$, CH_2Cl_2, toluene, and THF. Solvent-soluble poly(**3**) could not be obtained with any catalyst, although soluble oligomers (M_n < 5 000) formed by the polymerization at a very low catalyst concentration (0.050 mM). Grubbs 1st generation catalyst produced only oligomers from monomer **4**, while Grubbs 2nd generation catalyst gave transparent viscous rubbery poly(**4**). Monomer **5** afforded a polymer with a narrow MWD by using Grubbs 2nd generation catalyst, although it gave no polymer with Grubbs 1st generation catalyst.

It has been reported that the catalytic activities of Grubbs 2nd catalyst generation and Grubbs-Hoveyda catalysts are almost the same each other, while that of Grubbs 1st generation is lower.[12] As mentioned above, the formation of solvent-insoluble polynorbornene and its derivatives is most probably attributable to their high molecular weights. It is likely that the formation of high-molecular-weight polymers is caused by the use of too active catalysts. Considering these facts, the results described above imply that the polymerizability of monomer **3** is the highest, followed by **2**, **4**, and **5**. The reactivity of monomer **1** seems to be almost the same as that of **2**. The monomer reactivity is explicable in terms of both the number of siloxane linkages and the steric effect of the substituent. It is important to choose a catalyst suitable for an individual norbornene monomer to obtain a solvent-soluble polymer in a high yield. Monomers **1**–**5** possessing siloxane linkages did not polymerize with WCl_6–Ph_4Sn and $MoCl_5$–Ph_4Sn catalyst systems.

Hydrogenation of Poly(1) and Poly(2). The hydrogenation of poly(**1**) and poly(**2**) was carried out with *p*-toluenesulfonhydrazide in xylene at 120 °C (Scheme 2). After the reaction for 12 h, hydrogenated poly(**1H**) and poly(**2H**) were isolated by precipitation with methanol. Poly(**1**) and poly(**2**) showed ^{1}H NMR signals assignable to *cis* and *trans* olefinic protons at 5.0–5.7 ppm, while poly(**1H**) and poly(**2H**) showed

Scheme 2. Hydrogenation of Poly(1) and Poly(2)



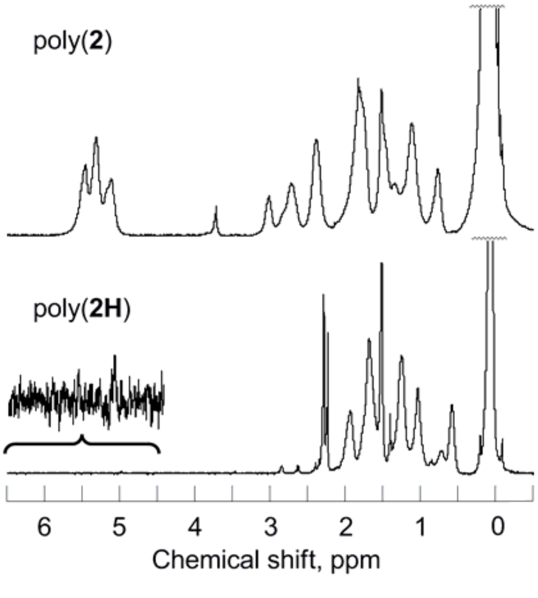


Figure 1. ^{1}H NMR spectra of poly(**2**) and poly(**2H**) measured in $CDCl_3$.

almost no signal in this region (Figure 1), indicating that both poly(**1**) and poly(**2**) were hydrogenated nearly quantitatively. The molecular weights of the hydrogenated polymers scarcely decreased compared to those of the starting polymers [poly(**1**): M_n = 253 800; poly(**1H**): M_n = 245 300; poly(**2**): M_n = 392 900; poly(**2H**): M_n = 337 000].

Thermal Properties. The thermal stability of the formed polymers was examined by TGA in air (Figure 2). The onset temperatures of weight loss (T_0) for all the polymers were 180–250 °C, and ashes composed of silica remained when the polymers were heated in air above 600 °C in all cases.

The glass transition temperatures (T_g) determined by DSC are shown in Table 4. Although no transition point was observed at a scanning rate of 10 °C/min, the increase of rate up to 100 °C/min and above resulted in clear appearance of the T_g peaks.[13] The T_g values were calculated as described in the experimental section. Poly(**1**) having two branched trimethylsiloxy groups showed a T_g at 27 °C, while poly(**2**) with three trimethylsiloxyl groups showed it at a much higher temperature (101 °C). The T_g values of poly(**3**), poly(**4**), and poly(**5**) having linear oligo(dimethylsiloxane) moieties were lower (–23, –89, and –115 °C) than those of poly(**1**) and poly(**2**). The T_g decreased with increasing length of the oligomeric

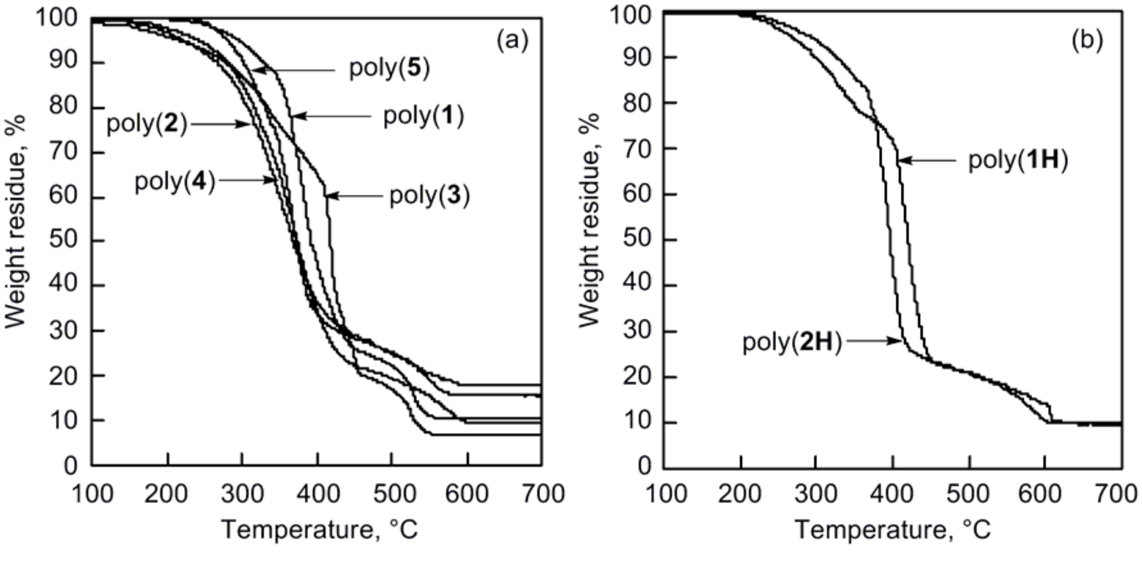


Figure 2. TGA curves of (a) poly(**1**)–poly(**5**) and (b) poly(**1H**) and poly(**2H**) (in air, heating rate 10 °C/min).

Table 4. Glass Transition Temperatures (T_g) of the Polymers[a]

	T_g, °C		T_g, °C
poly(**1**)	27	poly(**1H**)	–12
poly(**2**)	101	poly(**2H**)	62
poly(**3**)	–23	PNB	39
poly(**4**)	–89	PDMS	–126
poly(**5**)	–115		

[a] Determined by DSC.

pendant group, and poly(**5**) bearing decamers of dimethylsiloxane showed almost the same T_g (–115 °C) as that of poly(dimethylsiloxane) (PDMS). The incorporation of linear siloxane pendant groups led to lower T_g than that of polynorbornene (PNB; T_g = 39 °C). Polymers having spherical and/or branched siloxane linkages showed higher T_g values than those of the polymers with linear ones, which is attributable to much higher flexibility of the side groups of the latter polymers. The T_g values of poly(**1H**) and poly(**2H**) were lower than those of precursors [poly(**1**) and poly(**2**)], presumably because the disappearance of double bonds along the polymer backbone led to the enhancement of flexibility.

Gas Permeation Properties. The free-standing membranes of poly(**1**), poly(**2**), and poly(**2H**) could be fabricated by casting from polymer solutions, while the membranes of poly(**3**)–poly(**5**) and poly(**1H**) could not because the T_g values of these polymers were lower than room temperature. Table 5 lists the gas permeation properties of the polymer membranes in this study, along with those of polynorbornene derivatives shown in Chart 2 for comparison. The oxygen permeability coefficient (P_{O_2}) of unsubstituted polynorbornene (PNB) is no more than 2.8 barrers, whereas PTMSNB having trimethylsilyl groups showed a P_{O_2} value almost 10 times higher.[9a] The most oxygen-permeable ROMP-based polynorbornene derivative reported so far is bis(trimethylsilyl)-substituted polynorbornene (PDSNB,

Chart 2. Polynorbornene and Its Derivatives Based on ROMP

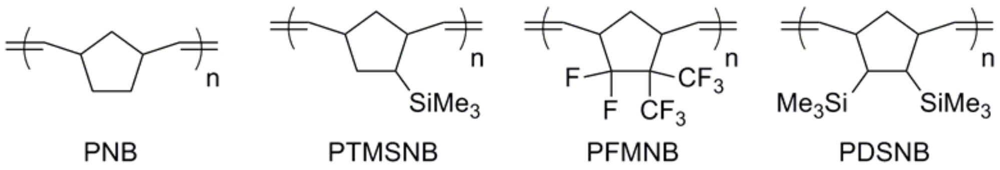

PNB PTMSNB PFMNB PDSNB

Table 5. Gas Permeability Coefficients (*P*) of Poly(1), Poly(2), Poly(2H) and Related ROMP Polymers at 25 °C

polymer	He	H_2	O_2	N_2	CO_2	CH_4	P_{O_2}/P_{N_2}
	P^a						
poly(**1**)	150	230	99	30	430	87	3.3
poly(**2**)	290	430	290	93	910	260	3.1
poly(**2H**)	200	320	160	55	610	160	2.9
PNB[b]	—	21	2.8	1.5	15	2.5	1.9
PTMSNB[c]	—	140	30	7.2	89	8.5	4.2
PFMNB[b]	—	170	50	17	200	13	2.9
PDSNB[c]	240	375	95	25	445	45	3.8

[a] In the unit of barrer (1 barrer = 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)). [b] Data from ref 9c. [c] Data from ref 9a.

P_{O_2} = 95 barrers).[9a] The polymers in the present study showed higher gas permeability, and especially the P_{O_2} of poly(**2**) reached 290 barrers, which is attributable to the presence of two or three trimethylsilyl groups. The gas permeability of poly(**2H**) was lower than that of poly(**2**) as a result of decrease of both main-chain rigidity and affinity to gases after hydrogenation.

Table 6 shows the solubility and diffusion coefficients (*S* and *D*) of poly(**1**) and poly(**2**) along with some polynorbornene derivatives for carbon dioxide and methane gases. The *S* values of both poly(**1**) and poly(**2**) were lower than those of trimethylsilyl or trifluoromethyl-containing polymers (PTMSNB, PFMNB, and

Table 6. Gas Solubility and Diffusion Coefficients (*S* and *D*) at 25 °C

	$S \times 10^{2a}$		$D \times 10^{7b}$	
	CO_2	CH_4	CO_2	CH_4
poly(**1**)	1.0	0.33	42	26
poly(**2**)	1.7	0.65	53	39
PNB[c]	0.96	0.87	1.6	0.36
PTMSNB[d]	5.0	0.78	3.3	1.4
PFMNB[c]	24	3.9	0.84	0.33
PDSNB[d]	8.5	2.6	4.0	1.3

[a] In the units of cm^3 (STP) cm^{-3} $cmHg^{-1}$. [b] In the units of cm^2 s^{-1}. [c] Data from ref 9c. [d] Data from ref 9a.

PDSNB); especially, the *S* value of poly(**1**) for methane gas is approximately one-tenth of that of PFMNB. On the other hand, the *D* values of the present polymers were approximately 10 and 30–100 times larger than those of the reported ones for carbon dioxide and methane, respectively. This suggests that the incorporation of siloxane moieties having large local mobility leads to enhanced gas permeability due to high diffusivity of gases in polymer membranes.

Conclusions

The ROMP of norbornene derivatives bearing branched or linear oligomeric dimethylsiloxane pendant groups was carried out with Grubbs 1st and 2nd generation Grubbs-Hoveyda catalysts. Monomer **1** having two branched siloxane linkages polymerized quantitatively. The monomer/catalyst ratio hardly affected the molecular weight and MWD of the formed polymer, indicating the non-living nature of the polymerization of **1**. Monomers **2**–**5** gave polymers in high yields. Poly(**1**) and poly(**2**) were quantitatively hydrogenated using *p*-toluenesulfonhydrazide keeping the molecular weights. All the polymers exhibited moderate thermal stability (T_0 =

180–250 °C). The T_g decreased with increasing length of the pendant siloxane groups. The oxygen permeability coefficient of poly(**2**) was 290 barrers, which is the largest among the ROMP-polynorbornene derivatives reported so far. This is attributable to the large local mobility of the siloxane pendant groups.

Experimental Section

Instrumentation. The molecular weights of polymers were estimated by gel permeation chromatography (THF as eluent, Showa Denko Shodex KF-805L × 3 polystyrene calibration). ^{1}H NMR (400 MHz) spectra were measured in $CDCl_3$ on a JEOL EX-400 spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C NMR were referenced to the resonances of the internal solvent and shown relative to tetramethylsilane (TMS). Gas permeability coefficients of polymer membranes were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C. Thermogravimetric analyses (TGA) were conducted in air with a Shimadzu TGA-50 thermal analyzer. Differential scanning calorimetry (DSC) analyses were performed using a Perkin-Elmer PYRIS Diamond DSC under a nitrogen atmosphere at scanning rates of 100, 120, 140, 160, and 180 °C/min. Glass transition temperatures extrapolated to the scanning rate of 0 °C/min were calculated by using the following equation (ϕ: scanning rate, C: constant value, E: activation energy, R: gas constant, and T_g: glass transition temperature).[14]

$$\ln \frac{\phi}{T_g^{\,2}} = \mathrm{C} - \frac{E}{RT_g}$$

Materials. Grubbs 2nd generation and Grubbs-Hoveyda catalysts were donated by Materia (USA) and used without further purification. Grubbs 1st generation catalyst was purchased from Aldrich. 5-$\{SiMe(OSiMe_3)_2\}$norbornene [**1**: purity 99% (by GC); bp 108 °C/2 mmHg], 5-$Si(OSiMe_3)_3$norbornene [**2**: purity 90 % (by GC); bp 140–143 °C/15 mmHg], 5-($SiMe_2OSiMe_2OSiMe_3$)norbornene [**3**: purity 98% (by GC); bp 94–96 °C/3 mmHg], 5-$\{SiMe_2(OSiMe_2)_3OSiMe_3\}$norbornene [**4**:

purity 97% (by GC); bp 128–130 °C/3 mmHg], and 5-{$SiMe_2(OSiMe_2)_8OSiMe_3$}norbornene [**5**: purity 88 % (by GC)] were offered by Shin-etsu chemical Co, Ltd. (Japan). Toluene and THF used as solvents for polymerization were distilled by the standard procedures before use.

Polymerization. Unless otherwise specified, polymerizations were carried out in an argon atmosphere. A detailed procedure of polymerization is as follows: A monomer solution was prepared in a Schlenk tube with a three-way stopcock by mixing monomer **1** (1.9 g, 6.0 mmol) and toluene (50 mL), and another Schlenk tube was charged with Grubbs 1st generation catalyst (4.9 mg, 6.0 μmol) and toluene (10 mL). Polymerization was initiated by adding the catalyst solution to the monomer solution, and continued at 30 °C for 30 minutes. Then the reaction was quenched by adding ethyl vinyl ether (0.5 mL, 9.2 mmol), and stirred for 15 minutes. The polymerization mixture was poured into a large amount of methanol, and the polymer precipitated was filtered and dried under vacuum to constant weight. The yield was determined by gravimetry.

Hydrogenation of Polymers. A ROMP polymer (2.0 mmol) was dissolved in xylene (50 mL) in an autoclave. To this solution, *p*-toluenesulfonhydrazide, a hydrogenation agent (2.79 g, 15 mmol; 7.5 equiv to the monomer unit of the polymer), and a trace amount of 2,6-di-*tert*-butyl-4-methylphenol (inhibitor) was added. The solution of polymer and hydrogenation agent was degassed thrice via a freeze-pump-thaw cycle and sealed, and then stirred at 120 °C for 12 h. A hydrogenated polymer was obtained by precipitating with methanol. The polymer was filtered and dried under vacuum to constant weight, whose yield was determined by gravimetry.

Membrane Fabrication. Membranes (thickness ca. 50–80 μm) of poly(**1**), poly(**2**) and poly(**2H**) were fabricated by casting toluene solutions of the polymers (concentration ca. 1.0–2.0 wt %) onto a flat-bottomed Petri dish. The Petri dish was covered with a glass vessel to slow solvent evaporation (ca. 3–5 days).

Gas Diffusivity and Solubility of Polymer Membranes. The gas permeability coefficients (P) were calculated from the slopes of time-pressure curves in the steady state where Fick's law holds.[15] The diffusion coefficients (D) were determined by the time lag method using the following equation:

$$D = l^2/6\theta$$

where l is membrane thickness and θ is time lag, which is given by the intercept of the asymptotic line of the time-pressure curve to the time axis. The solubility coefficients (S) were calculated by using the equation $S = P/D$.

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Part II

Synthesis and Organic Radical Battery Properties of Free Radical-Containing Polymers

Chapter 6

Synthesis, Characterization, and Charge/Discharge Properties of Polynorbornenes Carrying 2,2,6,6-Tetramethylpiperidine-1-oxy (TEMPO) Radicals

Abstract

TEMPO-containing norbornene monomers **1**–**8** (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxy) were synthesized and polymerized via ring-opening metathesis using a ruthenium carbene catalyst. The TEMPO moiety did not inhibit the polymerization, and the monomers gave corresponding polymers in good to high yields. Poly(**2**) and poly(**3**) were soluble in common solvents and possessed high molecular weight, while other polymers were insoluble. The resulting polymers were thermally stable up to ca. 240 °C according to TGA measurements in air. In the case of poly(**1**)–poly(**3**), the charge/discharge capacities of the polymer-based cells were largely dependent on the spatial arrangement of the two TEMPO moieties on each repeating unit. Quite interestingly, the capacity of the poly(**2**)-based cell reached its theoretical value (109 A h/kg) and a large capacity (>90 A h/kg) was retained even at high current densities up to 6 A/g, indicating the possibility of very fast charging (within 1 minute). The cells utilizing the present polymers as cathode-active materials demonstrated excellent cycle life; e.g., the discharge capacities of poly(**2**) and poly(**3**) showed no more than 10% decrement even after 400 cycles.

Introduction

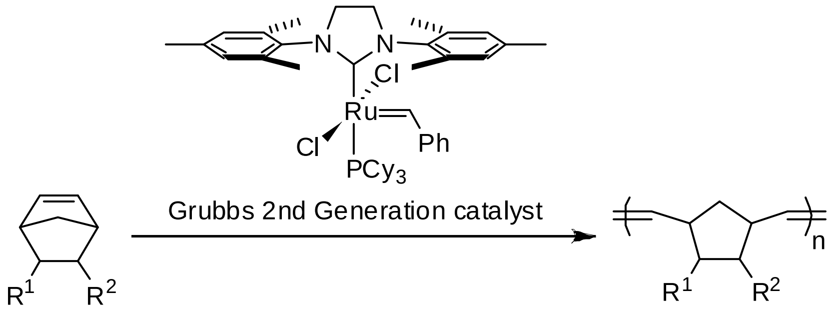
The olefin metathesis reaction has emerged as a powerful technique for the redistribution of carbon-carbon double bonds thus offering a variety of excellent methodologies for the synthesis of organic molecules and novel polymers. In the field of polymer synthesis, ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polycondensation are frequently employed to synthesize a wide range of functionalized polymers.[1] In particular, the recent development of ruthenium-based olefin metathesis catalysts has enabled the polymerization of various cycloolefin monomers possessing ether, ester, amide, alcohol and carboxylic acid moieties owing to their excellent tolerance toward polar functional groups and the use of polar and protic solvents as well.[2] Polynorbornene and its derivatives can be easily obtained by ROMP of norbornene monomers by making use of metathesis catalysts.

Nitroxy radical-containing polymers can be synthesized in two ways; one is the oxidation of amine or hydroxyamine moieties of precursor polymers after the polymerization of monomers possessing these groups, while the other is the direct polymerization of nitroxy radical-containing monomers. As far as the former strategy is concerned, it can make use of not only the ionic and transition metal-catalyzed polymerization but radical polymerization as well; however, it is difficult to achieve quantitative incorporation of free radical moieties into the polymer chain as the formation of free radical is based on the subsequent polymer reaction. On the other hand, although radical polymerization cannot be exploited in the polymerization of radical-containing monomers, the resultant polymers should possess free radicals quantitatively. To date, there have been a few reports concerning the investigation of nitroxy radical-containing polymers, which include poly[4-(*N*-*tert*-butyl-*N*-oxylamino)styrene],[3] poly(methyl methacrylate) labeled with 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO),[4] and TEMPO-containing polyethers.[5] The former two polymers have been synthesized through the polymer reaction, and the latter one has been obtained by direct polymerization of the corresponding monomer. Although the use of transition metal catalysts for the polymerization of radical-containing acetylenic monomers is rare,[6] Rh catalysts have successfully been exploited for the polymerization of monosubstituted acetylenes carrying free radical moieties,[6e] whereas W and Mo catalysts which are well known as metathesis polymerization catalysts are incapable even to effect the polymerization of phenylacetylene in the presence of a stable free radical compound, presumably due to their deactivation by the free radical moieties. It has been reported that the ruthenium carbene complexes are immune to TEMPO and related free radical moieties,[6b–d] and thus can be envisaged as suitable ROMP catalysts for the synthesis of polynorbornenes possessing TEMPO moieties at a high density.

Nitroxy radicals such as TEMPO are well known stable organic radicals finding a variety of applications including spin labels in the study of conformation and structural mobility of biological systems,[7] radical scavengers,[8] and oxidizing agents.[9] Polymers carrying stable organic radicals have also been intensively investigated with respect to electron spin resonance[10] and molecular motion,[11] and frequently employed as functional materials such as polymeric stabilizers,[12] oxidants of alcohols,[6d,13] and spin- and charge-storage materials.[14]

The charge-storage materials based on polyradicals such as TEMPO- and PROXY-carrying (PROXY = 2,2,5,5-tetramethylpyrroline-1-oxy) polymers can be applied as cathode-active materials in organic radical batteries, which exhibit unique characteristics of high power density and quick charge/discharge ability, unlike the lithium ion batteries, and thus expected to serve as novel functional materials. Nakahara et al. have reported the synthesis of poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMA), and the batteries using PTMA as a cathode material have displayed an average discharge voltage of 3.5 V and a discharge capacity of 77 A h/kg which corresponds to 70% of its theoretical value.[15] The author have preliminarily reported the synthesis and charge/discharge properties of a few TEMPO-containing polyacetylene and polynorbornene derivatives, among which the discharge capacity of poly(NB-2,3-*endo,exo*-(COO-4-TEMPO)$_2$) (NB = norbornene) attains the theoretical value (109 A h/kg).[6c] Moreover, the PROXY-containing polyacetylenes and polynorbornenes,[6b] and TEMPO-containing polyacetylenes[6f] have also been investigated and some of these polymers displayed high capacity (up to 117 A h/kg) and quick discharge properties.

The present chapter deals with the synthesis of various TEMPO-carrying polynorbornenes by direct polymerization of the corresponding monomers (Scheme 1) with a ruthenium based metathesis catalyst. Furthermore, the fundamental properties of the resulting polymers and their performance as cathode-active materials in organic radical batteries have been delineated in detail.

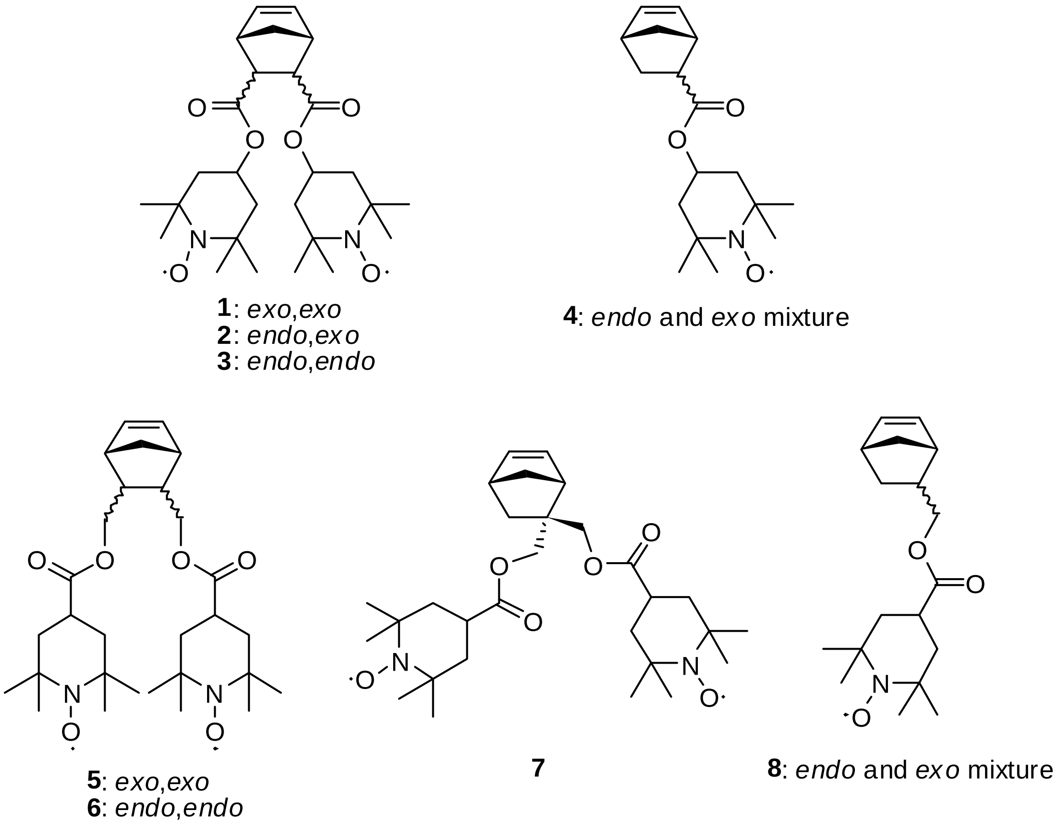


Scheme 1. Polymerization of Norbornenes

Results and Discussion

Monomer Synthesis. Norbornene monomers **1**–**8** (Chart 1) were synthesized by the condensation of anhydride, carboxylic acid, or hydroxy group of norbornene derivatives with hydroxy or carboxylic acid functionality of the TEMPO derivatives (Scheme 2). The attempted synthesis of norbornene-*endo*,*endo*-dicarboxylic acid di-TEMPO ester monomer **3** using 5-norbornene-*endo*-2,3-dicarboxylic anhydride provided a mixture of two isomers, although there had been no such description in the literature.[6d] Since it was impossible to measure the highly resolved ^{1}H and ^{13}C NMR spectra of the isomers due

Chart 1. Structures of Monomers 1–8



1: *exo*,*exo*
2: *endo*,*exo*
3: *endo*,*endo*

4: *endo* and *exo* mixture

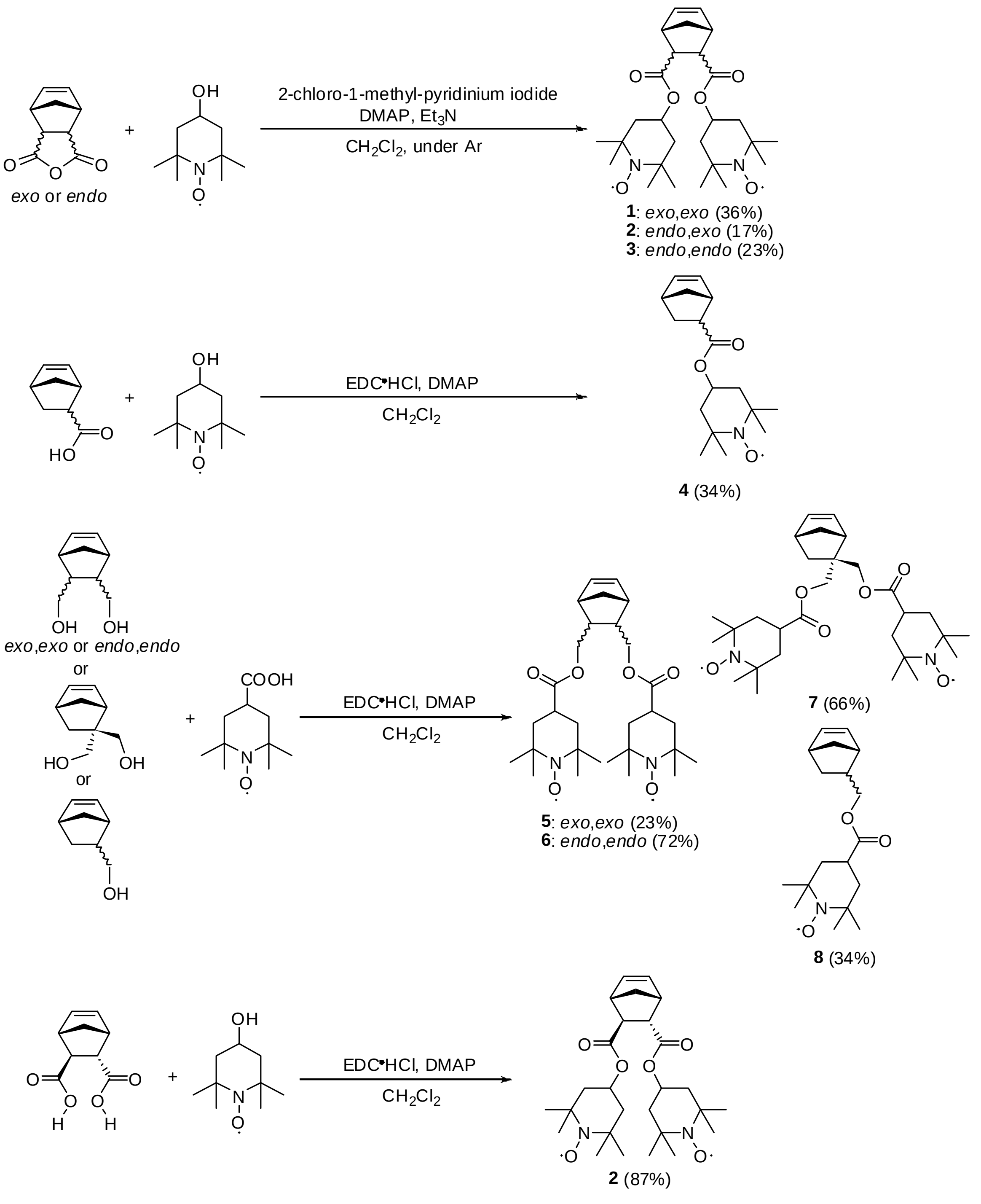
5: *exo*,*exo*
6: *endo*,*endo*

7

8: *endo* and *exo* mixture

to the presence of free radicals, they were converted into the corresponding hydroxy compounds in order to measure their NMR spectra. One hydroxy compound showed single peaks based on the carbonyl and olefinic carbons in the ^{13}C NMR spectrum, from which the *endo* orientation for both ester groups can reasonably be concluded; i.e., it was identified as **3'**. The other exhibited two carbonyl carbon signals and two olefinic carbon signals in the ^{13}C NMR spectrum (see the Experimental Section), thus providing the evidence that one of the ester groups is oriented in *endo* and the other in *exo* configuration. Therefore this compound is identified to be **2'**. Further evidence was obtained by the single-crystal X-ray diffraction analysis. Monomer **2** could afford needle-like crystals, which were too thin to carry out the X-ray crystallographic analysis, while a slow evaporation of a hexane/$CHCl_3$ solution of **3** yielded a single crystal suitable for X-ray analysis. The crystal data of **3** manifested that both the

Scheme 2. Monomer Synthesis



ester groups are oriented in the *endo* configuration. An alternative route for the synthesis of monomer **2** is the condensation of 5-norbornene-2,3-*exo*,*endo*-dicarboxylic acid with two equivalents of 4-hydroxy-TEMPO, which is preferable from the viewpoint of high yield (87%) and no necessity for the isolation of isomers, although the starting compound is somewhat expensive. NMR measurements were also employed to identify monomers **5**–**7**. The structures of monomers **1**–**8** were further confirmed by IR spectra and elemental analysis.

Polymer Synthesis. Table 1 summarizes the conditions and the results of ROMP of the norbornene monomers **1**–**8** using the Grubbs 2nd generation catalyst. Norbornenedicarboxylic acid ester **1** gave the polymer in a high yield (98%), which was insoluble in organic solvents after isolation by precipitation, although the reaction solution was homogeneous during polymerization (run 1 in Table 1). On the other

Table 1. Polymerization of TEMPO-Containing Norbornenes 1–8 with the Grubbs 2nd Generation Catalyst

run	monomer	polymer[c]		
		yield, %	M_n[d]	M_w/M_n[d]
1[a]	**1**	98	—[e]	—[e]
2[b]	**2**	59	185 000	1.92
3[a]	**3**	100	137 000	2.31
4[a]	**4**	100	—[f]	—[f]
5[a]	**5**	88	—[f]	—[f]
6[a]	**6**	72	—[f]	—[f]
7[a]	**7**	92	—[f]	—[f]
8[a]	**8**	96	—[f]	—[f]

[a] In CH_2Cl_2, 45 min, 30 °C; $[M]_0 = 0.50$ M, [Ru] = 5.0 mM. [b] In CH_2Cl_2, 30 min, 30 °C; $[M]_0 = 1.0$ M, [Ru] = 10 mM. [c] MeOH-insoluble part. [d] Determined by GPC (THF, polystyrene calibration). [e] Although the polymerization system was homogeneous, the isolated polymer was insoluble in any common organic solvents. [f] Insoluble in any solvents.

hand, the polymerization of norbornenedicarboxylic acid esters **2** and **3** yielded organosoluble polymers with fairly high molecular weights in 59% and quantitative yields, respectively (runs 2 and 3 in Table 1). Although the polymerization solutions of **4**–**8** were homogeneous at the start (polymerization conditions: in CH_2Cl_2, 45 min, 30 °C, $[M]_0 = 0.50$ M, $[Ru] = 5.0$ mM), the solution viscosity continued to increase with the passage of time and finally led to the formation of transparent gels. These gels were insoluble in common organic solvents such as toluene, acetone, THF, CH_2Cl_2, and $CHCl_3$, probably due to very high molecular weight or cross-linking of the polymers. Despite being insoluble, poly(**1**) and poly(**4**)–poly(**8**) could be used as cathode-active materials for a rechargeable battery.

Characterization of the Polymers. Though no evident information was obtained by IR and NMR spectroscopies, it is likely that poly(**1**)–poly(**8**) were formed by ROMP of the norbornene moiety. IR spectra of all the polymers showed strong absorption maxima at 1364 cm^{-1} assignable to the stretching vibration of N–O· bonds, indicating the incorporation of TEMPO moiety into the polymers. Poly(**2**) and poly(**3**) were soluble in relatively nonpolar organic solvents including toluene, $CHCl_3$, CH_2Cl_2 and THF, while the rest of the polymers were insoluble in any of the common organic solvents. Figure 1 illustrates the TGA thermograms of poly(**1**)–poly(**8**), whose onset temperatures of weight loss were in the range of 220–240 °C (under air) thus possessing moderate thermal stability. The decomposition of all the TEMPO-containing polymers followed basically the same fashion, suggesting that the ester linkage is cleaved at first followed by the degradation of the main chain.

The ultraviolet-visible (UV-Vis) spectra of poly(**2**) and poly(**3**) and the corresponding monomers (**2**, **3**) are shown in Figure 2. All the monomers and polymers displayed weak absorptions around 450 nm, originating from the free radical electrons located in the non-bonding singly occupied molecular orbitals (SOMOs). The spectral features of monomers and polymers were hardly different from each other in terms of the absorption wavelength (λ_{max}) and molar absorptivity (ε), hence ruling

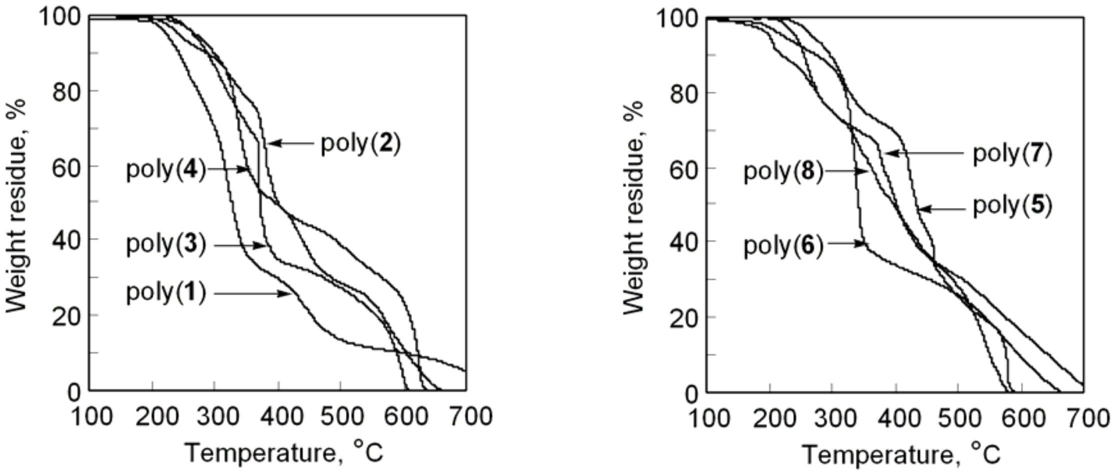


Figure 1. TGA curves of TEMPO-containing polynorbornenes poly(**1**)–poly(**8**) (measured in air; heating rate 10 °C/min).

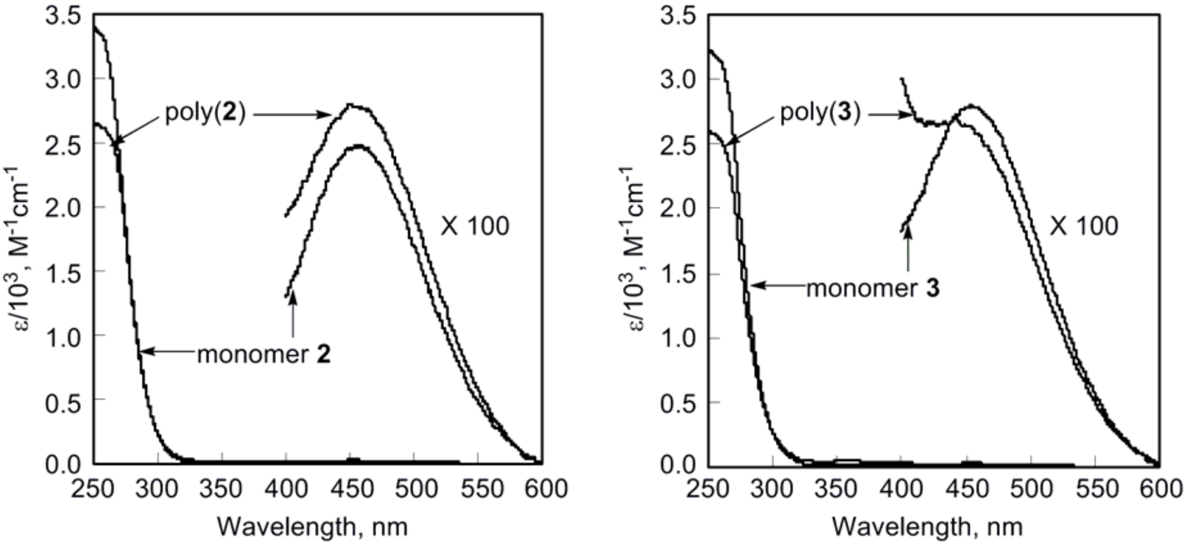


Figure 2. UV-Vis spectra of poly(**2**) and poly(**3**) (measured in $CHCl_3$, $c = 1.0–1.4 \times 10^{-3}$ M).

out any possibility of the disappearance of the radical moieties in the course of polymerization. All the polymers possessed orange-red color similar to those of the monomers. Table 2 summarizes the ESR data of poly(**1**)–poly(**3**). The ESR spectra of all the polymers exhibited a sharp single peak based on the TEMPO moiety at g =2.0064–2.0073 which is close to g = 2.0055 of the TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy) crystal but slightly higher probably due to the effect of the polymer backbone. Precise determination of the spin concentrations of poly(**1**)–poly(**3**) was carried out, and all of the TEMPO-containing polynorbornenes were found to possess free radical moieties in approximately quantitative amounts, i.e., nearly two per repeating unit in poly(**1**) and poly(**2**) and slightly less than two in poly(**3**). Both the Curie-Weiss temperature Θ and the frequency dependence of ESR line width are consistent with the 1-D magnetic interaction between TEMPO radicals attached to the polymer backbone. The Θ of the polymers with the 1-D chain of TEMPO radicals should be lower than that of the TEMPOL crystal (7 K) in which the 3-D magnetic interaction dominates the Θ value. The ESR line widths in the 1-D electronic systems should depend on the ESR frequency,[16] as demonstrated in Table 2.

The cyclic voltammograms (CV) of poly(**2**) and poly(**3**), displaying reversible oxidation and reduction based on the TEMPO radical, are depicted in Figure 3. The difference in the redox potentials for both poly(**2**) and poly(**3**) at a sweep rate of 0.01 V/s is 0.123 V, which is smaller than those of other electroactive organic materials such as PTMA (ca. 0.146 V).[15c] This indicates that the electron-transfer rate constants of poly(**2**) and poly(**3**) are larger than that of PTMA and therefore that the redox reactions of the present polymers are faster than that of PTMA.[17] The CV spectra of the two samples did not undergo any change during five cycles, thus

Table 2. Magnetic Properties of Poly(1)–Poly(3)

polymer	number of spins per monomer unit	Curie-Weiss temperature Θ (K)	ESR g-factor	ESR line width (G)	
				~50 MHz	~9 400 MHz
poly(**1**)	2.0±0.1	1.8	2.0073	17.9	10.7
poly(**2**)	1.9±0.1	1.5	2.0064	16.0	10.1
poly(**3**)	1.8±0.1	1.5	2.0066	17.0	9.9

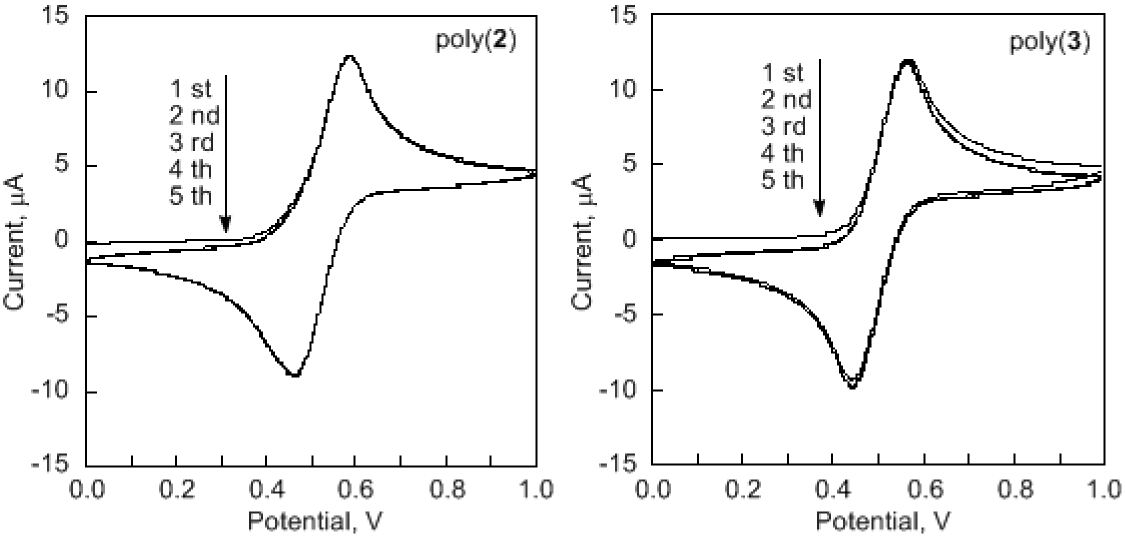


Figure 3. Cyclic voltammograms of poly(**2**) and poly(**3**) (1.0 mM) measured in CH_2Cl_2 solution in the presence of TBAP (tetrabutylammonium perchlorate) (0.10 M) with consecutive scans at 0.1 V/s.

displaying stable redox behavior and the absence of side reactions.

Charge/Discharge Properties. The charge/discharge curves of the cells fabricated with poly(**1**)–poly(**8**) were measured at a constant current density of 0.088 mA/cm^2 (0.034–0.12 A/g), in a cell voltage range of 2.5–4.2 V. Figures 4 and 5 show clear voltage plateaus in both charge and discharge curves with all the cells, advocating the applicability of the TEMPO-containing polynorbornenes as cathode-active materials for a rechargeable battery. The plateau voltages of the charge/discharge processes are in the range of 3.4–3.8 V starting from approximately 3.6 V vs. Li/Li$^+$, which corresponds to the redox potential of the TEMPO radical. It is reasonable to assume that the charge process at the cathode is oxidation of TEMPO moieties (**9**) in the polymers to oxoammonium salt (**10**), and the discharge process is the reverse reaction, namely, reduction of the salt (Scheme 3). Taking into account the fact that each TEMPO moiety furnishes a single electron in this redox process, the theoretical capacities of the cells fabricated with poly(**1**)–poly(**8**) were estimated to be 87.5–109.3 A h/kg (Table 3); meanwhile the actual initial discharge capacities of the

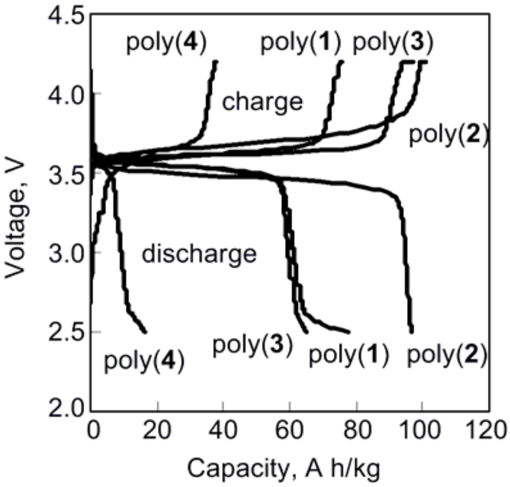


Figure 4. Charge/discharge curves of poly(**1**)–poly(**4**) at a current density of 0.088 mA/cm^2 (0.034–0.081 A/g) in a cell voltage range of 2.5–4.2 V.

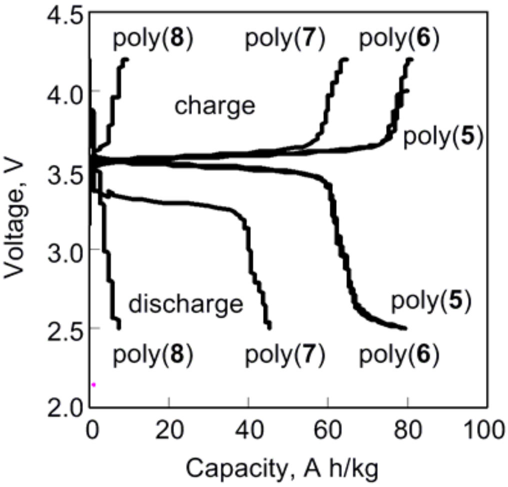
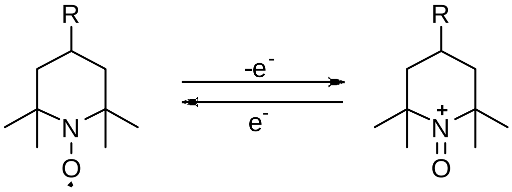


Figure 5. Charge/discharge curves of poly(**5**)–poly(**8**) at a current density of 0.088 mA/cm^2 (0.084–0.12 A/g) in a cell voltage range of 2.5–4.2 V.

Scheme 3. Reversible Oxidation of TEMPO Moiety



9 **10**

Table 3. Capacity Data of the Poly(1)–Poly(8)

polymer	m/e[a]	theoretical capacity, A h/kg[b]	observed capacity, A h/kg[c]	observed capacity/ theoretical capacity, %
poly(**1**)	245.3	109.3	77.5	70.9
poly(**2**)	245.3	109.3	109.3	100
poly(**3**)	245.3	109.3	65.2	59.7
poly(**4**)	292.4	91.7	16.4	17.9
poly(**5**)	259.4	103.3	79.2	76.7
poly(**6**)	259.4	103.3	78.3	75.8
poly(**7**)	259.4	103.3	45.4	4 3.9
poly(**8**)	306.4	87.5	7.2	8.2

[a] The polymer mass required per exchangeable unit. [b] Theoretical capacity (A h/kg), namely, specific charge calculated according to reference.[21] [c] Observed capacity (A h/kg): Initial discharge capacity at a current density of 0.088 mA/cm^2 (0.034–0.12 A/g) and a cut off at 2.5 V.

cells evaluated from the values at 3 V in Figures 4 and 5 were found to be 7.2–109.3 A h/kg at a current density of 0.088 mA/cm^2 (0.034–0.12 A/g).

It is noteworthy that poly(**1**)–poly(**3**) exhibited considerably different charge/discharge performance from one another, although their monomers differ only in the configuration of the substituents. Quite interestingly, the average of the three charge capacity measurements (96, 120, 112 A h/kg) for poly(**2**)-based cell attained the theoretical value (109 A h/kg), while those for poly(**1**) and poly(**3**) remained 77.5 and 65.2 A h/kg, respectively. X-ray crystallographic data of **3** as shown in Table S1 (in Supporting Information) has suggested a distance of 10 Å between the two radical moieties, oriented in the *endo*,*endo* fashion, in one repeating unit of poly(**3**) which should be the same for poly(**1**) having the *exo*,*exo*-orientation of substituents, whereas a comparatively large distance is expected between the TEMPO moieties of poly(**2**) because of their *endo*,*exo*-orientation. Although poly(**1**)–poly(**3**) are isomers and all of them possess free radicals quantitatively, quite different tendencies observed in their charge/discharge capacities signify the importance of configuration or three-dimensional arrangement of TEMPO moieties along the polymer backbone. Whether a polymer is soluble in nonpolar solvents or not usually does not largely affect the charge/discharge capacity. The appearance of a polymer sample may have influence, and if the sample is too hard to pulverize, the capacity may become lower than expected; however, it is not the case with poly(**1**)–poly(**3**). Thus the author think that the configurational difference is the main reason for the difference in capacity.

The theoretical capacities of the cells based on poly(**1**)–poly(**3**), possessing lesser methylene groups and thus higher radical concentrations per repeating unit, should be higher than those for poly(**5**)–poly(**7**); but experimental facts were not quite in accordance with the expected ones suggesting the presence of multiple factors affecting the actual capacity of the polymer-based cells. The observed discharge capacities of poly(**4**) and poly(**8**) having one nitroxy radical in the monomer unit were even lower than expected as compared to those having two radical moieties per repeat unit, which might result from the increased crystallinity, regular structure, and/or large particle size due to the smaller number of substituents.

Figure 6 depicts the charge/discharge curves of poly(**2**) observed at different current densities. A slight decrement in the charge/discharge capacity was witnessed with increasing current density, which is attributable to the polarization of TEMPO. The poly(**2**)-based cell, however, displayed excellent charge/discharge characteristics even at extremely large current densities; *e.g.*, the capacity estimated at a current density of 6.3 A/g (8.8 mA/cm^2) was ca. 90 A h/kg, which corresponds to 83% of the discharge capacity at 0.063 A/g (0.088 mA/cm^2) current density, evaluated at the same voltage (2.5 V).

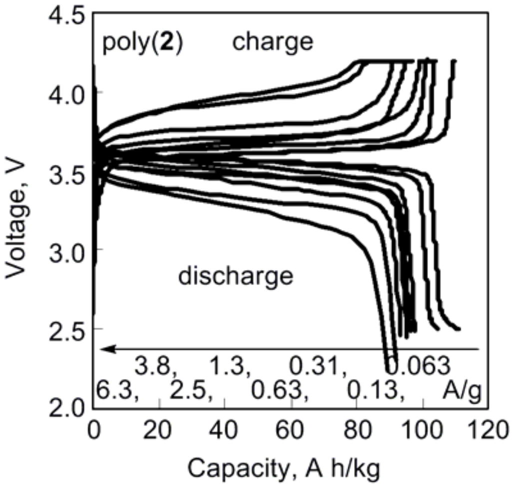


Figure 6. Charge/discharge curves of poly(**2**) at different current densities in a cell voltage range of 2.5–4.2 V.

The relationship between the capacity and current density of poly(**1**)–poly(**8**) is illustrated in Figure 7. An increase in current density led to a significant decrease in the charge capacities of poly(**1**)- and poly(**4**)–poly(**8**)-based cells, especially in the range of low current densities. On the contrary, the large capacities of poly(**2**) and poly(**3**) were retained even though the current density was increased up to more than 6 A/g (8.8 mA/cm^2), hence indicating the capability of being charged and discharged at a much faster rate (90 A h/kg / 6.3 A/g = 0.014 h = 51 sec) than the rest of the polymers. Few secondary batteries have been known which are characterized by such a high capacity and a high charge speed. Therefore, it can be said that especially poly(**2**) is a promising organic radical battery material.

Figure 8 delineates the cycle performance of the poly(**1**)–poly(**8**)/Li batteries, in which charge and discharge were repeated at a current density of 0.088 mA/cm^2 (0.034–0.12 A/g), under the application of cell voltage of 2.5–4.2 V. All the cells fabricated with the polymers under study as the cathode material possessed long cycle life; i.e., the discharge capacities hardly deteriorated after 100 cycles, and especially with poly(**2**) and poly(**3**) decreased by no more than 10% of the initial values even after 500 and 400 cycles, respectively. The capacity of poly(**5**) clearly increased with

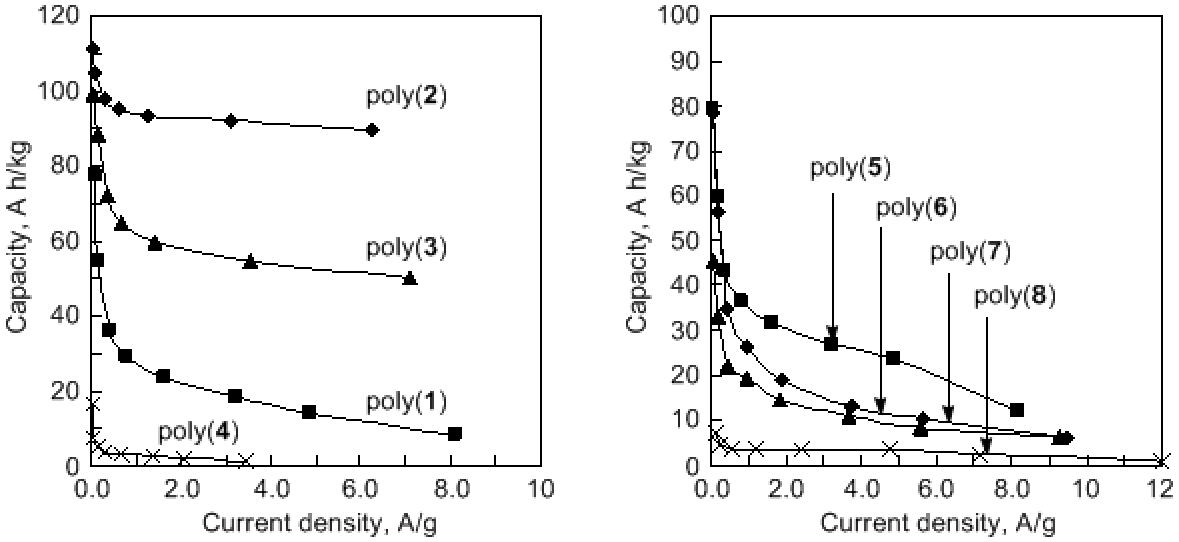


Figure 7. Dependence of capacity on current density in poly(**1**)–poly(**8**) in a cell voltage range of 2.5–4.2 V.

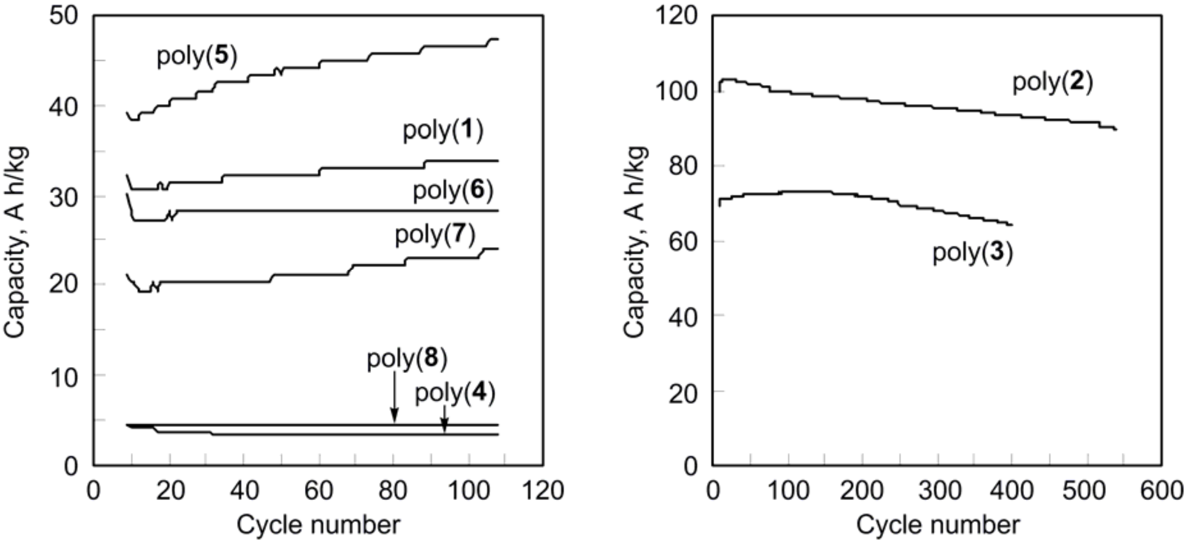


Figure 8. Dependence of capacity on cycle number in poly(**1**)–poly(**8**). Charge and discharge were repeated at a current density of 0.088 mA/cm^2 (0.034–0.12 A/g) in a cell voltage range of 2.5–4.2 V.

increasing cycle number, which is probably due to the increase in the area of contact between the electrode and the electrolyte, resulting from the swelling of the polymer upon repeated charge and discharge. The cycle life of poly(**2**) was better than those of the corresponding PROXY-containing polymer[6b] and TEMPO-carrying polyacetylenes,[6f] and comparable to that of the reported PTMA system.[15a]

The extraordinary characteristics of high charge capacity, excellent charge/discharge performance, and long cycle life of poly(**2**) are expected to signify its capability as a power source in a wide range of potential applications.

Conclusions

In the present study, a group of TEMPO-containing norbornene monomers **1**–**8** were synthesized and polymerized with a ruthenium-based metathesis catalyst. Monomers **2** and **3** gave polymers with number-average molecular weights of 185 000 and 137 000 in 59 and 100% yield, respectively, while monomers **1** and **4**–**8** gave insoluble polymers in 72–100% yield. All of the polymers were observed to be thermally stable up to ca. 240 °C, under air. The ESR spectra of poly(**1**)–poly(**3**) exhibited a sharp single peak with g-factors typical of nitroxy radicals (around 2.0065) and the number of spins per repeating unit was almost quantitative. The most interesting feature of the present research is the very high charge capacity displayed by the poly(**2**)-based cell (109 A h/kg) which attained the theoretical value, and a large capacity (up to 90 A h/kg) was retained even at a high current density of ca. 6 A/g. The cell fabricated with poly(**2**) as a cathode material demonstrated a promising cycle life and the deterioration of charge capacity was hardly observed even after 500 cycles. Thus, poly(**1**)–poly(**8**), especially poly(**2**), are expected to find applications as charge-storage materials in organic radical batteries.

Experimental Section

Measurements. IR and UV-Vis spectra were measured on a JASCO FT/IR-4100 and JASCO V-550 spectrophotometers, respectively. Cyclic voltammograms (CV) were recorded with an HCH Instruments ALS600A-n electrochemical analyzer. Melting points (mp) were determined with a Yanaco micro melting point apparatus and elemental analyses were conducted at the Kyoto

University Elemental Analysis Center. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a JASCO Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns KF-805L × 3), using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standards at 40 °C. ESR spectra were recorded with a JEOL JES-FR30 X-band (9.48 GHz) spectrometer. A frequency counter (Anritsu, MF76A) and an NMR field meter (Echo Electronics, EFM-2000AX) were used for the determination of g-factor. The precise number of free radicals was estimated with a Quantum Design MPMS susceptometer and a home-built low-frequency ESR-NMR apparatus operated around 50 MHz.[18]

Crystallographic Study. A single crystal of **3** obtained by recrystallization from hexane/$CHCl_3$ solution was subjected to X-ray crystallographic analysis and the measurement was made on a Rigaku RAPID-F imaging plate area detector with graphite-monochromated Mo Kα radiation. The structure was elucidated by a direct method using SIR92[19] and expanded by Fourier techniques (DIRDIF99).[20]

Materials. The solvents used for polymerization were distilled according to the standard procedure before use. The Grubbs 2nd generation catalyst was purchased from Materia, Inc., and used as received. 4-Carboxy-TEMPO (TCI), 4-hydroxy-TEMPO (TCI), 5-norbornene-*endo*,*exo*-2,3-dicarboxylic acid (Aldrich), 5-norbornene-*exo*-2,3-dicarboxylic anhydride (Aldrich), 5-norbornene-*endo*-2,3-dicarboxylic anhydride (Aldrich), 5-norbornene-*exo*,*exo*-2,3-dimethanol (Aldrich), 5-norbornene-*endo*,*endo*-2,3-dimethanol (Aldrich), 5-norbornene-2,2-dimethanol (Aldrich), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC•HCl; Eiweiss Chemical corporation), 4-dimethylaminopyridine (DMAP; Wako) were purchased and used without further purification.

Monomer Synthesis.

5-Norbornene-*exo,exo*-2,3-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-oxy)] ester (**1**) was synthesized from 5-norbornene-*exo*-2,3-dicarboxylic anhydride and 4-hydroxy-TEMPO according to the literature method.[6d] The crude product was purified by flash column chromatography (eluent: ethyl acetate/hexane = 1/4). Yield 36%, pale red solid, mp 148.5–149.5 °C. IR (KBr, cm^{-1}): 2976, 2938, 1720 ($\nu_{C=O}$), 1464, 1364, 1316, 1266, 1242, 1176 (ν_{C-O}), 1111, 1012, 989, 900, 702. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 65.97; H, 8.40; N, 5.64.

5-Norbornene-*exo,endo*-2,3-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-oxy)] ester (**2**) was synthesized as follows: 5-Norbornene-*exo*,*endo*-2,3-dicarboxylic acid (1.31 g, 4.00 mmol) was added to a solution of EDC•HCl (3.03 g, 8.80 mmol) and DMAP (1.08 g, 8.80 mmol) in CH_2Cl_2 (80 mL) at room temperature. 4-Hydroxy-TEMPO (1.52 g, 8.80 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (100 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed to afford a crude product. It was purified by flash column chromatography (eluent: ethyl acetate/hexane = 1/2). Yield 1.70 g (87%), pale red solid, mp 183.0–184.0 °C. IR (KBr, cm^{-1}): 2977, 2939, 1739 ($\nu_{C=O}$), 1464, 1345, 1250, 1191 (ν_{C-O}), 1158, 1076, 1048, 905, 731. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 66.11; H, 8.64; N, 5.66.

5-Norbornene-*endo,endo*-2,3-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-oxy)] ester (**3**) was synthesized from 5-norbornene-*endo*-2,3-dicarboxylic anhydride and 4-hydroxy-TEMPO according to the literature method.[6d] The crude product was a mixture of about same amounts of isomers **2** and **3**. These isomers were separated by flash column chromatography (eluent: ethyl acetate/hexane = 1/2). Yield of **3** 23%, pale red solid, mp 157.0–158.0 °C. IR (KBr, cm^{-1}): 2976, 2938, 2872, 1720 ($\nu_{C=O}$), 1463, 1364, 1317, 1266, 1175 ($\nu_{C\text{–}O}$), 1111, 1009, 989, 962, 713. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 66.09; H, 8.75; N, 5.62.

5-Norbornene-2-carboxylic acid 4-(2,2,6,6-tetramethylpiperidine-1-oxy)] ester (**4**) was synthesized as follows: 5-Norbornene-2-carboxylic acid (415 mg, 3.00 mmol) was added to a solution of EDC•HCl (864 mg, 3.30 mmol) and 4-dimethylaminopyridine (403 mg, 3.30 mmol) in CH_2Cl_2 (50 mL) at room temperature. 4-Hydroxy-TEMPO (517 mg, 3.00 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (50 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed to afford a crude product. It was purified by flash column chromatography (eluent: ethyl acetate/hexane = 1/4). Yield 34%, pale red solid, mp 89.0–90.0 °C. IR (KBr, cm^{-1}): 3063, 2973, 2943, 2870, 1725 ($\nu_{C=O}$), 1465, 1337, 1271, 1174 ($\nu_{C\text{–}O}$), 1112, 1021, 900, 839, 711. Anal. Calcd for $C_{17}H_{26}NO_3$: C, 69.83; H, 8.96; N, 4.79. Found: C, 69.78; H, 8.90; N, 4.79.

5-Norbornene-*exo*,*exo*-2,3-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-oxy 4-carboxylate) (**5**) was synthesized form 5-norbornene-*exo*,*exo*-2,3-dimethanol and two equivalents of 4-carboxy-TEMPO by following the same procedure as for/in a manner similar to **4**. Yield 23%, pale red solid, mp 148.5–149.5 °C. IR (KBr, cm^{-1}): 2970, 2938, 1726 ($\nu_{C=O}$), 1457, 1311, 1243, 1158 ($\nu_{C\text{–}O}$), 1011, 970, 698. Anal. Calcd for $C_{29}H_{46}N_2O_6$: C, 67.15; H, 8.94; N, 5.40. Found: C, 67.11; H, 8.94; N, 5.12.

5-Norbornene-*endo*,*endo*-2,3-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-oxy 4-carboxylate) (**6**) was synthesized from 5-norbornene-*endo*,*endo*-2,3-dimethanol and two equivalents of 4-carboxy-TEMPO in a manner similar to **4**. Yield 72%, pale red solid, mp 156.5–157.5 °C. IR (KBr, cm^{-1}): 3052, 2974, 2945, 1735 ($\nu_{C=O}$), 1457, 1323, 1292, 1192, 1163 ($\nu_{C\text{–}O}$), 972, 747. Anal. Calcd for $C_{29}H_{46}N_2O_6$: C, 67.15; H, 8.94; N, 5.40. Found: C, 66.96; H, 8.77; N, 5.34.

5-Norbornene-2,2-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-oxy 4-carboxylate) (**7**) was synthesized from 5-norbornene-2,2-dimethanol and two equivalents of 4-carboxy-TEMPO in a manner similar to **4**. Yield 66%, pale red solid, mp 152.0–153.0 °C. IR (KBr, cm^{-1}): 3070, 2972, 2874, 1718 ($\nu_{C=O}$), 1467, 1365, 1254, 1167 ($\nu_{C–O}$), 1013, 725, 712. Anal. Calcd for $C_{29}H_{46}N_2O_6$: C, 67.15; H, 8.94; N, 5.40. Found: C, 67.18; H, 8.87; N, 5.27.

5-Norbornene-2-methyl (2,2,6,6-tetramethylpiperidine-1-oxy 4-carboxylate) (**8**) was synthesized from 5-norbornene-2-methanol and 4-carboxy-TEMPO in a manner similar to **4**. Yield 34%, pale red solid, mp 93.4–94.5 °C. IR (KBr, cm^{-1}): 3069, 2975, 2875, 1726 ($\nu_{C=O}$), 1469, 1367, 1254, 1150 ($\nu_{C–O}$), 1013, 899, 710. Anal. Calcd for $C_{17}H_{26}NO_3$: C, 69.83; H, 8.96; N, 4.79. Found: C, 69.75; H, 8.99; N, 4.70.

Norbornene-2,3-*exo*,*exo*-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine 1-hydroxy)] ester (**1’**) was synthesized by hydrogenation of **1** according to the literature method.[6d] Yield 100%, white solid, mp 58.5–58.9 °C. ^1H NMR ($CDCl_3$) δ 6.20 (2H, =CH–), 5.16–4.92 (2H, –OCH<), 4.06 (2H, –OH), 3.06 (2H, =CH–C*H*–), 2.54 (2H, >CHCOO), 2.01–1.78 (2H, =CH–CHCH_2CH<), 1.74–1.42 (8H, –OCHCH_2C–), 1.20 (24H, >C(CH_3)$_2$). ^{13}C NMR ($CDCl_3$) δ 171.7, 136.7, 65.6, 57.8, 46.1, 46.0, 44.5, 42.7, 30.8, 19.0. IR (KBr, cm^{-1}): 3 445 ($\nu_{O–H}$), 2 974, 2 937, 2 873, 1 728 ($\nu_{C=O}$), 1 469, 1 372, 1 315, 1 242 ($\nu_{C–O}$), 1 196, 1 162, 1 097, 1 041, 1 014, 955, 728, 600. HRMS (FAB): $[M+H]^+$, found 493.3276. $C_{27}H_{45}N_2O_6$ requires 493.3278.

Norbornene-2,3-*endo*,*exo*-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-hydroxy)] ester (**2’**) was synthesized from **2** in a manner similar to **1’**. Yield 80%, white solid, mp 149.5–151.0 °C. ^1H NMR ($CDCl_3$) δ 6.29 (1H, =CH–), 6.07 (1H, =CH–), 5.19–4.94 (2H, –OCH<), 4.40 (2H, –OH), 3.32 (1H, >CHCOO), 3.24 (1H, >CH–COO), 3.09 (1H, =CH–C*H*–), 2.63 (1H, =CH–C*H*–), 2.09–1.78 (2H, =CH–CHCH_2CH<), 1.78–1.42 (8H, –OCHCH_2C–),1.20 (24H, >C(CH_3)$_2$). ^{13}C NMR ($CDCl_3$) δ 173.7, 172.5, 137.3, 134.7, 66.9, 66.7, 58.7, 47.8, 47.5, 47.1, 46.9, 45.4, 43.5, 31.8, 31.7, 20.1. IR (KBr, cm^{-1}): 3500 ($\nu_{O–H}$), 2976, 2943, 1727 ($\nu_{\mathrm{C=O}}$), 1467, 1362, 1315, 1267 ($\nu_{\mathrm{C–O}}$), 1177, 1011, 962, 712. HRMS (FAB): $[M+H]^+$, found 493.3270. $C_{27}H_{45}N_2O_6$ requires 493.3278.

Norbornene-2,3-*endo*,*endo*-dicarboxylic acid bis[4-(2,2,6,6-tetramethylpiperidine-1-hydroxy)] ester (**3’**) was synthesized from **3** in a manner similar to **1’**. Yield 90%, white solid, mp 165.5–167.0 °C. ^{1}H NMR ($CDCl_3$) δ 6.05 (2H, =CH–), 5.10–4.90 (2H, –OCH<), 4.22 (2H, –OH), 3.22 (2H, >CHCOO), 3.14 (2H, =CH–CH–), 2.00–1.78 (2H, =CH–CHCH_2CH<), 1.65–1.40 (8H, $–CH_2C(CH_3)_2–$), 1.16 (24H, $>C(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ 170.8, 133.6, 65.5, 57.9, 47.5, 47.0, 45.2, 42.7, 31.1, 19.0. IR (KBr, cm^{-1}): 3503 ($\nu_{\mathrm{O–H}}$), 2976, 2941, 1739 ($\nu_{\mathrm{C=O}}$), 1468, 1362, 1342, 1254 ($\nu_{\mathrm{C–O}}$), 1193, 1076, 963, 726. HRMS (FAB): $[M+H]^+$, found 493.3277. $C_{27}H_{45}N_2O_6$ requires 493.3278.

5-Norbornene-*exo*,*exo*-2,3-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-hydroxy 4-carboxylate) (**5’**) was synthesized from **5** in a manner similar to **1’**. Yield 100%, white solid, mp 115.0–116.0 °C. ^{1}H NMR ($CDCl_3$) δ 6.20 (2H, =CH–), 4.52–3.42 (5H, $–OCH_2–$, –OH), 2.89–2.50 (4H, =CH–CH–, –OCOCH<), 2.12–1.84 (2H, $–OCH_2$CH<), 1.84–1.55 (8H, –C$H_2$$C(CH_3)_2–$), 1.55–1.29 (2H, =CH–CHCH_2CH<)), 1.16 (24H, $>C(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ 171.0, 133.2, 61.3, 54.3, 40.5, 38.5, 37.4, 35.5, 30.7, 28.3, 15.2. IR (KBr, cm^{-1}): 3 390 ($\nu_{\mathrm{O–H}}$), 2 975, 2 936, 2897, 1 733 ($\nu_{\mathrm{C=O}}$), 1 457, 1 362, 1 329, 1 307, 1 244 ($\nu_{\mathrm{C–O}}$), 1 193, 1 164, 1 047, 1 013, 962, 708. HRMS (CI): $[M+H]^+$, found 520.3519. $C_{29}H_{49}N_2O_6$ requires 521.3591.

5-Norbornene-*endo*,*endo*-2,3-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-hydroxy 4-carboxylate) (**6’**) was synthesized from **6** in a manner similar to **1’**. Yield 100%, white solid, mp 120.0–121.0 °C. ^{1}H NMR ($CDCl_3$) δ 6.18 (2H, =CH–), 4.32–3.45 (5H, $–OCH_2–$, –OH), 2.92 (2H, =CH–CH<), 2.77–2.60 (2H, –OCOCH<), 2.60–2.41 (2H, $–OCH_2$CH<), 1.96–1.58 (8H, –C$H_2$$C(CH_3)_2–$), 1.58–1.30 (2H, =CH–CHCH_2CH<), 1.30–0.99 (24H, $>C(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ 173.1, 133.5, 62.5, 56.3, 46.9, 43.3, 39.6, 38.5, 32.9, 30.3, 17.3.

IR (KBr, cm^{-1}): 3 496 ($\nu_{O\text{–}H}$), 2 978, 2 941, 1 728 ($\nu_{C=O}$), 1 467, 1 363, 1 317, 1 245 ($\nu_{C\text{–}O}$), 1 175, 1 112, 1 050, 1 012, 963, 898, 735. HRMS (CI): $[M+H]^+$, found 521.3553. $C_{29}H_{49}N_2O_6$ requires 521.3591.

5-Norbornene-2,2-dimethyl bis(2,2,6,6-tetramethylpiperidine-1-hydroxy 4-carboxylate) (**7'**) was synthesized from **7** in a manner similar to **1'**. Yield 100%, white solid, mp 142.5–143.5 °C. ^{1}H NMR ($CDCl_3$) δ 6.22 (1H, =CH–), 6.04 (1H, =CH–), 4.54–3.21 (5H, $–OCH_2–$, –OH), 2.89 (1H, =CH–C*H*–), 2.82–2.43 (3H, =CH–C*H*–, –OCOCH<), 1.99–1.00 (36H, $–CH_2C(CH_3)_2–$, $–OCH_2CCH_2<$, $=CH–CHCH_2CH<$, $>C(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ 171.5, 171.3, 134.2, 130.2, 64.0, 63.1, 54.6, 43.4, 42.4, 42.2, 38.7, 37.84, 37.77, 31.1, 29.4, 28.6, 15.6. IR (KBr, cm^{-1}): 3 445 ($\nu_{O\text{–}H}$), 2 974, 2 937, 2873, 1 728 ($\nu_{C=O}$), 1 469, 1 372, 1 315, 1 242 ($\nu_{C\text{–}O}$), 1 196, 1 162, 1 041, 1 014, 955, 728. HRMS (FAB): $[M+H]^+$, found 521.3600. $C_{29}H_{49}N_2O_6$ requires 521.3591.

Polymerization. Polymerization of norbornene monomers was carried with Grubbs second generation as a catalyst in dry CH_2Cl_2 at 30 °C for 30 or 45 minutes under the following conditions: $[\text{monomer}]_0$ = 1.0 M, [catalyst] = 10 mM or $[\text{monomer}]_0$ = 0.50 M, [catalyst] = 5.0 mM. The polymers were isolated by precipitation in methanol.

IR (KBr, cm^{-1}) Data of the Polymers. poly(**1**): 3500, 2976, 2945,1751, 1637, 1560, 1541, 1470, 1394, 1364, 1290, 1210, 1155, 1137, 983, 967, 935, 916, 874, 818, 766, 745, 711, 649, 564. poly(**2**): 2976, 2941, 2363, 1732, 1465, 1364, 1178, 1010, 985, 752. poly(**3**): 2976, 2941, 2363, 2328, 1734, 1466, 1364, 1177, 1010, 982. poly(**4**): 3444, 2975, 2929, 1734, 1676, 1628, 1560, 1542, 1525, 1449, 1458, 1364, 1306, 1242, 1164, 1085, 1014, 937, 906, 743, 713, 582, 557. poly(**5**): 3492, 2973, 2933, 1734, 1676, 1646, 1638, 1628, 1560, 1542, 1458, 1390, 1378, 1364, 1310, 1194, 1162, 1085, 1041, 1014, 968, 867, 850, 751, 648, 558. poly(**6**): 3498, 2974, 2936, 1734, 1647, 1638, 1570, 1509, 1450, 1466, 1377, 1364, 1313, 1167, 1085, 1046, 1009, 968, 800, 741, 681, 557, 536. poly(**7**): 3486, 2974, 2943, 1732, 1459, 1377, 1364, 1309, 1243, 1190, 1165, 1104, 1086, 1040, 970, 748, 680, 650, 557. poly(**8**): 3444, 2973, 2945, 2863, 1733, 1458, 1390, 1377, 1363, 1308, 1243, 1195, 1166, 1012, 966, 755, 667, 647.

Fabrication and Electrochemical Properties of the Batteries. A coin-type cell was fabricated by stacking electrodes with porous polyolefin separator film. A cathode was prepared by pressing the composites of a polymer (10 wt%), carbon fiber (80 wt%), and fluorinated polyolefin binder (10 wt%) as described in a previous paper.[6c] The cathode was set to a coin-type cell with a lithium metal anode. A composite solution of ethylene carbonate/diethyl carbonate (30/70 v/v) containing 1 M $LiPF_6$ was used as an electrolyte. Charge and discharge properties were measured at 25 °C using a computer controlled automatic battery charge and discharge instrument (Keisokukiki, Co. Ltd., Battery Labo System BLS5500).

Theoretical Capacity of the Polymer-Based Cell. The theoretical capacity (C, in A h/kg) of an electroactive polymer is calculated from the polymer mass required per exchangeable unit charge.[21]

$$\mathrm{C\,(A\ h/kg)} = \frac{N_{\mathrm{A}} \times \mathrm{e}}{3600 \times (M_{\mathrm{w}}/1000)}$$

where $N_{\mathrm{A}} \times \mathrm{e}$ is the Faraday constant (96 484 C/mol); while M_{w} is the equivalent weight (or mass) of polymer in g, and defined as the molecular weight (molar mass) of the repeating unit of polymer divided by the number of electrons exchanged or stored by it (which may be a fractional number), or as the molecular weight of the set of repeating units exchanging (storing) one electron in polymers.

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Chapter 7

Synthesis and Charge/Discharge Properties of Polyacetylenes Carrying 2,2,6,6-Tetramethyl-1-piperidinoxy (TEMPO) Radicals

Abstract

TEMPO-containing acetylenic monomers, $HC{\equiv}CC_6H_3$-*p,m*-(CONH-4-TEMPO)$_2$ (**1**), $HC{\equiv}CC_6H_3$-*p,m*-(COO-4-TEMPO)$_2$ (**2**), (*S,S,S,S*)-$HC{\equiv}CC_6H_3$-*p,m*-[CO-NHCH{COO-(4-TEMPO)}CH_2COO-(4-TEMPO)]$_2$ (**3**) (*S,S*)-$HC{\equiv}CC_6H_4$CO-NHCH{COO-(4-TEMPO)}CH_2COO-(4-TEMPO) (**4**), $HC{\equiv}CC_6H_4$-*p*-OCO-4-TEMPO (**5**), $HC{\equiv}CCH_2C(CH_3)(CH_2OCO\text{-}4\text{-}TEMPO)_2$ (**6**), $HC{\equiv}CCH_2NHCO$-4-TEMPO (**7**), and $HC{\equiv}CCH_2OCO$-4-TEMPO (**8**) (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy) were polymerized to afford novel polymers containing the TEMPO radical at high densities. Monomers **1**, **3–6,** and **8** provided polymers with number-average molecular weights of 10 000–136 500 in 62–99% yields in the presence of a Rh catalyst, while monomers **2** and **7** gave insoluble polymers in 100% yields. The formed polymers were thermally stable up to ca. 274 °C according to TGA. All the TEMPO-containing polymers demonstrated reversible charge/discharge processes, whose discharge capacities were 21.3–108 A h kg^{-1}. In particular, the capacity of a poly(**1**)-, poly(**4**)-, and poly(**5**)-based cell reached 108, 96.3, and 89.3 A h kg^{-1} respectively, which practically coincided with their theoretical value.

Introduction

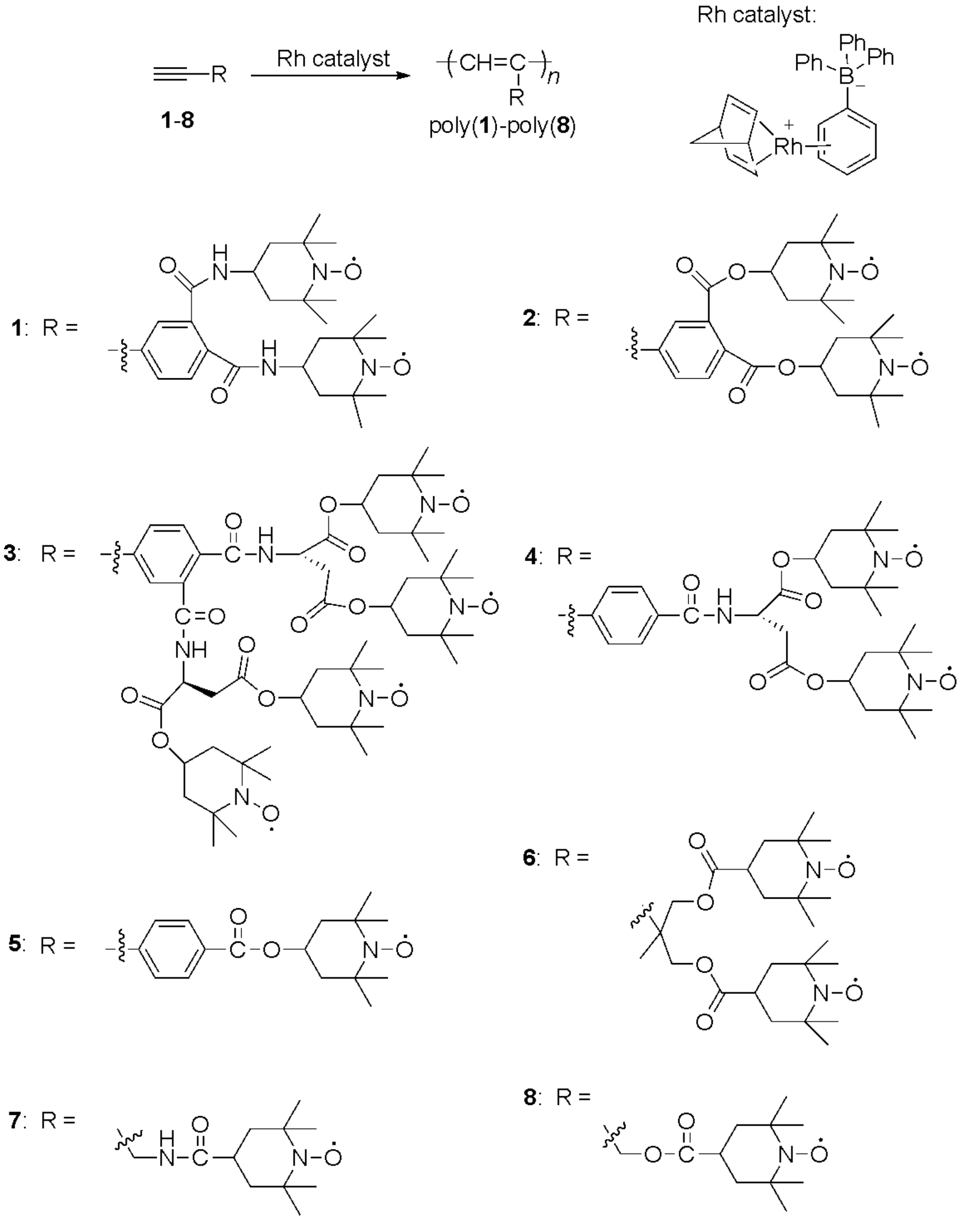
Stable organic radicals are widely used as spin labels[1] for monitoring the functions of biomolecules and as spin traps or radical scavengers[2] of organic materials and biological systems. Polymers carrying stable organic radicals have been intensively studied as subjects of electron spin resonance[3] and molecular motion,[4] and frequently employed as functional materials such as polymeric stabilizers,[5] oxidants of alcohols,[6] and spin- and charge-storage materials.[7] Among these applications, polymers having π-conjugated radicals,[8] especially polyacetylenes containing stable radicals,[9] have been extensively studied in the search for organic ferromagnetic materials.

2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and its derivatives are well known stable nitroxy radicals[10] and have found applications in a variety of fields such as spin labels in the study of conformation and structural mobility of biological systems,[11] scavengers of unstable radical species,[12] and oxidizing agents.[13] The TEMPO radical is a typical oxygen-centered radical involving a resonance structure in which odd electron is delocalized to nitrogen, which contributes to its high stability. The TEMPO radical displays two redox couples, namely, oxidation to a cation and reduction to an anion. It can be oxidized to form the corresponding oxoammonium cation; the oxidation process of the radical is reversible and leads to p-type doping of the radical material. It can also be reduced to the aminoxy anion resulting in n-type doping of the material. By using the oxidation process to the cation, TEMPO-carrying polymers can be applied to cathode-active materials in secondary batteries, and such batteries can be called organic radical batteries. As compared to currently popular Li-based batteries, organic radical batteries feature high-speed charging and discharging.

Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) was examined as a material for the first-generation organic radical batteries, which would be quickly chargeable and have a high power density.[14] Thus far, polymers carrying nitroxy free radicals such as PTMA have usually been synthesized by an indirect method, i.e., synthesis of precursor polymers having the corresponding amino group, followed by the oxidation to afford polymers containing stable radicals.[15] The indirect route is adopted due to lack of capability of radical-bearing monomers to undergo radical polymerization. However, this method is often accompanied by incomplete oxidation, resulting in less than quantitative incorporation of the radical into the polymers.[14] As a consequence, PTMA contained not the quantitative amount but ca. 70% of radicals against the theoretical value, and the batteries using this polymer showed an average discharge voltage of 3.5 V and a discharge capacity of 77 A h kg^{-1} (70% of the theoretical value). Noting that transition metal catalysts may polymerize radical-bearing monomers, the author have recently investigated the preparation and charge/discharge properties of several of polyacetylenes and polynorbornenes containing TEMPO groups as a preliminary study, and revealed that the discharge capacity of the cell fabricated with poly(norbornene-2,3-*endo,exo*-(COO-4-TEMPO)$_2$) reached the theoretical value (109 A h kg^{-1}) expected for the molecular structure.[16] More recently, Nishide and coworkers have reported poly[4-(*N*-*tert*-butyl-*N*-oxylamino)styrene], poly[3,5-di(*N*-*tert*-butyl-*N*-oxylamino)styrene], and poly[4-(*N*-*tert*-butyl-*N*-oxylamino)-3-trifluoromethylstyrene] possessed radical densities of 1.82–4.27×10^{21} unpaired electrons g^{-1}, and these polymers might be applicable as an electrode-active material with a high charge/discharge capacity.[17]

Substituted polyacetylenes exhibit unique properties such as chromism, semiconductivity, paramagnetism, high gas permeability, helix formation, and nonlinear optical properties.[18] Introduction of TEMPO moieties into polyacetylene may lead to new functional materials based on the synergistic effect of stable organic radical and conjugated polyacetylene main chain. The present chapter deals with the synthesis of TEMPO-carrying polyacetylenes by direct polymerization of TEMPO-containing acetylenes (Scheme 1) with a Rh-based transition metal catalyst, and reports on the fundamental properties such as charge/discharge characteristics of the formed polymers as cathode-active materials in the organic radical battery.

Scheme 1. Polymerization of TEMPO-containing Acetylenes 1–8.



Results and Discussion

Monomer Synthesis. Scheme 2 illustrates the synthetic routes for monomers **1**–**6**. Acetylene ester and amide monomers **1** and **2** were synthesized by the reaction of 4-ethynylphthalic anhydride with the hydroxy or amino group of TEMPO derivatives. Monomers **3** and **4** were synthesized by the reaction of 4-hydroxy-TEMPO with **3’** (M_w = 420.33) (for **3**) and *N*-(4-ethynyl benzoyl)-L-aspartic acid (for **4**) which were prepared from 4-ethynylphthalic anhydride and 4-ethynylbenzoic acid reaction with L-H-Glu(OMe)-OMe·HCl, then by removing the methyl group of products. Monomer **5** was prepared by condensation of the hydroxy group of 4-hydroxy-TEMPO with the carboxy group of 4-ethynylbenzoic acid. Monomer **6** was synthesized by the reaction of 1-pentyne-4,4-dimethanol with two equivalents of 4-carboxy-TEMPO. Monomers **1**–**6** were purified silica gel column chromatography eluted by ethyl acetate/*n*-hexane (1/4 volume ratio). Due to the presence of free radicals, it was impossible to measure the NMR spectra of the monomers. The structures of the monomers were confirmed by IR spectra and elemental analysis.

Polymer Synthesis. The polymerization of acetylene monomers **1**–**8** was carried out using (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ as a catalyst at 30 °C for 24 h, the conditions and results of which are summarized in Table 1. Polymeric compounds were obtained quantitatively by the polymerization of **2** and **7**, but they were insoluble in common organic solvents including THF, $CHCl_3$, and DMF (runs 2 and 7 in Table 1). However, poly(**2**) which was obtained under a lower monomer concentration ($[M]_0$ = 0.10 M) was soluble in organic solvents, although the polymer yield was rather low (38%). On the other hand, **1**, **3–6,** and **8** gave solvent-soluble polymers with number-average molecular weights of 10 000–136 500 in 62–99% yields (runs 1, 3–6, and 8 in Table 1). All the polymers were colored orange, which is attributable to TEMPO side chains and/or the conjugated main chain.

Structure of the Polymers. Poly(**1**)–poly(**8**) exhibited no IR absorptions at

Scheme 2. Preparation of Monomers 1–6.

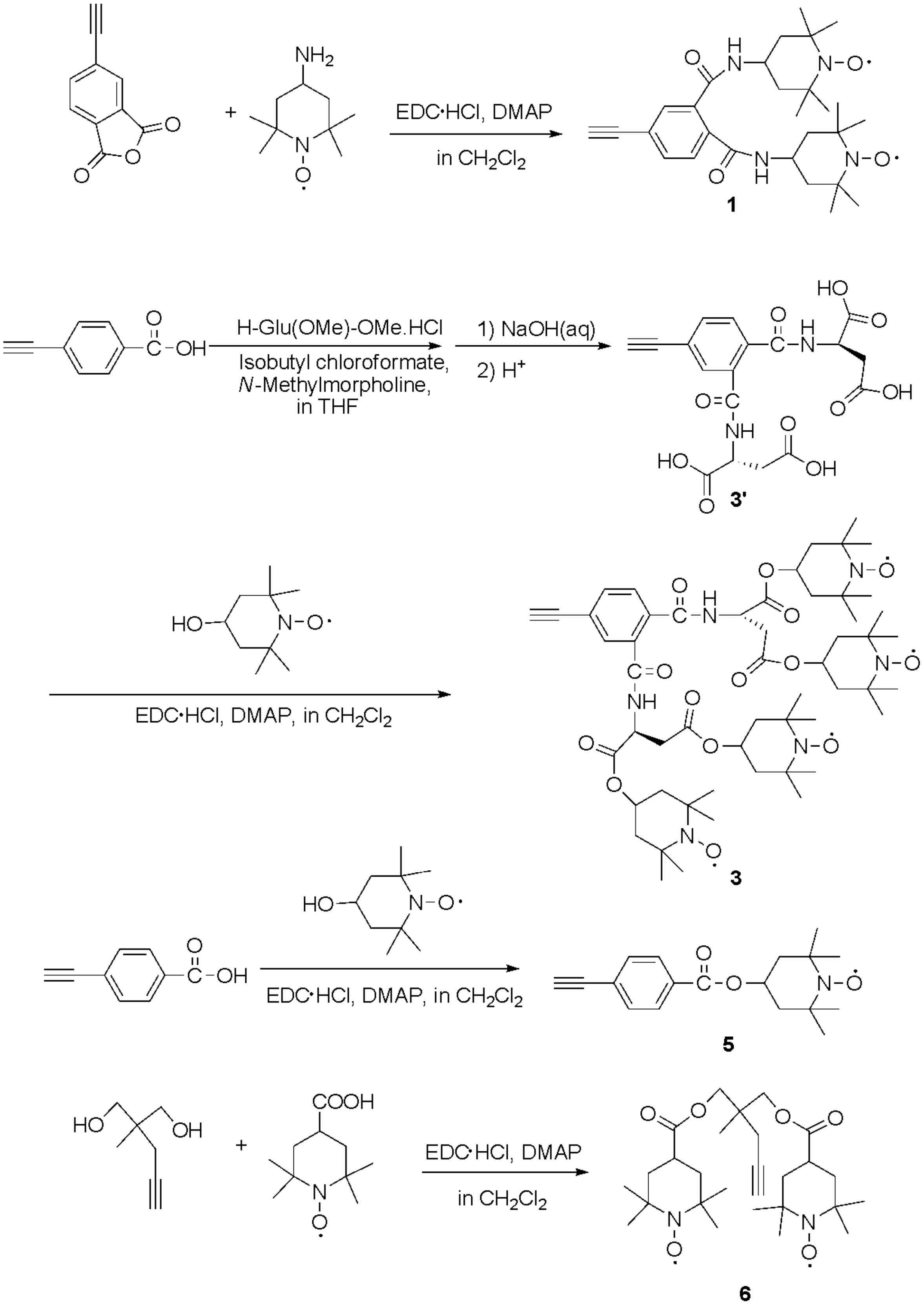


Table 1. Polymerization of Acetylenic Monomers 1–8 with $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$

run	monomer	polymer		
		yield, %[d]	M_n[e]	M_w/M_n[e]
1[a]	**1**	99	108 900	4.75
2[a]	**2**	100	—[f]	—[f]
3[b]	**3**	95	125 700	4.43
4[b]	**4**	99	83 800	3.39
5[b]	**5**	97	136 500	4.68
6[c]	**6**	62	10 000	1.36
7[c]	**7**	100	—[f]	—[f]
8[c]	**8**	66	47 000	2.01

[a] In THF, 24 h, 30 °C; $[M]_0$ = 0.50 M, [Rh] = 10 mM. [b] In THF, 24 h, 30 °C; $[M]_0$ = 0.25 M, [Rh] = 2.5 mM. [c] In $CHCl_3$, 24 h, 30 °C; $[M]_0$ = 0.25 M, [Rh] = 2.5 mM. [d] MeOH-insoluble part. [e] Determined by GPC (THF, polystyrene calibration). [f] Insoluble due to gelation.

about 3300 and 2120 cm^{-1} due to the stretching vibrations of H–C≡ and –C≡C–, respectively, indicating that the ordinary acetylene polymerization took place. The IR spectra of all the polymers showed a strong absorption maximum at 1364 cm^{-1} assignable to the nitroxy radical, implying that the TEMPO moiety is present in the polymers.

Properties of the Polymers. Poly(**1**), poly(**3**)–poly(**5**), and Poly(**8**) were soluble in relatively nonpolar organic solvents including toluene, $CHCl_3$, CH_2Cl_2 and THF, but insoluble in *n*-hexane, methanol and diethyl ether. Poly(**6**) was soluble in $CHCl_3$ and THF, partly soluble in toluene and CH_2Cl_2, and insoluble in *n*-hexane, methanol and diethyl ether. Poly(**2**) and poly(**7**) were insoluble in common organic

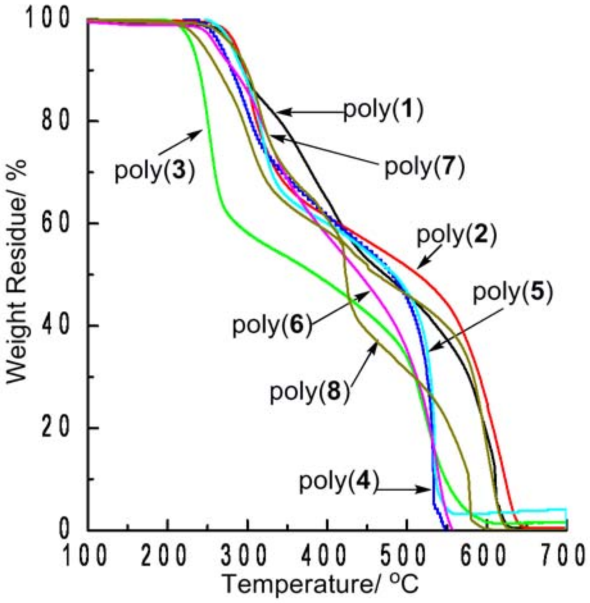


Figure 1. TGA curves of poly(**1**)–poly(**8**) measured at a heating rate of 10 °C min^{-1} in air.

solvents. Figure 1 illustrates the TGA traces of the present polymers. The onset temperatures of weight loss of poly(**1**)–poly(**8**) were all around 220–274 °C under air. All of the polymers containing TEMPO decomposed in similar fashions. All of the present polymers completely decomposed when temperature was raised above 650 °C.

The cyclic voltammetry (CV) curves of poly(**1**) and poly(**4**) are shown in Figure 2. Reversible oxidation and reduction based on the TEMPO radical are observed for all the polymers. Poly(**1**) exhibits an oxidation potential peak at 0.507 V versus Ag/Ag^+, and a reduction potential peak at 0.459 V versus Ag/Ag^+ at a sweep rate of 0.01 V s^{-1}, while poly(**4**) shows the corresponding peaks at 0.504 and 0.431 V, respectively. It is noted that the distances between the oxidation and reduction potential peaks of poly(**1**) and poly(**4**) are 0.048 and 0.073 V, respectively, which are by far smaller than those of other electroactive organic materials such as PTMA (ca. 0.146 V).[14] The small gaps between the reduction and oxidation peaks generally imply large electrode reaction rates of the polymers, which suggests that these polymers will exert high power rates in the charge/discharge processes of battery

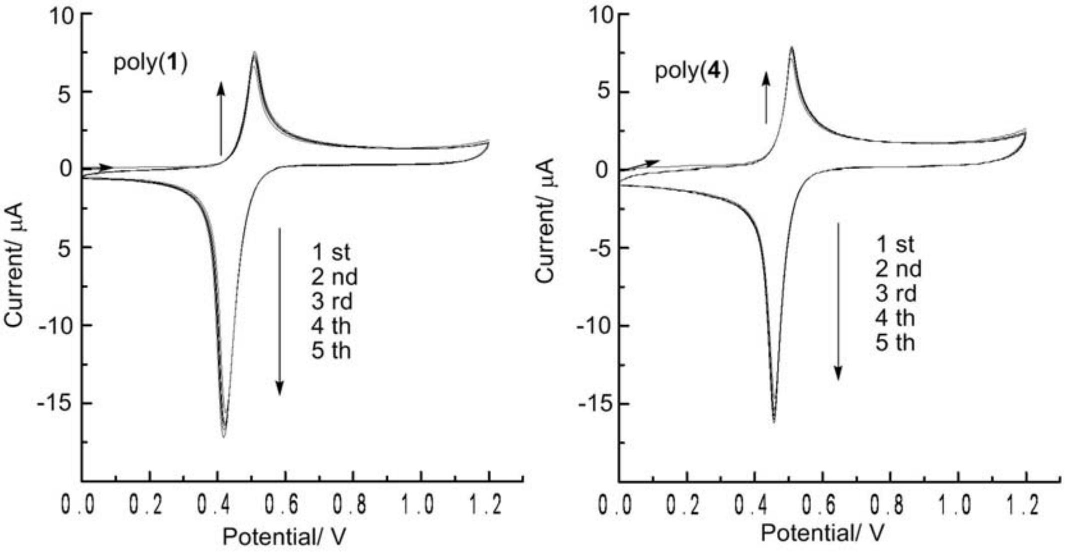


Figure 2. Cyclic voltammograms of poly(**1**) and poly(**4**) measured at a scan rate of 0.01 V s^{-1} vs. Ag/Ag^+ in TBAP solution.

under the constant battery process conditions. The oxidation and reduction peaks of poly(**1**) and poly(**4**) scarcely changed after five CV scans, indicating that they were electrochemically quite stable.

Figure 3 shows the electron spin resonance (ESR) spectrum of poly(**1**) and poly(**2**). The ESR spectrum of poly(**1**) and poly(**2**) exhibited a sharp singlet signal

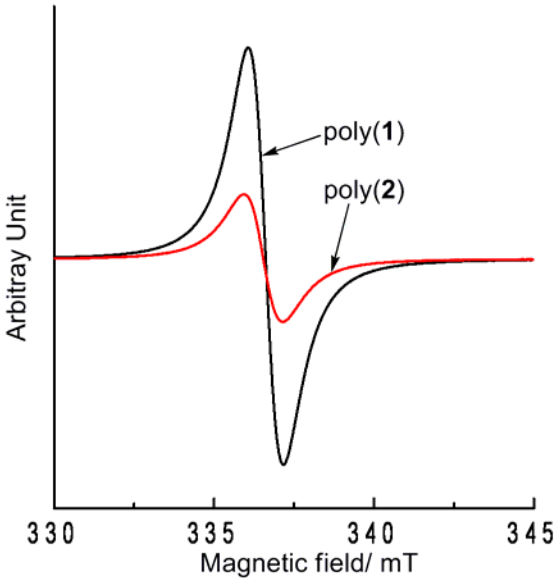


Figure 3. ESR spectrum of poly(**1**) and poly(**2**) measured in the powdery state .

based on the TEMPO moiety at g = 2.0070 and 2.0064 respectively, which are close to g = 2.0055 of the TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) crystal, but with the small enhancement probably due to the effect of the polymer backbone. The spin concentration of poly(**1**) and poly(**2**) were tested up to 2.53×10^{21} and 2.41×10^{21} spins g^{-1} respectively, and much larger than that of PTMA, hence the local spin concentration within the macromolecular domain of poly(**1**) and poly(**2**) are higher than that of PTMA. The ESR spectra of other polymers were similar to that of poly(**1**). Further the author precisely determined the spin concentrations and magnetic properties of poly(**1**), poly(**2**), and poly(**7**), which are listed in Table 2. As seen from Table 2, poly(**1**), poly(**2**), and poly(**7**) possess approximately quantitative amounts of free radicals, i.e., relatively close to one in poly(**7**) and around 2 in poly(**1**) and poly(**2**) per repeating unit. Both of the Curie-Weiss temperature Θ and the frequency dependence of the ESR line width are consistent with the 1-D magnetic interaction between TEMPO radicals attached to the polymer backbone. The Θ of the polymers with the 1-D chain of TEMPO radicals should be smaller than about 7 K of the TEMPOL crystal in which the 3-D magnetic interaction dominates the Θ. The ESR line widths vary with the ESR frequency in the 1-D electronic systems,[23] as demonstrated in Table 2.

Table 2. Magnetic Properties of Polymers

polymer	number of spins per monomer unit	Curie-Weiss temperature Θ [K]	ESR g-factor	ESR line width/ G	
				~50 MHz	~9 400 MHz
poly(**1**)	2.03±0.10	1.9	2.0070	13.9	9.9
poly(**2**)	1.96±0.10	1.8	2.0064	12.6	8.9
poly(**7**)	0.83±0.05	1.5	2.0064	13.0	8.6

Figure 4 exhibits the charge/discharge curves of the cells fabricated using poly(**1**)–poly(**8**) measured at a constant current density of 0.030–0.096 A g^{-1} in the voltage range of 2.5–4.2 V. During the charge process of poly(**1**), the voltage sharply increased from 3.0 V to 3.5 V in a range of 0–10 A h kg^{-1} cell capacity, followed by a highly steady voltage plateau at about 3.5–3.7 V up to a cell capacity of 95 A h kg^{-1}, and the voltage finally increased to a top cutoff voltage of 4.2 V. Similarly, during the discharge process of poly(**1**), the voltage quickly reduced from 4.2 V to 3.7 V within 0–8 A h kg^{-1} cell capacity, followed by a steady voltage plateau at about 3.7–3.4 V until the capacity up to 97 A h kg^{-1}, and the voltage then gradually decreased to a bottom cutoff voltage at 2.5 V. The plateau voltages of the charge/discharge processes are in the range of 3.4–3.7 V starting from approximately 3.6 V, which corresponds to the redox potential of the TEMPO radical. The charge/discharge process of poly(**2**)–poly(**8**) behaved similarly to poly(**1**). Namely, all of the present polymers exhibit clear voltage plateaus at about 3.6 V in both charge and discharge curves, indicating that the polymers can be used as cathode-active materials of a rechargeable battery.

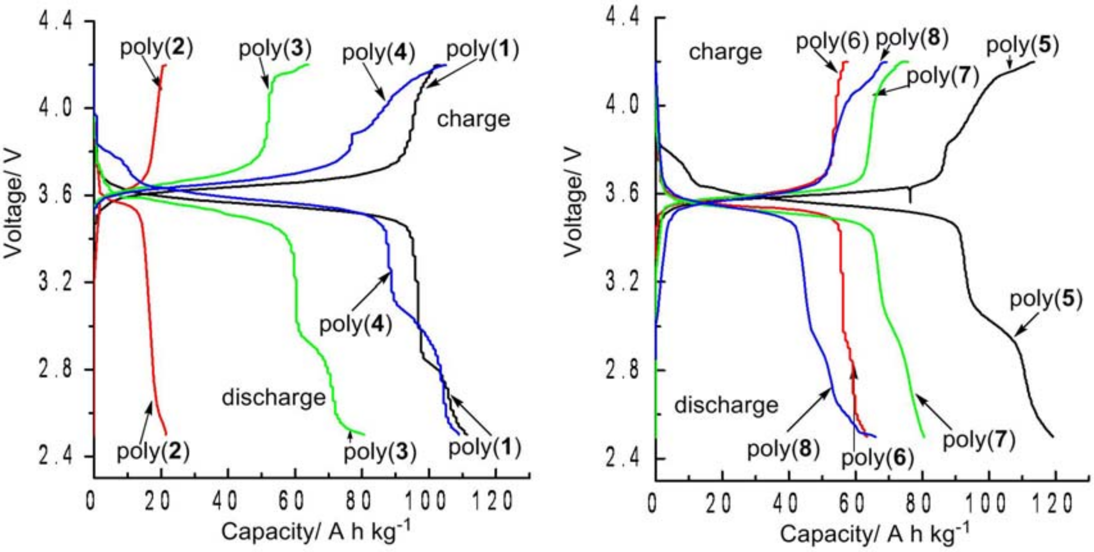


Figure 4. Charge-discharge curves of poly(**1**)–poly(**8**) at a current density of 0.030–0.096 A g^{-1} in a range of 2.5–4.2 V cell voltage.

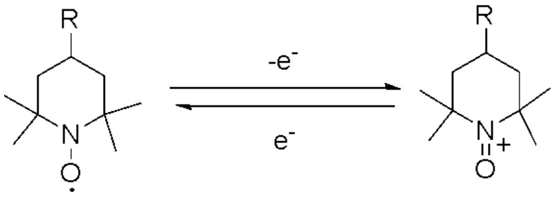
It is reasonable to assume that the charge process at the cathode is oxidation of TEMPO (**9**) in the polymers to oxoammonium salt (**10**), and the discharge process is the opposite reaction, namely, reduction of the salt (Scheme 3). Taking it into account that one TEMPO moiety provides one electron in this redox process, the author can estimate the theoretical capacities of the cells based on poly(**1**)–poly(**8**) to be 89.3–113 A h kg^{-1} (Table 3). Evaluating from the values at 2.5 V in Figure 3, the initial discharge capacities of the cells using poly(**1**)–poly(**8**) are determined to be 21.3–108 A h kg^{-1} per polymer weight at a current density of 0.030–0.096 A g^{-1}. The observed discharge capacity of poly(**1**), poly(**4**), and poly(**5**) was 108, 96.3, and 89.3 A h kg^{-1}, respectively, which agreed with the theoretical capacity. This demonstrates that poly(**1**), poly(**4**), and poly(**5**) displays high capacity which will lead to a wide

Table 3. Capacity Data of Poly(1)–poly(8)

polymer	m/e[a]	theoretical capacity, A h kg^{-1}[b]	observed Capacity, A h kg^{-1}[c]	observed capacity/ theoretical capacity, %
poly(**1**)	248.3	108.0	108.0	100
poly(**2**)	249.3	107.5	21.3	19.8
poly(**3**)	252.3	106.2	62.3	58.7
poly(**4**)	277.8	96.5	96.3	100
poly(**5**)	300.2	89.3	89.3	100
poly(**6**)	246.3	108.9	63.0	58.0
poly(**7**)	227.3	113.0	80.5	71.2
poly(**8**)	238.3	112.0	66.0	58.9

[a] The polymer mass required per exchangeable unit. [b] Theoretical capacity (A h kg^{-1}), namely, specific charge calculated according to reference.[25] [c] Observed capacity (A h kg^{-1}): Initial discharge capacity at a current density of 0.030–0.096 A g^{-1}, cut off at 2.5 V.

Scheme 3. Redox Reaction of Nitroxy Radical.



9 **10**

range of potential applications as a power source. On the other hand, the capacities of the poly(**2**)-, poly(**3**)- and poly(**6**)–poly(**8**)-based cells remained 21.3, 62.3, 63.0, 80.5, and 66.0 A h kg^{-1}, respectively (Table 3), clearly lower than that of the poly(**1**)-based counterpart, although their theoretical capacities are all about 100 A h kg^{-1}. This seems to be due to differences in both molecular scale structures (e.g., spacial arrangement of the TEMPO radicals) and macroscopic aggregation states (e.g., the size and hardness of polymer powders) but not in the spin concentration (because the spin concentrations of poly(**2**) and poly(**7**) are all quantitative).

Figure 5 depicts the charge/discharge curves of poly(**1**) and poly(**5**) observed at different current densities. The charge and discharge capacities gradually decreased with increasing current densities. An effective capacity of ca. 53.0 A h kg^{-1} was

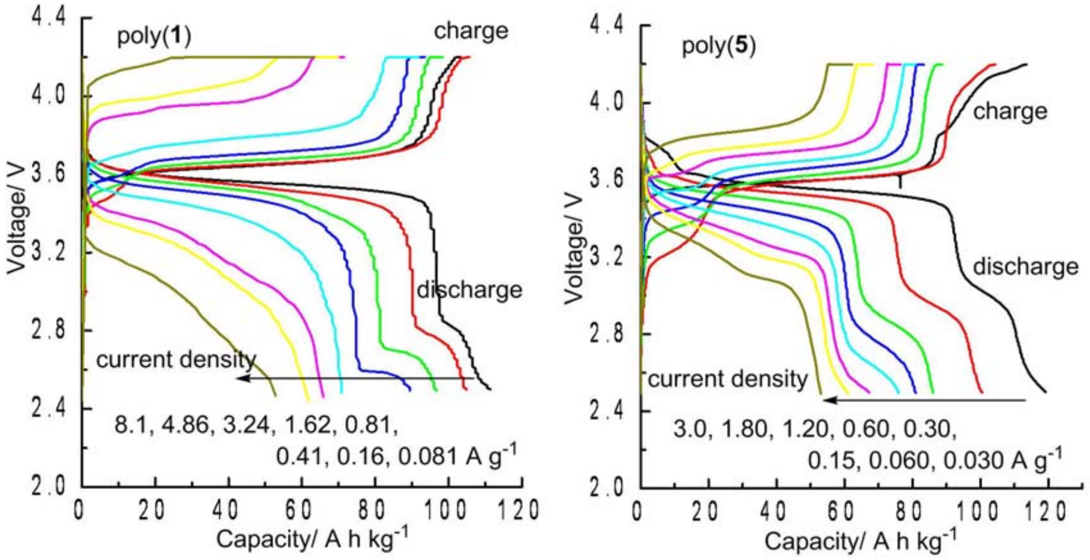


Figure 5. Charge/discharge curves of poly(**1**) and poly(**5**) at different currents in a range of 2.5–4.2 V cell voltage.

attained at a current density of 8.10 A g^{-1} based on a cutoff voltage of 2.5 V with poly(**1**), which corresponds to 50% of the discharge capacity at 0.081 A g^{-1}, indicating that the poly(**1**)-based cell displays the excellent charge/discharge characteristics under the extremely large currents. The fabricated cell contains 1.23 mg of poly(**1**) as an electro-active material, and so the cell capacity of 108 A h kg^{-1} is calculated as 0.133 mA h. In this experiment, the current density of 8.1 A/g corresponds to 10 mA, which is capable of charging and discharging the cell within 0.0133 hrs (47.9 sec). The poly(**5**)-based cell, in which the discharge capacity at 3.0 A g^{-1} was above 50 A h kg^{-1}, exhibited a similar performance to that of poly(**1**).

Figure 6 depicts the relationship between capacity and current densities of poly(**1**)–poly(**8**). The large capacity of poly(**4**) was maintained fairly well even though the current densities was increased to 7.3 A g^{-1}. On the other hand, the capacity of the other polymers decreased more with increasing current densities. Thus the largest capacity is available in the discharge of poly(**4**) among the present polymers irrespective of the current densities. Poly(**1**), poly(**3**), and poly(**5**) displayed pretty large capacities even though high current densities up to 3–9 A g^{-1}

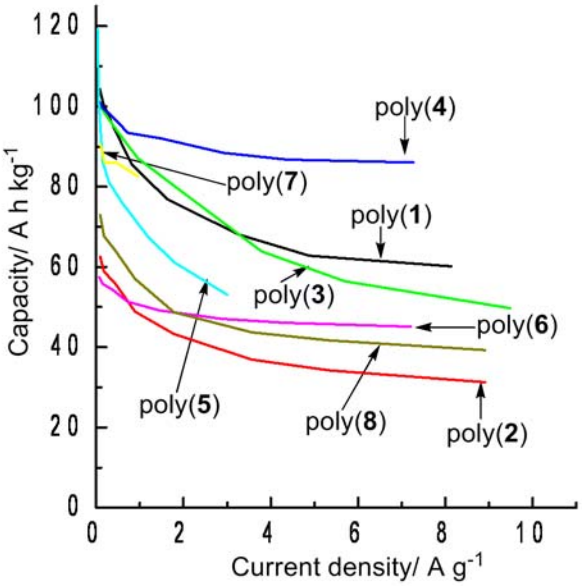


Figure 6. Dependence of capacity on current densities in poly(**1**)–poly(**8**).

were applied. On the other hand, poly(**2**) and poly(**6**)-poly(**8**) showed worse behavior.

Figure 7 illustrates the cycle performance of the poly(**1**)–poly(**6**)/Li cells, in which charging and discharging were repeated at a 0.30–0.96 A g^{-1} current density (1 mA current per 1.04–2.72 mg) under application of 2.5–4.2 V cell voltages. The capacity of the cell using poly(**1**) maintained over 85% after 100 cycles. Poly(**2**) exhibited a different cycle performance; namely, the increase in capacity was observed, which appears to arise from the increase in the contact surface between the electrode and the electrolyte probably because of swelling of the polymer during the charge/discharge process. The discharge capacity of poly(**3**) did not deteriorate even after 100 cycles. The cycle-lives of poly(**4**)–poly(**6**)-based cells were similar to that of poly(**1**). It seems that the cycle-lives of poly(**1**)–poly(**6**)-based cells are comparable to that of the reported PTMA system.[14]

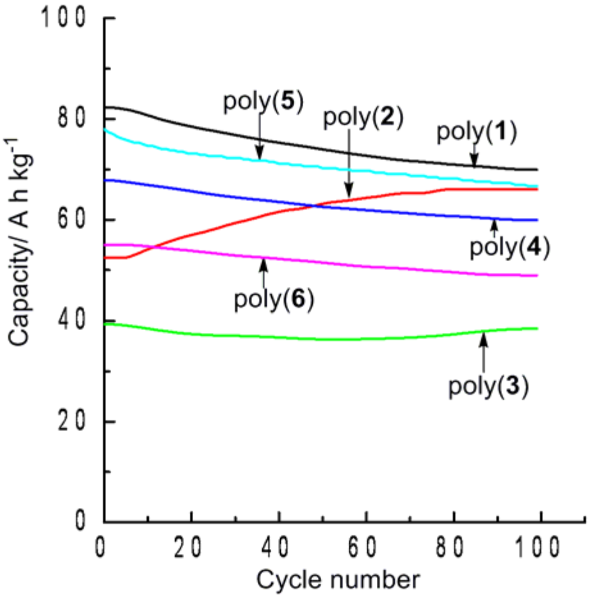


Figure 7. Dependence of capacity on cycle number in poly(**1**)–poly(**6**). Charging and discharging were repeated at a current density of 0.30–0.96 A g^{-1} in a range of 2.5–4.2 V cell voltage.

Conclusions

In the present research, the author have synthesized a group of acetylenic monomers containing TEMPO, **1**–**8**, and polymerized them with a rhodium catalyst. Monomers **1**, **3–6,** and **8** provided polymers with number-average molecular weights of 10 000–108 900 in 62–99% yields, while monomers **2** and **7** gave insoluble polymers in 100% yields. The separations of the oxidation and reduction potential peaks of these polymers in CV were by far smaller than those of other electroactive organic materials, indicative of high power rate in the charge/discharge processes of battery. The ESR spectra of poly(**1**) and poly(**2**) exhibited a sharp singlet, and poly(**1**) and poly(**2**) possessed practically quantitative amounts of free radicals based on the TEMPO moiety, namely, around two spins per repeating unit. The capacity of the poly(**1**)-, poly(**4**)-, and poly(**5**)-based cell reached 108, 96.3 and 89.3 A h kg^{-1}, respectively, corresponding to 100% of their theoretical capacity value. The cells fabricated with poly(**1**)–poly(**6**) as cathodes demonstrated a promising cycle-life, i.e., the capacity hardly deteriorated even after 100 cycles. Charge-storage materials based on poly(**1**)–poly(**8**) can be applied to cathode-active materials in organic radical batteries, which feature quick charging and discharging, and high power density. Among the present polymers, poly(**4**) exhibited a high capacity up to 96.3 A h kg^{-1}, which did not decrease below 90 A h kg^{-1} even at a high current densities up to 7.3 A g^{-1} and the excellent performance was kept even after 100 cycles.

Experimental Section

Materials. Solvents used for polymerization were distilled before use according to the standard procedures. 4-Carboxy-TEMPO (TCI), 4-hydroxy-TEMPO (TCI), L-Glutamic acid-α,γ-dimethyl ester hydrochloride (L-H-Glu(OMe)-OMe·HCl) (Watanabe Chemical Industries, Ltd), propargyl alcohol (Aldrich), propargylamine (Aldrich), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl; Eiweiss Chemical Corporation), 4-dimethylaminopyridine (DMAP; Wako) were purchased and used without further purification. 4-Carboxy-2,2,6,6-tetramethyl-1-piperidinoxy *N*-propargylamide,[16] 4-Carboxy-2,2,6,6-tetramethyl-1-piperidinoxy propargyl ester,[16] 1-Pentyne-4,4-dimethanol,[19] 4-ethynylbenzoic acid,[20] *N*-(4-ethynyl benzoyl)-L-aspartic acid methyl ester,[21] and (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$[22] were synthesized according to the literature.

Measurements. IR spectra were measured using a JASCO FT/IR-4100 spectrophotometer. Melting points (m.p.) were measured on a Yanaco micro melting point apparatus. Elemental analysis was conducted at the Kyoto University Elemental Analysis Center. The number- and weight-average molecular weights (M_n and M_w, respectively) of polymers were determined by gel permeation chromatography (GPC) on a JASCO Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with Shodex columns KF805-L × 3, using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, calibrated with polystyrene standards at 40 °C. Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7. ESR spectra were measured on a JEOL JES-FR30 type X-band (9.48 GHz) spectrometer. The precise number of free radicals was estimated with a Quantum Design MPMS susceptometer and a home-built low-frequency ESR-NMR apparatus operated around 50 MHz, 4-hydroxy-TEMPO as a reference radical, the samples were tested in solid state.[23] Cyclic voltammograms were observed with an HCH Instruments ALS600A-n electrochemical analyzer. The measurements were carried out with a modified ITO substrate as the working electrode coupled with a Pt plate counter electrode and an Ag/AgCl reference electrode[Ag/AgCl/ KCl (saturated)], using a solution of a polymer (1 mM) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in CH_2Cl_2.

Monomer Synthesis. 4-Ethynylphthalic acid 1,2-di[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)]amide (**1**) was prepared as follows: 4-Amino-TEMPO (500 mg, 2.90 mmol) was added to a solution of EDC·HCl (581 mg, 3.04 mmol) and DMAP (37 mg, 0.30 mmol) in CH_2Cl_2 (30 mL) at room temperature. 4-Ethynylphthalic anhydride (250 mg, 1.46 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (20 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation to afford the crude product. It was purified on a silica gel column with a hexane/ethyl acetate mixture (4/1 volume ratio) as eluent. An orange-red solid of **1** was obtained in 64% yield (921 mg), m.p. 204.0–205.0 °C; IR (KBr): ν bar = 3257 (H–C≡), 3068 (N–H), 2976, 2938, 2104 (C≡C), 1645 (C=O), 1561 (N–H), 1329, 1243, 1179, 847 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{40}O_4N_4$: C 67.71, H 8.12, N 11.28; found: C 67.50, H 8.39, N 11.50.

4-Ethynylphthalic acid 1,2-di[4-(2,2,6,6-tetramethyl-1-piperidinyloxy)] ester (**2**) was synthesized from 4-ethynylphthalic anhydride and two equivalents of 4-hydroxy-TEMPO in a manner similar to **1**. Yield 80%, orange-red solid, m.p. 140.0–141.0 °C; IR (KBr): ν bar = 3224 (H–C≡), 2976, 2935, 2106 (C≡C), 1736 (C=O), 1714 (C=O), 1603, 1465, 1365, 1295 (C–O), 1193, 1133, 1069, 963, 789, 769, 564 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{38}O_6N_2$: C 67.45, H 7.68, N 5.62. Found: C 67.30, H 7.59, N 5.50.

Compound **3’** (in scheme 2) was synthesized from 4-ethynylphthalic anhydride and two equivalents of L-H-Glu(OMe)-OMe·HCl, then by removing the methyl group of products according to the literature.[22] Yield 34%, white solid, ^{1}H NMR (400 MHz,$CDCl_3$, 25 °C, TMS): δ = 2.16 (q, 2H, *J* =7.26 Hz, -2CHC*H*$_2$COOH), 2.47 (q, 2H, *J* = 7.26 Hz, -2CHC*H*$_2$COOH); 3.22 (s, 1H, ≡C*H*), 4.81 (q, 2H, *J* = 6.99 Hz, -2NHC*H*COOH), 7.54–7.80 (m, 3H, Ar), 8.11 (d, 2H, -2NH); ^{13}C NMR (100 MHz,$CDCl_3$, 25 °C, TMS): δ = 30.2 (CH*C*H$_2$COOH), 52.4 (NH*C*HCOOH), 81.4 (≡*C*H), 82.3 (≡*C*-), 125.7, 127.1, 132.0, 132.2, 132.5, 133.4 (Ar), 166.3 (*C*ONH), 172.3 (CH*C*OOH), 173.7 (CHCH$_2$*C*OOH).

Monomer **3** was synthesized from **3**’ and 4-hydroxy-TEMPO in a manner similar to **2**. Yield 80%, orange-red solid, m.p. 137.0–139.0 °C; IR (KBr): ν bar = 3243 (H–C≡), 2974, 2927, 2102 (C≡C), 1712 (C=O), 1604, 1562, 1465, 1365, 1307, 1268 (C–O), 1173, 1 103, 971, 906, 856, 763, 663, 556 cm^{-1}; elemental analysis calcd (%) for $C_{54}H_{80}O_{14}N_6$: C 62.53, H 7. 77, N 8.10; found: C 62.30, H 7.59, N 8.30.

Monomer **4** was synthesized from *N*-(4-ethynyl benzoyl)-L-aspartic acid which was prepared form *N*-(4-ethynyl benzoyl)-L-aspartic acid methyl ester and 4-hydroxy-TEMPO in a manner similar to **3**. Yield 80%, orange-red solid, m.p. 127.0–129.0 °C; IR (KBr): ν bar = 3251 (H–C≡), 2969, 2889, 2105 (C≡C), 1731 (C=O), 1604, 1562, 1504, 1465, 1403, 1373, 1365, 1292 (C–O), 1200, 1164, 1084, 987, 856, 759, 674, 578 cm^{-1}; elemental analysis calcd (%) for for $C_{31}H_{43}O_7N_3$: C 65.36, H 7.61, N 7.38; found: C 65.50, H 7.59, N 7.50.

4-Ethynylbenzoic acid 4-(2,2,6,6-tetramethyl-1-piperidinyloxy) ester (**5**) was prepared in a manner similar to **1**. Yield 82%, orange-red solid, m.p. 121.0–123.0 °C; IR (KBr): ν bar = 3243 (H–C≡), 2974, 2931, 2102 (C≡C), 1712 (C=O), 1604, 1455, 1365, 1307, 1268, 1238, 1194, 1168 (C–O), 1106, 971, 856, 767, 686, 648 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{22}NO_3$: C 71.97, H 7.38, N 4.66; found: C 72.01, H 7.32, N 4.61.

1-Pentyne-4,4-dimethyl di(2,2,5,5-tetramethyl-1-piperidinyloxyl-carboxylate) (**6**) was synthesized from 1-pentyne-4,4-dimethanol and two equivalents of 4-carboxy-TEMPO in a manner similar to **1**. Yield 32%, orange-red solid, m.p. 112.0–113.0 °C; IR (KBr): ν bar = 3433, 3314, 2972, 2931, 2120, 1725 (C=O), 1473, 1376, 1364 (N–O), 1292, 1243, 1167, 1040, 973, 871, 747, 647, 632 cm^{-1}, elemental analysis calcd (%) for $C_{27}H_{44}N_2O_6$: C 65.83, H 9.00, N 5.69; found: C 65.62, H 8.67, N 5.57.

Polymerization. Polymerizations of monomers **1**–**8** were carried out with $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ as a catalyst in dry solvents at 30 °C for 24 h. After polymerization, the resultant solutions were poured into a large amount of methanol to precipitate the formed polymers. They were filtered and then dried under reduced pressure.

IR (KBr) Data of the Polymers. Poly(**1**): 3460, 2974, 2945, 1733, 1458, 1363, 1310, 1168, 968, 649 cm^{-1}; poly(**2**): 3456, 2976, 2937, 1718, 1364, 1288, 1240, 1131, 1067, 970, 732, 645 cm^{-1}; poly(**3**): 3478, 2978, 2937, 1724, 1605, 1515, 1434, 1380, 1364, 1257, 1162, 1110, 1049, 910, 852, 744 cm^{-1}; poly(**4**): 3444, 2977, 2935, 1735, 1646, 1600, 1515, 1461, 1373, 1364, 1303, 1253, 1191, 1149, 1064, 995, 856, 671 cm^{-1}; poly(**5**): 3444, 2973, 2897, 1716, 1605, 1562, 1465, 1364, 1311, 1272, 1176, 1106, 1014, 802, 763, 482 cm^{-1}; poly(**6**): 3464, 2974, 2938, 1734, 1459, 1377, 1364, 1306, 1242, 1193, 1164, 1104, 1018, 971, 722, 648 cm^{-1}; poly(**7**): 3469, 2978, 2937, 1734, 1458, 1364, 1308, 1240, 1162, 964 cm^{-1}; poly(**8**): 3450, 3054, 3016, 2954, 2897, 1596, 1494, 1440, 1364, 1248, 1118, 856, 833, 689, 553 cm^{-1}.

Fabrication and Electrochemical Measurements of the Batteries Using the Polymers. A coin-type cell was fabricated by stacking electrodes (1.13 cm^2) with porous polyolefin separator films. A cathode was formed by pressing the composites of a polymer (10 wt%), carbon fiber (80 wt%), and fluorinated polyolefin binder (10 wt%) as described in a previous paper.[25] The cathode was set to a coin-type cell possessing a lithium metal anode. A composite solution of ethylene carbonate (30 vol%)/diethyl carbonate (70 vol%) containing 1 M of LiPF_6 was used as an electrolyte. Charge/discharge properties were measured at 25 °C using a computer controlled automatic battery charge and discharge instrument (Keisokukiki, Co. Ltd., Battery Labo System BLS5500).

Theoretical Capacity of Polymer-Based Cell. The theoretical capacity (in A h/kg) of an electroactive polymer was calculated from the molecular weight required per exchangeable unit charge in a polymer:[26]

$$\mathrm{C\,(A\,h/kg)} = \frac{N_{\mathrm{A}} \times \mathrm{e}}{3600 \times (M_{\mathrm{w}}/1000)}$$

where $N_{\mathrm{A}}\times\mathrm{e}$ is the Faraday constant (96 487 C mol^{-1}), while M_{w} is the equivalent weight (or mass) of polymer in g, and defined as the molecular weight (molar mass) of the repeating unit of polymer divided by the number of electrons exchanged or stored by it (which may be a fractional number), or as the molecular weight of the set of repeating units exchanging (storing) one electron in polymers.

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Chapter 8

Synthesis and Properties of Polyacetylene and Polynorbornene Derivatives Carrying 2,2,5,5-Tetramethyl-1-pyrrolidinyloxy (PROXY) Moieties

Abstract

PROXYL-containing propargyl ester $HC{\equiv}CCH_2OCO$-3-PROXYL (**1**), *N*-propargylamide $HC{\equiv}CCH_2NHCO$-3-PROXYL (**2**), 1-pentyne-4,4-dimethyl ester $HC{\equiv}CCH_2C(CH_3)(CH_2OCO\text{-3-PROXYL})_2$ (**3**) and norbornene diester monomers, NB-2,3-*exo,exo*-$(CH_2OCO\text{-3-PROXYL})_2$ (**4**), NB-2,3-*endo,endo*-$(CH_2OCO\text{-3-PROXYL})_2$ (**5**), and NB-2,2-$(CH_2OCO\text{-3-PROXYL})_2$ (**6**) (NB = norbornene, PROXYL = 2,2,5,5-tetramethyl-1-pyrrolidinyoxy) were polymerized to afford novel polymers containing the PROXYL radical. While **1** and **2** provided polymers with number-average molecular weights of 3300–29 800 in 60–65% yields in the presence of a Rh catalyst, monomers **4**–**6** gave polymers with number-average molecular weights up to 209 000–272 000 in 90–94% yields with a Ru catalyst. The formed polymers were thermally stable up to ca. 220 °C according to TGA, and soluble in common organic solvents including toluene, $CHCl_3$ and THF. Poly(**1**), poly(**2**), poly(**4**)–poly(**6**) hardly exhibited absorption above 400 nm, which corresponds with their very light color. The oxidation/reduction gaps in the cyclic voltammograms of the present polymers were as small as 0.072–0.092 V, indicating large electrode reaction rates. All the PROXYL-containing polymers demonstrated the reversible charge/discharge processes, whose capacities were larger than 85 A h/kg. In particular, the maximum capacity of poly(**1**)- and poly(**4**)-based cells reached 117 A h/kg and 107 A h/kg, which practically coincided with the theoretical capacity values (119 A h/kg and 109 A h/kg, respectively).

Introduction

Stable organic radicals have been utilized in the studies of spin trapping,[1] spin labeling,[2] organic ferromagnetism,[3] and so forth. Among them, nitroxyl radicals such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,2,5,5-tetramethyl-1-pyrrolidinyloxy (PROXYL) are well known and have found applications in a variety of fields, including spin labels to study the conformation and structural mobility of biological systems,[4] scavengers of unstable radical species,[5] and oxidizing agents.[6] Polymers carrying stable organic radicals have been intensively investigated in the fields of electron spin resonance[7] and molecular motion,[8] and frequently employed as functional materials such as polymeric stabilizers,[9] oxidants of alcohols,[10] and spin- and charge-storage materials.[11] Among these applications, polymers having radicals have been extensively studied in the search for organic ferromagnetic materials;[12] e.g., poly(triphenylamine-*alt*-phenylenevinylene)s,[13] poly(9,10-anthryleneethynylene),[14] poly(phenylacetylene),[15] dendritic-macrocyclic poly(arylmethyl) polyradical.[16] Charge-storage materials based on polyradicals such as TEMPO- and PROXYL-carrying polymers can be applied to cathode-active materials in organic radical batteries. To the best of our knowledge, however, the synthesis and battery properties of this type of polymers have been scarcely investigated.[17]

Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) has been prepared by the polymerization of a methacrylate monomer having the corresponding amine group followed by oxidation to generate the radical in the polymer.[17] This polymer was examined as a material for organic radical batteries which would be quickly chargeable and have a high power density.[18] It was found that this polymer contained ca. 70% of radical against the theoretical value and that the batteries using this polymer showed an average discharge voltage of 3.5 V and a discharge capacity of 77 A h/kg (70% of the theoretical value). Thus far, polymers carrying nitroxide free radicals have usually been synthesized by an indirect method, i.e., synthesis of precursor polymers having the corresponding amino group, followed by the oxidation to afford polymers containing stable radicals.[17] The indirect route is adopted due to lack of capability of radical-bearing monomers to undergo radical polymerization. However, this method is often accompanied by incomplete oxidation, resulting in the less than quantitative incorporation of the radical into the polymers. A feasible approach to circumvent this problem is to polymerize free radicals-containing monomers with transition metal catalysts, which are not affected by the radicals in the monomers.

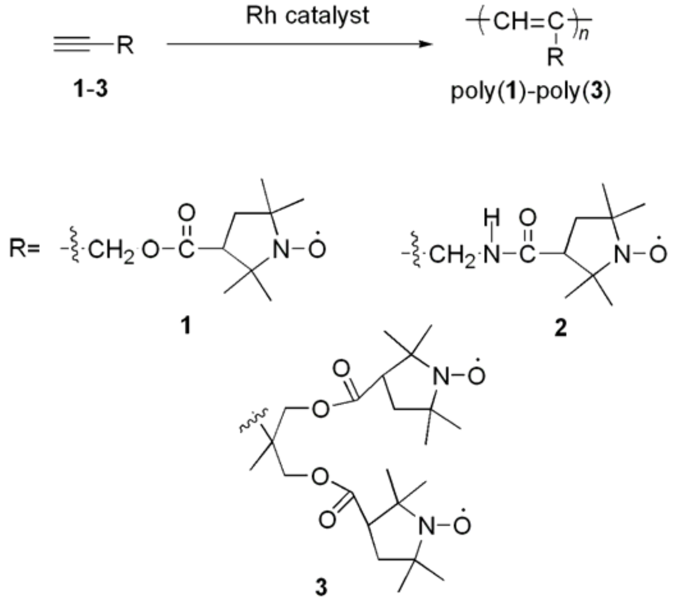
The author have recently studied the preparation and charge/discharge properties of a series of polyacetylenes and polynorbornenes containing TEMPO groups to find that the discharge capacity of the cell fabricated with poly(NB-2,3-*endo,exo*-(COO-4-TEMPO)$_2$) reaches the theoretical value (109 A h/kg) anticipated for the molecular structure.[19] Polymers containing PROXYLs are promising candidates as cathode-active materials in quickly chargeable/dischargeable and high power density batteries. However, the synthesis of polymers containing PROXYLs and their application to a rechargeable battery has not been reported so far.

The present chapter deals with the synthesis of PROXYL-carrying polymers by direct polymerization of PROXYL-containing acetylenes and norbornenes (Scheme 1) with transition metal catalysts, elucidation of the fundamental properties, and the evaluation of their performance as cathode-active materials in organic radical battery.

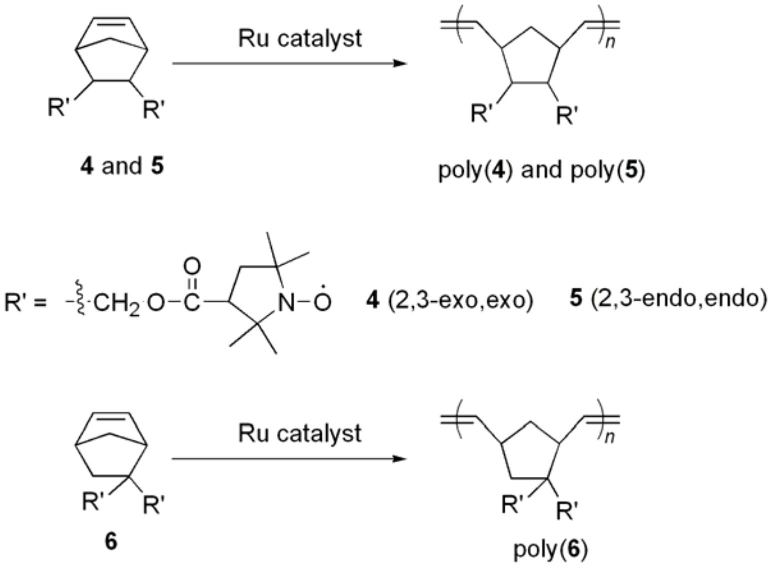
Results and Discussion

Monomer Synthesis. The synthetic routes for monomers **1**–**6** have been illustrated in Scheme 2. Acetylenic ester and amide monomers, namely 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy propargyl ester (**1**) and 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy *N*-propargylamide (**2)** were synthesized by condensation of the carboxy group of 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (3-carboxy-PROXYL) with the

Scheme 1. Polymerization of Monomers 1–6



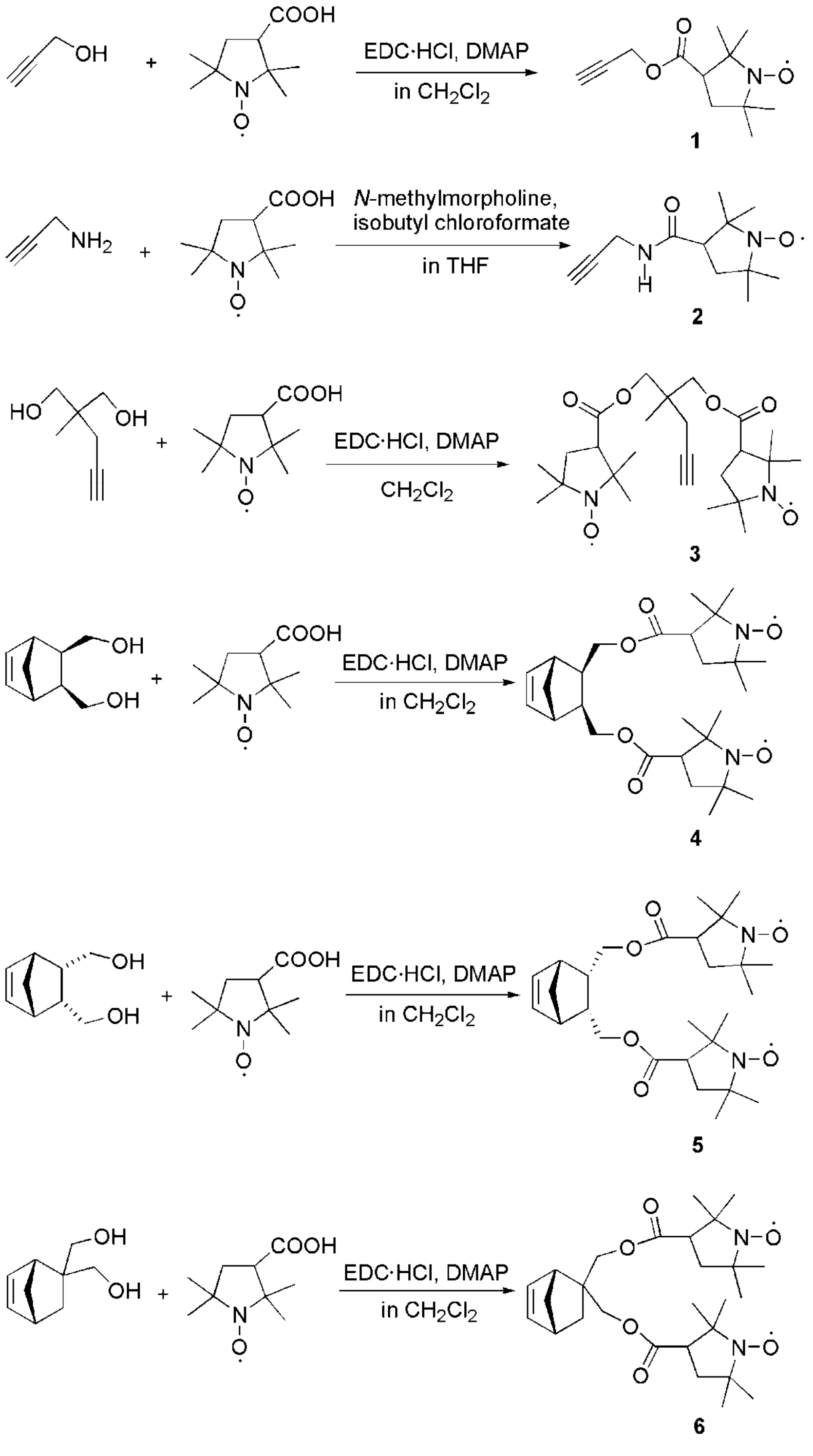
(a) Polymerization of PROXYL-containing acetylene monomers



(b) Polymerization of PROXYL-containing norbornene monomers

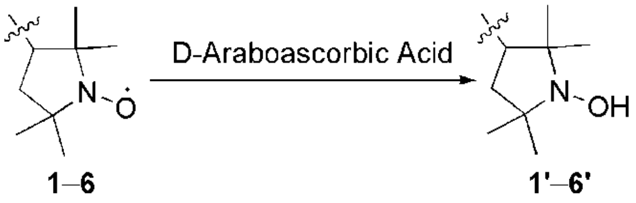
hydroxy or amino group of propargyl compounds. 1-Pentyne-4,4-dimethyl-di(2,2,5,5-tetramethyl-1-pyrrolidinyloxyl-carboxylate) ($HC\equiv CCH_2C(CH_3)(OCO$-3-PROXYL$)_2$ (**3**) was prepared by condensation of the carboxy group of 3-carboxy-PROXYL with the hydroxyl groups of

Scheme 2. Preparation of Monomers 1–6



1-pentyne-4,4-dimethanol. Norbornene diester monomers, namely 5-norbornene-2-exo, 3-exo-dimethyl-di(2,2,5,5-tetramethyl-1-pyrrolidinyloxy-carboxylate) (**4**), 5-norbornene-2-endo,3-endo-dimethyl-di(2,2,5,5-tetramethyl-1-pyrrolidinyloxy-carbo

Scheme 3. Conversion to Hydroxyamine



xylate) (**5**), and 5-norbornene-2,2-dimethyl-di(2,2,5,5-tetramethyl-1-pyrrolidinyloxy-carboxylate) (**6**) were synthesized by condensation of the hydroxy groups of norbornene derivatives and 3-carboxy-PROXYL. The monomers were purified by silica gel column chromatography eluted by ethyl acetate/*n*-hexane (1/4 volume ratio) or recrystallization using ethyl acetate/*n*-hexane (1/1 volume ratio). The presence of free radicals did not allow measuring the NMR spectra of the monomers. Hence they were converted to the corresponding hydroxyamine derivatives (**1'**–**6'**; Scheme 3) according to the literature method,[10c] and the ^{1}H and ^{13}C NMR spectra of these derivatives were measured, which supported that the monomers possessed the expected structures (see the Experimental part). Further confirmation for the structures of the monomers was furnished by IR spectra and elemental analysis.

Polymer Synthesis. The polymerization of acetylenic monomers **1**–**3** was carried out using $(\mathrm{nbd})\mathrm{Rh}^+[\eta^6\text{-}\mathrm{C_6H_5B^-(C_6H_5)_3}]$ as a catalyst at 30 °C for 24 h, the results of which are summarized in Table 1. Polymerizations of **1** were performed in toluene, $CHCl_3$, and THF, and the reaction mixtures were poured into a large excess of diethyl ether to give pale yellow powdery polymers. The polymer yields were in the range of 41–60%, and the polymers possessed M_n of 16 200–29 800. Among them, the polymerization in THF gave the best results with respect to polymer yield and the M_n, and the same behavior was observed for monomer **2**, i.e., polymer yield (65%) and M_n (3300) were highest in THF solution. This monomer hardly polymerized in toluene, which is attributable to the strong interaction between the Rh metal and the amide group in nonpolar toluene. However, the polymerization of **3** hardly afford

Table 1. Polymerization of Monomers 1–3 with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$]^a

			polymer^b		
run	monomer	solvent	yield, %	M_n^{c}	M_w/M_n^{c}
1	**1**	toluene	41	16 200	1.79
2	**1**	$CHCl_3$	59	19 300	1.69
3	**1**	THF	60	29 800	1.63
4	**2**	toluene	trace	—	—
5	**2**	$CHCl_3$	55	1 500	1.40
6	**2**	THF	65	3 300	1.20
7	**3**	THF	20	3 700	1.73

[a] Polymerized at 30 °C for 24 h; $[M]_0 = 0.25$ M, [Rh] = 2.5 mM. [b] Diethyl ether-insoluble part. The color of the polymers was pale yellow. [c] Determined by GPC eluted with THF, using a polystyrene calibration.

polymer probably owing to the steric hindrance of substituted groups.

Table 2 summarizes the conditions and results of ring-opening metathesis polymerization (ROMP) of norbornene monomers **4**–**6** using the Grubbs 2nd generation catalyst in CH_2Cl_2 at 30 °C for 2 h. The polymerization mixtures became deep yellow within 30 min, and gradually turned dark brown with the concomitant increase of viscosity. After polymerization, the reaction mixture was poured into a large amount of diethyl ether to precipitate the formed polymers. Gray solid polymers were obtained in 90–95% yields, whose M_n values were as high as 209 000–272 300. Both yield and M_n of the polymers scarcely changed even though the polymerization time was prolonged beyond 2 h.

Structure of the Polymers. Poly(**1**) and poly(**2**) exhibited no IR absorptions due to the stretching vibrations of C≡C and H–C≡, indicating that the ordinary acetylene polymerization took place. Polymerization of monomers **4**–**6** most likely takes place by ROMP of the norbornene moiety, although no clear information was

Table 2. Polymerization of Monomers 4–6 with the Grubbs 2nd Generation Catalyst[a]

		polymer[b]		
run	monomer	yield, %	M_n[c]	M_w/M_n[c]
1	**4**	94	272 300	3.53
2	**5**	90	210 600	3.67
3	**6**	95	209 000	4.24

[a] Polymerized in CH_2Cl_2 at 30 °C for 2 h; $[M]_0 = 0.50$ M, [Ru] = 5.0 mM. [b] Diethyl ether-insoluble part. The color of the polymers was gray. [c] Determined by GPC eluted with THF, polystyrene calibration.

obtained by IR spectroscopy. Strong absorption maxima at 1364 cm^{-1} assignable to the nitroxyl radical, were observed in the IR spectra of all the polymers, indicating the presence of PROXYL moiety in the polymers.

Properties of the Polymers. Poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) were soluble in relatively nonpolar common organic solvents including toluene, $CHCl_3$,

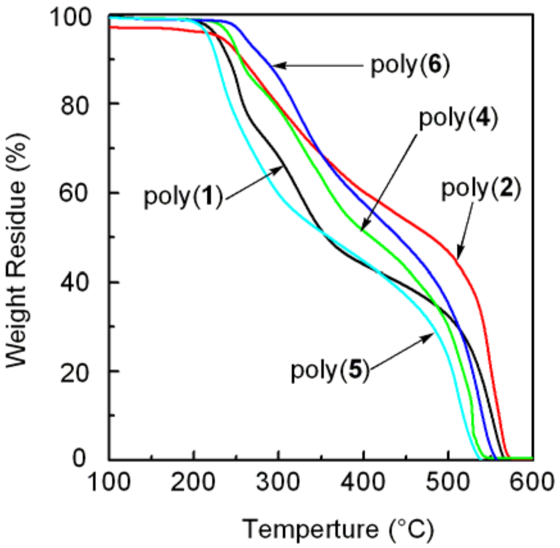


Figure 1. TGA curves of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) measured at a heating rate of 10 °C /min in air. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)–poly(**6**) : Table 2.

CH_2Cl_2 and THF, but insoluble in *n*-hexane and diethyl ether. TGA traces of the present polymers are shown in Figure 1. The temperatures for 5% weight loss for poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) were around 220–250 °C under air. All the polymers containing PROXYLs decomposed in similar fashions regardless of the main chain structure (polyacetylene and polynorbornene), suggesting that the thermolysis of the polymers initially occurs at the ester linkage which connects PROXYL moiety to the main chain, followed by the decomposition of the double bonds in the main chain.

Figure 2 depicts the UV-vis spectra of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) in $CHCl_3$, along with those of monomers **1**, **2**, and **4**–**6** for comparison. In all these spectra, the PROXYL moiety displays no absorption above 325 nm, which accounts for the almost white color of the monomers. Poly(**1**) and poly(**2**) with pale yellow color exhibited absorptions in the range 325–450 nm, which should originate from the conjugated polyacetylene main chain, while monomers **1** and **2** showed no absorption in this region. The observation that no absorption was seen above 325 nm in

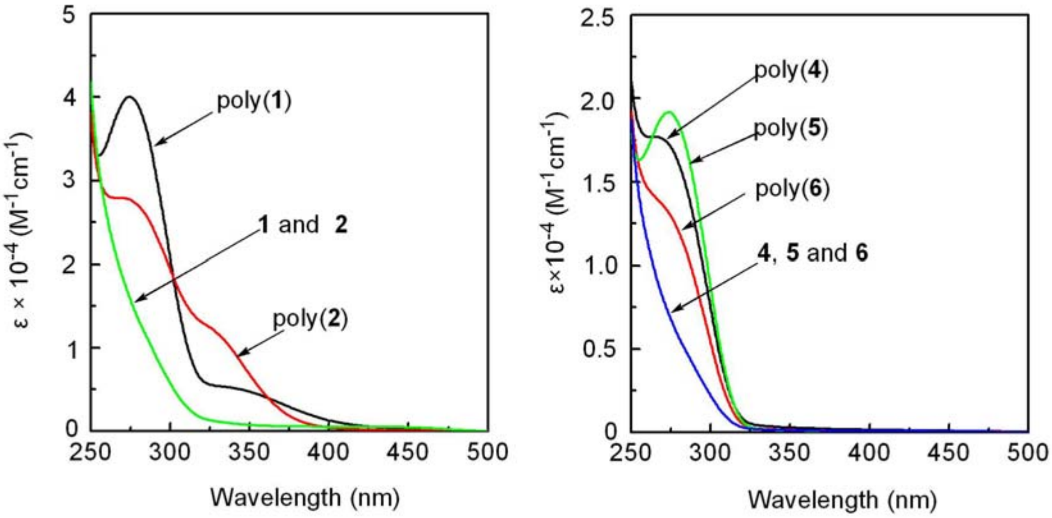


Figure 2. UV–vis spectra of **1**, **2** and **4**–**6** and poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) measured in $CHCl_3$. Concentration; **1** and poly(**1**): 4.46×10^{-5} M, **2** and poly(**2**): 4.48×10^{-5} M, **4**–**6** and poly(**4**)–poly(**6**): 2.04×10^{-5} M. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)–poly(**6**): Table 2.

poly(**4**)–poly(**6**) is consistent with their non-conjugated main chain.

The cyclic voltammetry (CV) curves of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) at the first cycle are shown in Figure 3. Reversible oxidation and reduction based on the PROXYL radical are observed for all the polymers. Poly(**1**) exhibits an oxidation potential peak at 0.55 V versus Ag/Ag$^+$, and a reduction potential peak at 0.47 V versus Ag/Ag$^+$, while poly(**2**) shows the corresponding peaks at 0.52 V and 0.44 V, respectively. Poly(**4**)–poly(**6**) showed similar oxidation peaks at 0.56, 0.57, and 0.56 V, and the corresponding reduction peaks at 0.49, 0.48, and 0.47 V, respectively. It is noted that the distances between the oxidation and reduction peak potentials of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) are 0.080, 0.081, 0.072, 0.090, and 0.092 V, respectively, at a sweep rate of 0.01 V/s, which are by far smaller than those of other electroactive organic materials such as PTMA (ca. 0.146 V),[17c] disulfide compounds (ca. 0.10–0.20 V)[20] and conducting polymers (ca. 0.20–0.80 V).[21] The small gaps between the reduction and oxidation peaks generally imply large electrode reaction rates of the polymers, which suggests that these polymers will exert high power rates

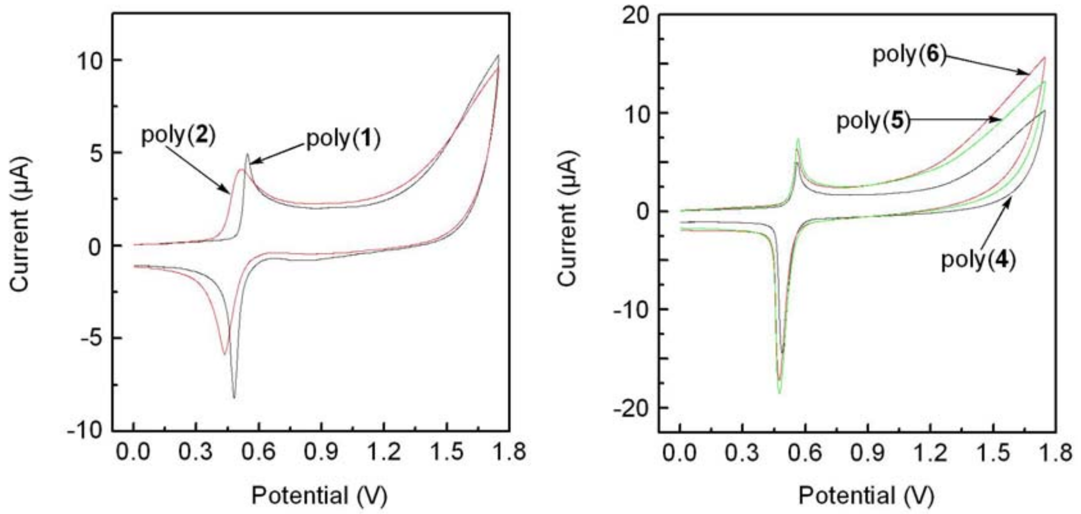


Figure 3. Cyclic voltammograms of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) measured at a scan rate of 0.01 V/s vs. Ag /Ag$^+$ in TBAP solution. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)–poly(**6**): Table 2.

in the charge/discharge processes of battery under the constant battery process conditions. Poly(**1**), poly(**2**) and poly(**4**) show larger oxidation/reduction rates among the present polymers, because the separation of its oxidation and reduction peak potentials is 0.072–0.081 V and smaller. Therefore, the poly(**1**), poly(**2**), and poly(**4**)-based batteries will exhibit high power-rate performance in the charge/discharge process. Although CV scans were continued in five cycles, the oxidation and reduction peaks of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) scarcely changed, indicating that the electrochemical properties of these PROXYL-containing polymers are sufficiently stable.

Figure 4 depicts the electron spin resonance (ESR) spectra of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**). All the ESR spectra exhibited a sharp singlet signal based on the PROXYL moiety with the ESR g-factor of 2.0063 which is slightly larger than 2.0055 for a typical nitroxyl radical of the TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) crystal, probably because of the interaction with the polymer backbone. The spin concentrations determined with X-band ESR were approximately in the range of 0.7×10^{21}–4.2×10^{21} spins/g, indicating

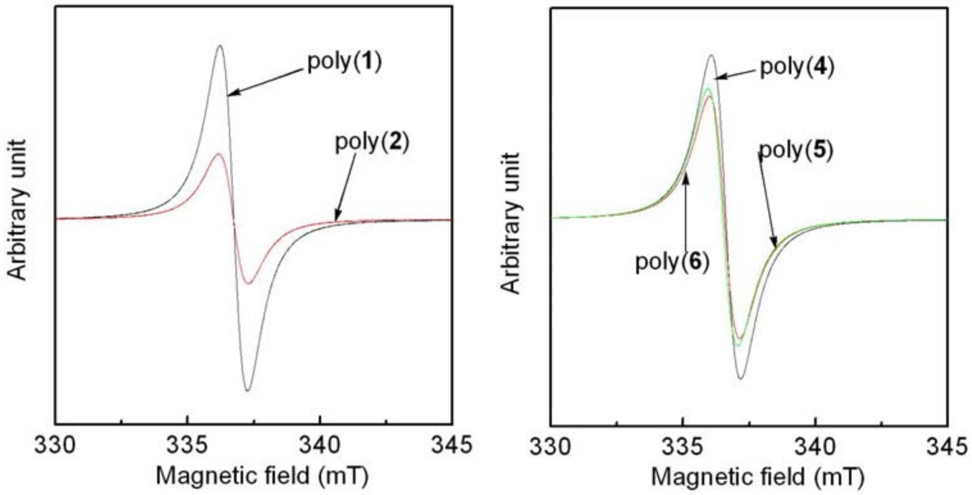


Figure 4. ESR spectra of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) measured in the powdery state. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)–poly(**6**): Table 2.

Table 3. Magnetic Properties of Polymers

polymer	number of free radicals per monomer unit	Curie-Weiss temperature Θ (K)	ESR g-factor	ESR line width (G)	
				~50 MHz	~9,400 MHz
poly(**4**)	2.06±0.10	2.2	2.0063	15.4	9.6
poly(**5**)	1.99±0.10	2.2	2.0063	15.6	9.7

that the local spin concentrations within the macromolecular domain are high. More precise determination was carried out for poly(**4**) and poly(**5**) with both SQUID susceptometer and ESR at low frequency (Table 3). Quite interestingly, it is clear that each repeating unit of both polymers possess around two radicals, namely quantitative amounts of spins, based on the PROXYL moiety. The Curie-Weiss temperature of 2.2 K is lower than 7 K for the TEMPOL crystal, suggesting anisotropic magnetic interaction between the PROXYL radicals of the polymers, in comparison with the 3D magnetic interaction in the TEMPOL crystal. The strong frequency dependence of the ESR line widths is also an indication of the anisotropic magnetic interaction, typical of the quasi-1D spin systems in the polymers.[22]

Coin-type cells were fabricated using poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) as cathodes, and the charge/discharge curves of the cells were observed at a constant current density of 0.089 mA/cm^2 in the voltage range of 3.0–4.0 V. Figure 5 shows clear voltage plateaus in both charge and discharge curves with all the cells, implying that the polymers are usable as cathode-active materials of a rechargeable battery. The plateau voltages of the charge/discharge processes are in the range of 3.4–3.8 V starting at approximately 3.6 V, which corresponds to the redox potential of the PROXYL radical. It is reasonable to assume that the charge process at the cathode is oxidation of PROXYL (**7**) in the polymers to oxoammonium salt (**8**), and the discharge process is the reverse reaction, namely, reduction of the salt (Scheme 4). Taking into account that one PROXYL moiety provides one electron in this redox

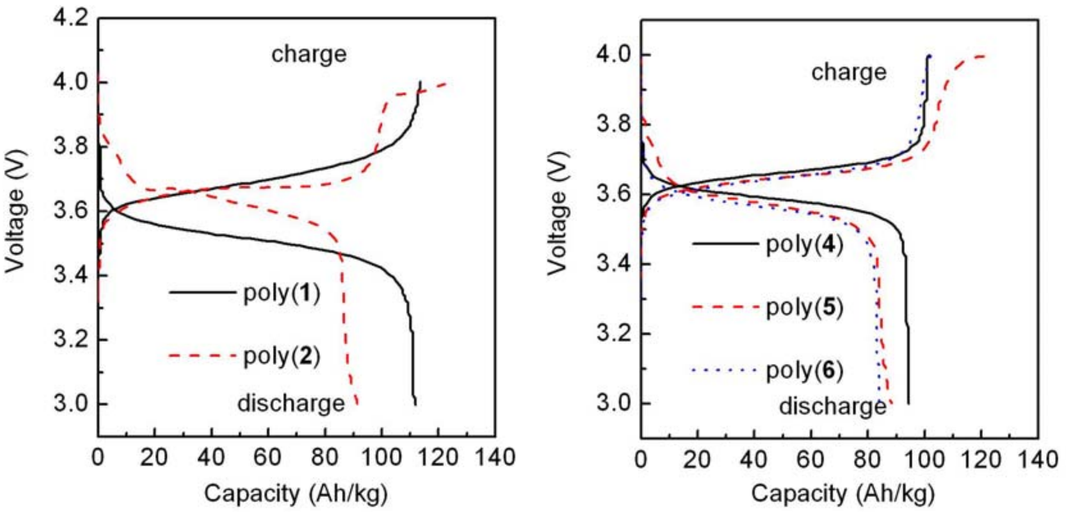
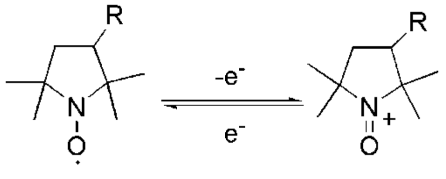


Figure 5. Charge/discharge curves of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) at a current density of 0.089 mA/cm^2 (100 mA /g$_{\text{–cathode active material}}$) in a voltage range of 3.0–4.0 V. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)–poly(**6**) : Table 2.

Scheme 4. Redox Reaction of Nitroxy Radical



(7) **(8)**

process, the author can estimate the theoretical capacities of the cells fabricated with poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) to be 109–120 A h/kg (Table 4). Evaluating from the values at 3 V in Figure 5, the initial discharge capacities of the cells fabricated with poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) are determined to be 85–117 A h/kg per polymer weight at a current density of 0.089 mA/cm^2.

The experimentally observed discharge capacity of poly(**1**) was 98% of the theoretical capacity, while that of poly(**2**) was no more than 79% of the theoretical capacity (Table 4). It is interesting to note that the observed discharge capacity of poly(**1**) and poly(**2**), 117 and 95 A h/kg, are much higher than those of the TEMPO-containing counterparts (66 and 81 A h/kg, respectively).[19,23] The average value of two experiments (103, 111 A h/kg) for the capacity of poly(**4**)-based cell was

Table 4. Capacity Data of Polymers

polymer	m/e[a]	theoretical capacity, A h/kg[b]	observed capacity, A h/kg[c]	observed capacity/ theoretical capacity, %
poly(**1**)[d]	224.3	119.6	117.2	98. 0
poly(**2**)[d]	223.1	120.0	94.7	78.9
poly(**4**)	245.2	109.3	107.0	98.0
poly(**5**)	245.2	109.3	89.0	81.4
poly(**6**)	245.2	109.3	84.9	77.7

[a] The molecular weight per exchangeable unit. [b] Theoretical capacity (A h/kg), namely specific charge (in A h/kg), was calculated according to reference 28. [c] Observed capacity (A h/kg): Initial discharge capacity at a current density of 0.089 mA/cm^2, cut off at 2.5 V. [d] Poly(**1**) sample from run 3 in Table 1, and poly(**2**) sample from run 6 in Table 1.

107 A h/kg, which reaches 98% of the theoretical capacity value (109 A h/kg). This ratio is the same as that of poly(**1**), indicating that poly(**1**) and poly(**4**) exhibit high capacity which will lead to a wide range of potential applications as a power source. On the other hand, the capacities of the poly(**5**)- and poly(**6**)-based cells remained 89 and 85 A h/kg, respectively, clearly lower than that of the poly(**4**)-based counterpart. This seems to be due to the difference in spatial arrangement of the PROXYL radicals; more specifically, a spatial arrangement that places the PROXYL groups far apart seems to favor a high capacity, as in the case of TEMPO-carrying polynorbornenes.[19] Another possible reason for the difference in capacity is a difference in the macroscopic aggregation state (e.g., the size and hardness of polymer powders) but not in the spin concentration (because the spin concentrations of poly(**4**) and poly(**5**) are

both quantitative). The capacities of the corresponding TEMPO-containing polymers for poly(**4**)–poly(**6**) are 68, 78, and 45, respectively,[24] which are obviously smaller than those of poly(**4**)–poly(**6**). The result that the PROXYL-containing polymers, poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) displays larger capacities than the TEMPO-bearing counterparts indicates that the PROXYL moiety is more efficient to achieve large capacity than is TEMPO.

Figure 6 depicts the charge/discharge curves of poly(**1**) observed at different currents. The charge and discharge capacities gradually decreased with increasing current, which is attributable to the polarization of PROXYL. A useful capacity of ca. 87 A h/kg was attained at 10 CmA, which corresponds to 74% of the discharge capacity at 0.1 CmA, indicating that the poly(**1**)-based cell displays the excellent charge/discharge characteristics under the extremely large currents. The poly(**4**)-based cell exhibited a similar performance to that of poly(**1**), whereas poly(**2**), poly(**5**), and poly(**6**) showed inferior properties under large currents.

Figure 7 depicts the relationship between capacity and discharge rate of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**). In this Figure, C is the unit for the current

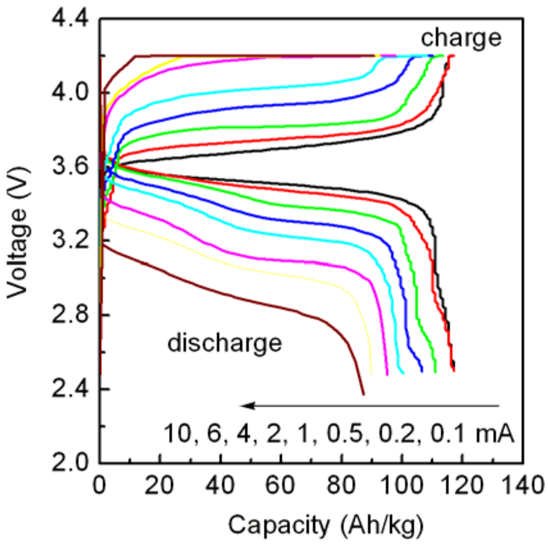


Figure 6. Charge/discharge curves of poly(**1**) at different currents in a voltage range of 2.5–4.2 V. Poly(**1**): run 3, Table 1.

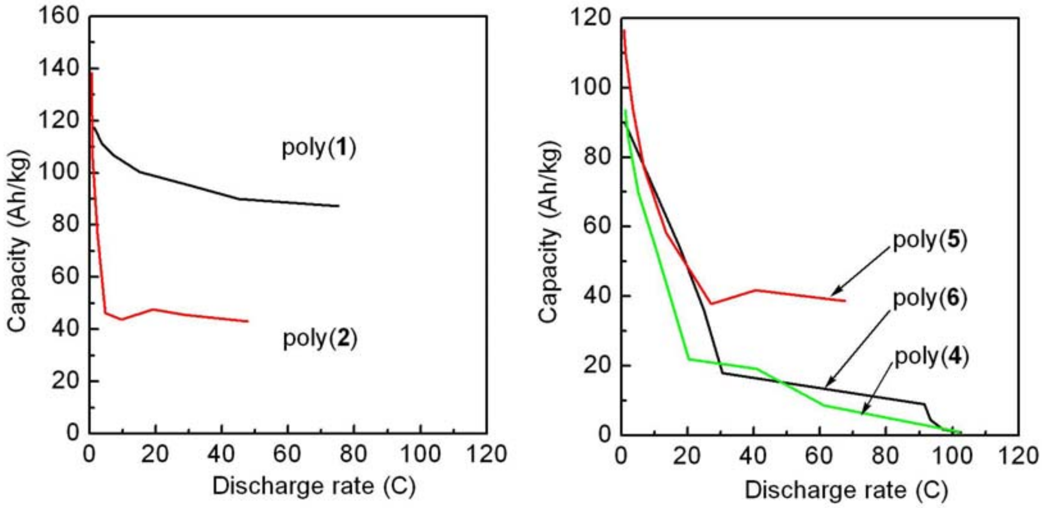


Figure 7. Dependence of capacity on discharge rate of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**). Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)–poly(**6**) : Table 2.

expressed as multiple of the nominal capacity of the cell, which was ca. 0.2 mA. The large capacity of poly(**1**) was maintained fairly well even though the discharge rate was increased to 80 C. By contrast, the capacity of poly(**2**), poly(**4**)–poly(**6**) decreased considerably with increasing discharge rate. This means that a large current is available in the discharge of poly(**1**).

Figure 8 illustrates the cycle performance of the poly(**1**), poly(**2**), and poly(**4**)–poly(**6**)/Li batteries, in which charging and discharging were repeated at a 0.089 mA/cm^2 current density under application of 3.0–4.0 V cell voltages. The cell using poly(**1**) retained about 85% of the capacity after 100 cycles. Poly(**2**) exhibited a different cycle performance; namely, the increase in capacity was observed during the initial 30 cycles, which appears to arise from the increase in the contact surface between the electrode and the electrolyte probably because of swelling of the polymer. The discharge capacity of poly(**4**) did not deteriorate even after 100 cycles, whereas the capacities of the poly(**5**) and poly(**6**) cells decreased to about 65 and 75% of the initial values, respectively. It seems that the cycle-lives of poly(**1**), poly(**2**), and poly(**4**)-based cells are comparable to that of the reported PTMA system.[17]

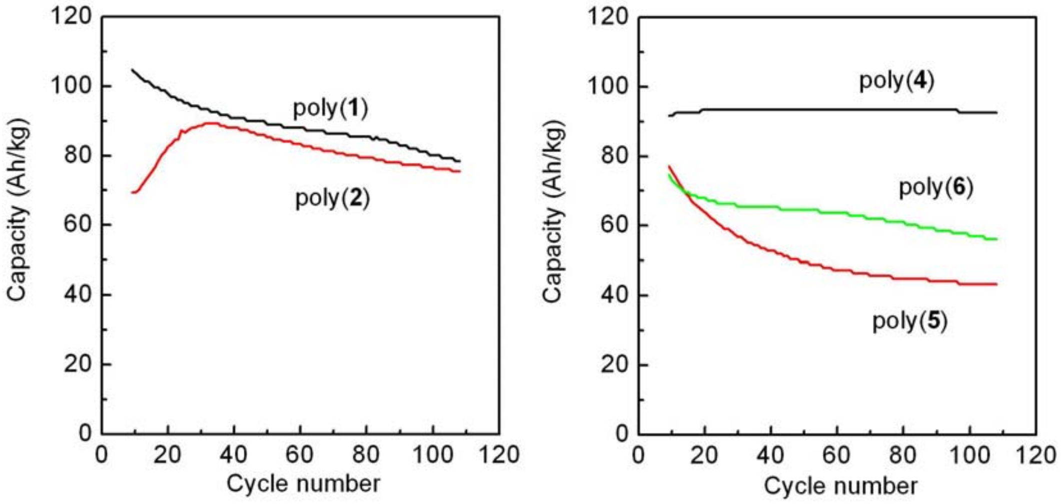


Figure 8. Dependence of capacity on cycle number of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**). Charging and discharging were repeated at a 0.089 mA/cm^2 current density in a range of 3.0–4.0 V cell voltage. Poly(**1**): run 3, Table 1; poly(**2**): run 6, Table 1; poly(**4**)–poly(**6**) : Table 2.

As discussed above, poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) can be applied to the cathode-active materials in organic radical batteries as charge-storage materials, which are promising as quickly chargeable/dischargeable and high power density batteries. Among the present polymers, poly(**1**) exhibited a high capacity up to 117 A h/kg, which is observed even at a high discharge rate up to 80 C. On the other hand, poly(**4**) is characterized by a high capacity up to 107 A h/kg, which is kept even after 100 cycles.

Conclusions

In the present research, the author synthesized a group of monomers containing PROXYL, **1**–**6**, and polymerized them with rhodium and ruthenium catalysts. While acetylenic monomers **1** and **2** yielded polymers with M_n of 3300–29 800 in 60–64% yields, norbornene derivatives **4**–**6** gave polymers with M_n of 209 000–272 000 in 90–94% yields. The formed polymers were thermally stable and soluble in common organic solvents. The separations of the oxidation and reduction potential peaks of these polymers in CV were by far smaller than those of other electroactive organic materials, indicative of high power rate in the charge/discharge processes of battery. The ESR spectra of poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) exhibited a sharp singlet, and poly(**4**) and poly(**5**) possessed practically quantitative amounts of free radicals based on the PROXYL moiety, namely, around two spins per repeating unit. The capacity of poly(**1**)-based cell was as large as 117 A h/kg, corresponding to 98% of the theoretical capacity value (119 A h/kg). The cell fabricated with poly(**4**) as cathode demonstrated a promising cycle-life, i.e., the discharge capacity did not deteriorate even after 100 cycles. The discharge rate of the poly(**1**)-based cells could be much faster than those of other polymers. Charge-storage materials based on poly(**1**), poly(**2**), and poly(**4**)–poly(**6**) can be applied to cathode-active materials in organic radical batteries. The high capacity and excellent charging and discharging characteristics of poly(**1**) indicate that a wide array of potential applications are expected as a power source for this type of polymer.

Experimental Section

Measurements. IR spectra were measured using a JASCO FT/IR-4100 spectrophotometer. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Elemental analysis was done at the Kyoto University Elemental Analysis Center. The number- and weight-average molecular weights (M_n and M_w, respectively) of polymers were determined by gel permeation chromatography (GPC) on a JASCO Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806), using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min at 40 °C with a polystyrene calibration. Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7 thermal analyzer. ESR spectra were measured on a JEOL JES-FR30 type X-band (9.48 GHz) spectrometer. The precise number of free radicals was estimated with a Quantum Design MPMS susceptometer and a home-built low-frequency ESR-NMR apparatus operated around 50 MHz.[25] Cyclic voltammograms were observed with an HCH Instruments ALS600A-n electrochemical analyzer. The measurements were carried out with a modified ITO substrate as the working electrode coupled with a Pt plate counter electrode and an Ag/AgCl reference electrode, using a solution of a polymer (1 mM) and tetrabutylammonium perchlorate (TBAP, 0.1 M) in CH_2Cl_2.

Materials. Solvents used for polymerization were distilled before use according to the standard procedures. The Grubbs 2nd generation catalyst was purchased from Materia, Inc., and used as received. 3-Carboxy-PROXYL (TCI), propargyl alcohol (Aldrich), propargylamine (Aldrich), 5-norbornene-2-exo,3-exo-dimethanol (Aldrich), 5-norbornene-2-endo,3-endo-dimethanol (Aldrich), 5-norbornene-2,2-dimethanol (Aldrich), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl; Eiweiss Chemical corporation), 4-dimethylaminopyridine (DMAP; Wako), *N*-methylmorpholine (Wako), and isobutyl chloroformate (Wako) were purchased and used without further purification. 1-Pentyne-4,4-dimethanol and $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ were synthesized according to the literature.[26, 27]

Monomer Synthesis. Monomer **1** was prepared as follows: 3-Carboxy-PROXYL (500 mg, 2.68 mmol) was added to a solution of EDC·HCl (796 mg, 3.04 mmol) and DMAP (37 mg, 0.34 mmol) in CH2Cl2 (15 mL) at room temperature. Propargyl alcohol (170 mg, 3.04 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (20 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation to afford the crude product. It was purified on a silica gel column with a hexane/ethyl acetate mixture (4/1 volume ratio) as eluent. A pale yellow liquid of **1** was obtained in 89% yield (500 mg). IR (KBr, cm^{-1}): 3294 ($\nu_{H\text{–}C\equiv}$), 2976, 2935, 2873, 2127 ($\nu_{C\equiv C}$), 1746 ($\nu_{C=O}$), 1463, 1365($\nu_{N\text{–}O}$), 1305, 1291, 1194, 1168 ($\nu_{C\text{–}O}$), 1017, 958, 686, 648. Anal. Calcd for $C_{12}H_{18}NO_3$: C, 64.26; H, 8.09; N, 6.25. Found: C, 64.20; H, 8.17; N, 6.24.

Monomer **2** was prepared as follows: *N*-Methylmorpholine (272 mg, 2.68 mmol) was added to a solution of 3-carboxy-PROXYL (500 mg, 2.68 mmol) in THF (10 mL) at room temperature. Isobutyl chloroformate (366 mg, 2.68 mmol) was added to the solution to precipitate *N*-methylmorpholine hydrochloride as a white mass. Then, propargylamine (148 mg, 2.68 mmol) was added, and the resulting mixture was stirred at room temperature overnight. The precipitate was removed by filtration, and the filtrate was concentrated by rotary evaporation. The residue was dissolved in ethyl acetate (20 mL) and washed with water three times, and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed to afford the crude product. It was purified by recrystallization from hexane/ethyl acetate (1/1 volume ratio). A pale yellow solid of **2** was obtained in 83% yield (500 mg). Mp 102–103 °C. IR (KBr, cm^{-1}): 3328 ($\nu_{N\text{–}H}$), 3214 ($\nu_{H\text{–}C\equiv}$), 2977, 2932, 2117 ($\nu_{C\equiv C}$), 1702, 1661 ($\nu_{C=O}$), 1528 (δN–H), 1364 ($\nu_{N\text{–}O}$), 1327, 1258, 1173, 1150, 1041, 709, 647. Anal. Calcd for $C_{12}H_{19}N_2O_2$: C, 64.55; H, 8.58; N, 12.55. Found: C, 64.27; H, 8.44; N, 12.51.

Monomer **3** was synthesized from 1-pentyne-4,4-dimethanol and two equivalents of 3-carboxy-PROXYL in a manner similar to **1**. Yield 74%, pale yellow liquid. IR (KBr, cm^{-1}): 3462, 3275, 2975, 2934, 2120, 1735 ($\nu_{C=O}$), 1458, 1379, 1363 ($\nu_{N\text{–}O}$), 1303, 1254, 1193, 1152, 1104, 1067, 1012, 781, 697, 647. Anal. Calcd for $C_{25}H_{40}N_2O_6$: C, 64.63; H, 8.68; N, 6.03. Found: C, 64.27; H, 8.44; N, 6.31.

Monomer **4** was synthesized from 5-norbornene-2-exo,3-exo-dimethanol and two equivalents of 3-carboxy-PROXYL in a manner similar to **1**. Yield 88%, pale yellow liquid. IR (KBr, cm^{-1}): 3465, 3058, 2970, 2934, 2871, 1734 ($\nu_{C=O}$), 1560, 1541, 1462, 1422, 1363 ($\nu_{N\text{–}O}$), 1303, 1253, 1197, 1163, 1104, 1067, 1005, 780, 730, 699, 646. Anal. Calcd for $C_{27}H_{42}N_2O_6$: C, 66.10; H, 8.63; N, 5.71. Found: C, 66.22; H, 8.61; N, 5.47.

Monomer **5** was synthesized from 5-norbornene-2-endo,3-endo-dimethanol and two equivalents of 3-carboxy-PROXYL in a manner similar to **1**. Yield 75%, pale yellow liquid. IR (KBr, cm^{-1}): 3450 ($\nu_{\mathrm{O–H}}$), 3059, 2976, 2975, 2933, 1735 ($\nu_{\mathrm{C=O}}$), 1637, 1574, 1464, 1422, 1363 ($\nu_{\mathrm{N–O}}$), 1325, 1303, 1253 ($\nu_{\mathrm{C–O}}$), 1195, 1163, 1149, 1105, 1067, 1047, 1005, 949, 754, 666, 640. Anal. Calcd for $\mathrm{C_{27}H_{42}N_2O_6}$: C, 66.10; H, 8.63; N, 5.71. Found: C, 65.92; H, 8.60; N, 5.64.

Monomer **6** was synthesized from 5-norbornene-2,2-dimethanol and two equivalents of 3-carboxy-PROXYL in a manner similar to **1**. Yield 82%, pale yellow liquid. IR (KBr, cm^{-1}): 3450, 3061, 2972, 2934, 2878, 1738 ($\nu_{\mathrm{C=O}}$), 1634, 1571, 1464, 1422, 1363 ($\nu_{\mathrm{N–O}}$), 1303, 1255, 1193, 1150, 1104, 1067, 1004, 952, 754, 720, 700, 657. Anal. Calcd for $\mathrm{C_{27}H_{42}N_2O_6}$: C, 66.10; H, 8.63; N, 5.71. Found: C, 65.82; H, 8.67; N, 5.57.

Since it was impossible to measure the NMR spectra of the monomers, the ^{1}H and ^{13}C NMR spectra of the hydroxyamine compounds (**1'–6'**; Scheme 3) were examined, whose data are as follows. **1'**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 4.72–4.62 (m, 2H, $\mathrm{CH_2CMe_2}$), 2.84 (s, 1H, HC≡), 2.40 (qu, 1H, CHC=O), 1.82 (s, 2H, $\mathrm{CH_2O}$), 1.35 (s, 3H, $\mathrm{CH_3}$), 1.23 (s, 3H, $\mathrm{CH_3}$), 1.17 (s, 3H, $\mathrm{CH_3}$), 1.06 (s, 3H, $\mathrm{CH_3}$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ): 162.3 (C=O), 83.4 ($\mathrm{CH_2\underline{C}}$≡), 74.6 (≡CH), 67.3 ($\mathrm{CH\underline{C}Me_2}$), 62.1 ($\mathrm{CH_2\underline{C}Me_2}$), 53.7 ($\mathrm{CH_2O}$), 51.6 ($\mathrm{\underline{C}HC{=}O}$), 36.9 ($\mathrm{\underline{C}H_2CMe_2}$), 26.4 ($\mathrm{CH_2C\underline{Me_2}}$), 25.5 ($\mathrm{CHC\underline{Me_2}}$); **2'**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 4.02–3.99 (m, 2H, $\mathrm{CH_2N}$), 2.61 (qu, 1H, CHC=O), 2.17 (s, 1H, HC≡), 2.0–1.37 (m, 2H, $\mathrm{CH_2CMe_2}$), 1.36–1.12 (m, 12H, 4Me). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ): 159.9 (C=O), 83.1 ($\mathrm{CH_2\underline{C}}$≡), 74.3 (≡CH) , 60.5 ($\mathrm{CH\underline{C}Me_2}$), 56.1 ($\mathrm{CH_2\underline{C}Me_2}$), 36.3 ($\mathrm{\underline{C}H_2C}$≡), 32.3 ($\mathrm{\underline{C}H_2CMe_2}$), 23.3 ($\mathrm{CH_2C\underline{Me_2}}$), 16.9 ($\mathrm{CHC\underline{Me_2}}$); **3'**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ): 3.85–4.05 (m, 4H, $\mathrm{2CCH_2O}$), 2.74 (s, 2H, $\mathrm{2COCHCMe_2}$), 2.23 (s, 2H, $\mathrm{CH_2C}$≡), 1.97–2.08 (m, 4H, $\mathrm{2CH_2CMe_2}$), 1.74 (s, 1H, HC≡), 1.29 (s, 3H, $\mathrm{CCH_3}$), 0.99–1.18 (m, 24H, 8Me). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ): 173 (C=O), 78.8 ($\mathrm{CH_2\underline{C}}$≡), 69.6 (≡CH), 66.7 ($\mathrm{C\underline{C}H_2O}$), 62.2 ($\mathrm{CH\underline{C}Me_2}$) 52.6 ($\mathrm{CH_2\underline{C}Me_2}$), 36.7 ($\mathrm{\underline{C}HCO}$), 36.1 ($\mathrm{CH\underline{C}H_2CMe_2}$), 31.7 ($\mathrm{CH_3\underline{C}CH_2}$), 26.6 ($\mathrm{\underline{C}H_2C}$≡), 19.3 ($\mathrm{CH_2C\underline{Me_2}}$), 18.6 ($\mathrm{CHC\underline{Me_2}}$), 7.52 ($\mathrm{CH_3\underline{C}CH_2}$); **4'**:

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.15 (s, 2H, –CH=), 3.80–3.62 (m, 4H, $2CH_2O$), 2.87 (brs, 2H, $2{=}CHC\underline{H}$), 2.10 (s, 2H, $2C\underline{H}CH_2O$), 1.97 (s, 2H, 2CHC=O), 1.79 (brs, 2H, $CHC\underline{H}_2CH$), 1.43–1.29 (m, 4H, $2CH_2CMe_2$), 1.19 (s, 24H, 8Me). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.8 (2C=O), 133.2 (2C=), 61.9 ($2CH\underline{C}Me_2$), 56.2 ($2CH_2\underline{C}Me_2$), 40.6 ($2CH_2O$), 39.8 ($CH\underline{C}H_2CH$), 38.5 ($2{=}CH\underline{C}H$), 35.7 ($2CH\underline{C}HCH_2$), 28.1 ($2\underline{C}HC{=}O$), 17.0 ($2\underline{C}H_2CMe_2$), 15.0 ($2CH_2C\underline{Me_2}$), 10.0 ($2CHC\underline{Me_2}$); **5'**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.14 (s, 2H, –CH=), 4.05–3.72 (m, 4H, $2CH_2O$), 2.87 (brs, 2H, 2CHC=), 2.50 (s, 2H, $2CHC\underline{H}CH_2$), 1.97 (s, 2H, 2CHC=O), 1.79 (s, 2H, $CHC\underline{H}_2CH$), 1.54 (s, 4H, $2C\underline{H}_2CMe_2$), 1.20 (m, 24H, 8Me). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 164.9 (2C=O), 130.1 (2C=), 70.2 ($2CH_2O$), 59.1 ($2CH\underline{C}Me_2$), 54.4 ($2CH_2\underline{C}Me_2$), 43.0 ($CH\underline{C}H_2CH$), 39.8 ($2{=}C\underline{C}H$), 39.6 ($2CH\underline{C}HCH_2$), 34.6 ($2\underline{C}HC{=}O$), 15.3 ($2\underline{C}H_2CMe_2$), 8.9 ($2CH_2C\underline{Me_2}$), 8.3 ($2CHC\underline{Me_2}$); **6'**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.19 (m, 2H, CH=CH), 4.06–3.69 (m, 4H, $2CH_2O$), 2.87 (s, 2H, $2{=}CC\underline{H}$), 2.68 (s, 2H, $={CCC}\underline{H_2}$), 2.00 (s, 2H, 2CHC=O), 1.79 (s, 2H, $CHC\underline{H}_2CH$), 1.53 (s, 4H, $2C\underline{H}_2CMe_2$), 1.20 (s, 24H, 8Me). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 160.3 (2C=O), 127.8 (C=C), 58.4 ($2\underline{C}H_2O$), 57.3 ($2CH\underline{C}Me_2$), 50.0 ($2CH_2\underline{C}Me_2$), 37.1 ($CH\underline{C}H_2CH$), 36.8 ($={C}\underline{C}HC$), 35.9 ($={C}\underline{C}HCH_2$), 32.0 ($O{=}C\underline{C}HCH_2$), 26.1 ($={CC}\underline{C}CH_2$), 23.1 ($2\underline{C}H_2CMe_2$), 10.9 ($={CC}\underline{C}H_2C$), 8.7 ($2CH_2C\underline{Me_2}$), 3.9 ($2CHC\underline{Me_2}$).

Polymerization. Polymerization of acetylenic monomers **1**–**3** were carried out with (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] as a catalyst in dry toluene, CHCl3 or THF at 30 °C for 24 h under the following conditions: $[\text{monomer}]_0$ = 0.25 M, [catalyst] = 2.5 mM. After polymerization, the resultant solution was poured into a large amount of diethyl ether to precipitate the formed polymer. It was filtered and then dried under reduced pressure.

Polymerization (ROMP) of norbornene monomers **4**–**6** were carried with the Grubbs 2nd generation catalyst in dry CH2Cl2 at 30 °C for 2 h under the following conditions: $[\text{monomer}]_0$ = 0.50 M, [catalyst] = 5.0 mM. The polymerization was quenched by adding *tert*-butyl vinyl ether (0.20 mL) and stirring the mixture at room temperature for 1 h. The polymers were isolated by precipitation in diethyl ether.

IR (KBr, cm^{-1}) Data of the Polymers. Poly(**1**): 3455, 2974, 2932, 2872, 1736, 1462, 1380, 1364, 1302, 1254, 1187, 1147, 1104, 1066, 997, 948, 877, 852, 747, 698, 668, 647, 561. Poly(**2**): 3450, 3321, 3058, 2975, 2932, 1657, 1533, 1462, 1364, 1302, 1225, 1169, 1149, 1105, 1035, 889, 852, 747, 689, 671, 654, 630. Poly(**4**): 3459, 2975, 2933, 1734, 1637, 1463, 1422, 1362, 1303, 1255, 1191, 1165, 1146, 1104, 1066, 1007, 947, 777, 695, 669, 649. Poly(**5**): 3455, 2973, 1736, 1637, 1560, 1541, 1464, 1422, 1363, 1303, 1254, 1192, 1147, 1104, 1067, 1003, 969, 838, 779, 754, 699, 670, 641. Poly(**6**): 3450, 2975, 1736, 1637, 1560, 1464, 1422, 1364, 1303, 1255, 1191, 1146, 1104, 1066, 1005, 779, 743, 700, 657, 646.

Fabrication and Electrochemical Properties of the Batteries Using the Polymers. A coin-type cell was fabricated by stacking electrodes with porous polyolefin separator films. A cathode was formed by pressing the composites of a polymer (10 wt%), carbon fiber (80 wt%), and fluorinated polyolefin binder (10 wt%) as described in a previous paper.[19] The cathode was set to a coin-type cell possessing a lithium metal anode. A composite solution of ethylene carbonate (30 vol%)/diethyl carbonate (70 vol%) containing 1 M of LiPF6 was used as an electrolyte. Charge/discharge properties were measured at 25 °C using a computer controlled automatic battery charge and discharge instrument (Keisokukiki, Co. Ltd., Battery Labo System BLS5500).

Theoretical Capacity of Polymer-Based Cell. The theoretical capacity (in A h/kg) of an electroactive polymer is calculated from the polymer mass or volume required per exchangeable unit charge.[28]

$$\text{Theoretical capacity (Ah/kg)} = \frac{N_A\, x\, e}{3600x\, (M_W/1000)}$$

where N_A×e is the Faraday constant (96484 C/mol); while M_w is the equivalent weight (or mass) of polymer in kg, and defined as the molecular weight (molar mass) of the repeating unit of polymer divided by the number of electrons exchanged or stored by it (which may be a fractional number), or as the molecular weight of the set of repeating units exchanging (storing) one electron in polymers.

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List of Publications

Chapter 1

"Polymerization of Substituted Acetylenes by the Grubbs-Hoveyda Ru Carbene Complex"

Katsumata. T.; Shiotsuki, M.; Kuroki, S.; Ando, I.; Masuda, T.

Polym. J. **2005**, *37*, 608–616.

Chapter 2

"Polymerization of Diphenylacetylenes with Polar Functional Groups by the Grubbs-Hoveyda Ru Carbene Catalyst"

Katsumata, T.; Shiotsuki, M.; Masuda, T.

Macromol. Chem. Phys. **2006**, *207*, 1244–1252.

Chapter 3

"Polymerization of *Ortho*-Substituted Phenylacetylenes with Ru Carbene Catalysts"

Katsumata, T.; Shiotsuki, M.; Masuda, T.

J. Polym. Sci., Part A: Polym. Chem. to be submitted

Chapter 4

"Synthesis and Properties of Various Poly(diphenylacetylenes) Containing *tert*-Amine Moieties"

Katsumata, T.; Maitani, M.; Huang, C. -C.; Shiotsuki, M.; Masuda, T.

Polymer **2008**, *49*, 2808–2816.

Chapter 5

"Synthesis and Properties of Polynorbornenes Bearing Siloxane Linkages"

Katsumata, T.; Shiotsuki, M.; Masuda, T.

Polymer submitted.

Chapter 6

"Polyacetylene and Polynorbornene Derivatives Carrying TEMPO. Synthesis and Properties as Organic Radical Battery Materials"
Katsumata, T.; Satoh, M.; Wada, J.: Shiotsuki, M.; Sanda, F.; Masuda, T.
Macromol. Rapid Commun. **2006**, *27*, 1206–1211.

"Synthesis, Characterization, and Charge/Discharge Properties of Polynorbornenes Carrying 2,2,6,6-Tetramethylpiperidine-1-oxy Radicals at High Density"
Katsumata, T.; Qu, J.; Shiotsuki, M.; Satoh, M.; Wada, J.; Igarashi, J.; Mizoguchi, K.; Masuda, T.
Macromolecules **2008**, *41*, 1175–1183.

Chapter 7

"Synthesis and Charge/Discharge Properties of Polyacetylenes Carrying 2,2,6,6-Tetramethyl-1-piperidinoxy Moieties"
Qu, J.; Katsumata, T.; Satoh, M.; Wada, J.; Igarashi, J.; Mizoguchi, K.; Masuda T.
Chem. Eur. J. **2007**, *13*, 7965–7973.

Chapter 8

"Synthesis and Properties of Polyacetylene and Polynorbornene Derivatives Carrying 2,2,5,5-Tetramethyl-1-pyrrolidinyloxy (PROXY) Moieties"
Qu, J.; Katsumata, T.; Satoh, M.; Wada, J.; Masuda, T.
Macromolecules **2007**, 40, 3136–3144.

Publications Not Included in This Thesis

1. "Novel Neodymium-Based Ternary Catalyst, Nd(O*i*-Pr)$_3$/[HNMe$_2$Ph]$^+$[B(C$_6$F$_5$)$_4$]$^-$/*i*-Bu$_3$Al, for Isoprene Polymerization"
   Taniguchi, Y.; Dong, A.; Katsumata, T.; Shiotsuki, M.; Masuda, T.
   Polym. Bull. **2005**, *54*, 173–178.

2. "Polymerization of Substituted Acetylenes by Various Rhodium Catalysts: Comparison of Catalyst Activity and Effect of Additives"
   Nakazato, A.; Saeed, I.; Katsumata, T.; Shiotsuki, M.; Masuda, T.; Zednik, J.; Vohlidal, J.
   J. Polym. Sci., Part A: Polym. Chem. **2005**, *43*, 4530–4536.

3. "Helical Polyacetylenes Carrying 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and 2,2,5,5-Tetramethyl-1-pyrrolidinyloxy (PROXYL) Moieties: Their Synthesis, Properties, and Function"
   Qu, J.; Fujii, T.; Katsumata, T.; Suzuki, Y.; Shiotsuki, M.; Sanda, F.; Satoh, M.; Wada, J.; Masuda, T.
   J. Polym. Sci., Part A: Polym. Chem. **2007**, *45*, 5431–5445.

4. "Synthesis of Poly(diphenylacetylene) Carrying Primary Amino Groups by the Protection/Deprotection Method and Its Properties"
   Maitani, M.; Katsumata, T.; Shiotsuki, M.; Masuda, T.
   Macromolecules to be submitted.

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