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**POLYMERIZATION AND
POLYMER PROPERTIES OF
SILICON- AND FLUORINE-CONTAINING
ACETYLENES**

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1992

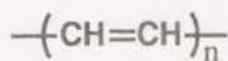
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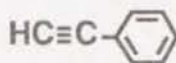
Introduction

First synthesized by Natta et al. in 1958,¹ polyacetylene (1) has attracted much attention, both in its synthesis and properties.² The trend has been accelerated in particular since the synthesis of a uniform polyacetylene film by Shirakawa et al. with use of $\text{Ti}(\text{O}-n\text{-Bu})_4\text{-Et}_3\text{Al}$ catalyst.³ The most salient feature of polyacetylene is the electrical conductivity that arises from conjugation of the main-chain which contains alternating double bonds, and reaches the metallic region upon doping. Despite such interesting properties, however, the polymer is insoluble, infusible, and unstable in air, making its manipulation, fabrication, and application difficult.

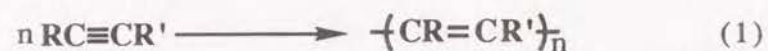
In sharp contrast to the extensive synthetic efforts for 1, the synthesis of high polymers from substituted acetylenes had been difficult for a long time, until Masuda and Higashimura found in 1974 that phenylacetylene (2) could be polymerized with WCl_6 and MoCl_5 to form high polymers.⁴ It has been revealed that group 6 transition metal halides (WCl_6 , MoCl_5 , etc.), either alone or in conjunction with suitable cocatalysts (e.g., Ph_4Sn), provide high-molecular-weight polymers particularly from acetylenes having bulky substituents (eq. 1). Since then, various monosubstituted and disubstituted acetylenes have been polymerized with those catalysts as well as NbCl_5 - and TaCl_5 -based catalysts. Unlike the unsubstituted counterpart (1), some of these substituted polyacetylenes are soluble in various organic solvents and have weight-average molecular weights (\bar{M}_w) around 1×10^6 .



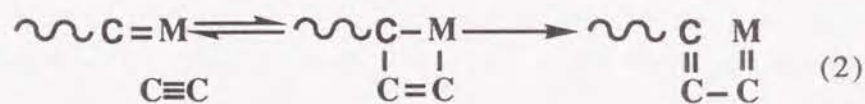
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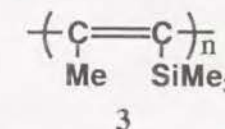
It was claimed⁵ that the transition metal-mediated polymerization of substituted acetylenes follows a metathesis polymerization mechanism as shown in eq. 2 like ring-opening polymerization of cycloolefins⁶; i.e., the monomer coordinates to a metal carbene, which contains a carbon-metal double bond, to form a metallacyclobutene that subsequently cleaves to regenerate a metal carbene.



Previous investigations have disclosed the following relationships between monomer structure and polymerization behavior of substituted acetylenes:⁷ i) Monosubstituted derivatives and disubstituted acetylenes carrying relatively small substituents polymerize with group 6 transition-metal (Mo, W) catalysts, whereas disubstituted acetylenes carrying bulky substituents with group 5 transition-metal (Nb, Ta) catalysts; ii) High-molecular-weight polymers are difficult to form from acetylenic monomers containing heteroatoms like oxygen and nitrogen with lone pair electrons; iii) The molecular weight of the polymers increases with increasing bulkiness of the substituents, though no polymerization occurs if the substituents are too bulky. More data should, however, be collected to predict the relationship between monomer structure and its reactivity.

It has also been revealed that substituted polyacetylenes show unique properties that clearly differ from those of polyacetylene. For example, substituted polyacetylenes are soluble in various organic solvents thanks to the interaction between their substituents and solvent. The extent of the main-

chain conjugation is lower than in polyacetylene because the backbone is twisted by the bulky substituents. Thus, substituted polyacetylenes exhibit colors ranging from purple to white and are stable in air. Another interesting property is the high gas permeability. This is noteworthy, particularly because these polymers are glassy at room temperature. Especially, poly[1-(trimethylsilyl)-1-propyne] [3, poly(TMSP)] is the most gas-permeable among the hitherto known synthetic polymers,⁸ and therefore its gas permeation behavior has been intensively studied.



Among a number of substituents that can be incorporated in acetylenic monomers silicon- and fluorine-based groups are of particular interest in terms of polymerization mechanism and polymer properties. For examples, silicon- and fluorine-containing polymers, in general, are known to show unique properties.⁹ The features of silicon-containing polymers include high thermal stability, high resistance to reactive ion etching (suited for photo-resists), and high gas permeability as demonstrated in poly(dimethylsiloxane). Fluorine-containing polymers are characterized by high thermal stability, resistance to chemicals, and unique solubility.¹⁰

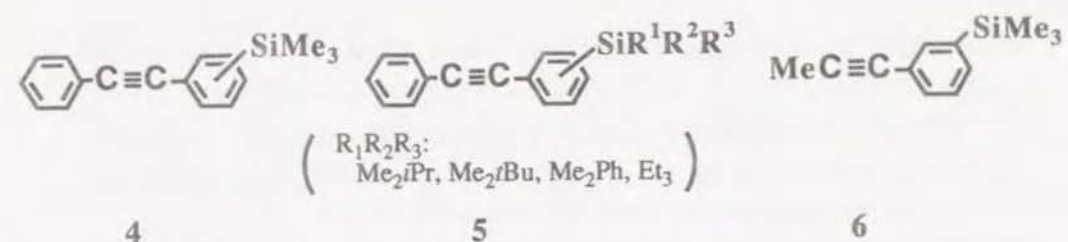
In view of the facts discussed above, silicon- and fluorine-containing acetylenes are heteroatom substituted acetylenes of particular interest in terms of both their polymerization behavior and polymer properties that should differ from those of hydrocarbon polyacetylenes. However, the synthesis of such polyacetylenes has not been attempted very much. Thus, the author decided in the present study to examine the polymerization and polymer properties of silicon- and fluorine-containing acetylenes, to specifically focusing on the relationship between monomer structure and either polymer yield or molecular weight and on the synthesis of polymers with unique properties.

For these research objectives, the author selected a series of silicon- and fluorine-containing acetylenes: the trialkylsilyl groups (typically trimethylsilyl, SiMe_3) in the monomers **4** - **9** are bulky and slightly electron-donating. On the other hand, the fluorine-containing groups in **11** and **12** are relatively compact and strongly electron-withdrawing. Thus, it is expected that the steric and electronic effects of substituents on polymerization become clear if the polymerization of silicon- and fluorine-containing acetylenes is examined. Equally important, these acetylenic monomers may be useful to clarify the relationship between the kind of pendant group and polymer properties.

This thesis consists of three parts. Part I and Part II deal with the polymerization and polymer properties of the silicon-containing acetylenes (**4** - **9**), while Part III concerns those of fluorine-containing acetylenes (**11** and **12**).

Part I delineates the polymerization of aromatic disubstituted acetylenes (**4** - **6**) having various silyl groups and their polymer properties, especially gas permeability.

Chapter 1 deals with diphenylacetylenes (**4**) carrying an SiMe_3 group at the para or meta position on one of the phenyl groups. Silylacetylenes **4** were polymerized by TaCl_5 -cocatalyst systems to form in good yield new polymers whose \bar{M}_w exceeded over 1×10^6 . Their polymerization behavior was similar to that of diphenylacetylene without an SiMe_3 group. The polymers were soluble in toluene and CHCl_3 owing to the presence of the SiMe_3 group, whereas poly(diphenylacetylene), free from a silyl group, is insoluble in any solvents. Free-standing films could be obtained from poly(**4**) by solution casting. The on-set temperatures of weight loss were over 400°C , indicating a fairly high thermal stability of the polymers.



Chapter 2 treats monomers **5**, which have bulky substituents on the silicon of **4**. The \bar{M}_w of the polymers obtained from **5** with TaCl_5 -cocatalyst reached several hundred thousand. The polymer yields for the para isomers were similar to those of **4**, while those for the meta isomers were smaller because of the steric hindrance of the meta-substituents. Most of the polymers were soluble in various organic solvents, whereas the polymers with very bulky substituents on the para silyl group were not.

Chapter 3 describes the polymerization of monomer **6**, which has a methyl group instead of a phenyl group in **4**. Not only TaCl_5 but also NbCl_5 produced polymers from **6**. The polymer was soluble in various organic solvents and had high molecular weight over 1×10^6 . When 1-phenyl-1-propyne, an SiMe_3 free parent form of **6**, is polymerized by NbCl_5 and TaCl_5 alone, polymer degradation occurs after the polymerization.¹¹ No degradation was, however, observed for **6**, showing that introduction of a bulky SiMe_3 group inhibits such a polymer degradation. During the polymerization of **6**, the molecular weight of polymer increased approximately in proportion to monomer conversion. This indicates the presence of a long-lived propagating species.

In Chapter 4, the gas permeability of the silicon-containing polymers synthesized in this thesis was examined. Poly(**4**)s were found to show very high gas permeability of ca. 1/4 the value of poly(TMSP) and of about two-fold that of poly(dimethylsiloxane). The gas permeability of the substituted polyacetylenes depended on the structure of the substituents. It was revealed that bulky

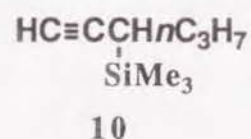
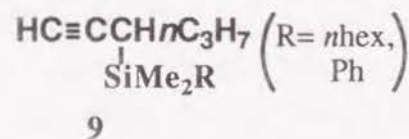
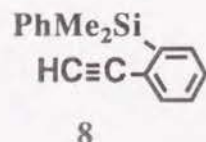
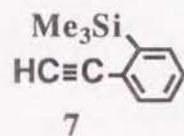
substituents on the silicon atom tended to reduce gas permeability.

Part II discusses the polymerization and polymer properties of monosubstituted acetylenes with bulky silyl groups.

Chapter 5 concerns monomer 7, which has an SiMe₃ group at the ortho position of phenylacetylene. A high polymer was obtained from 7 by using WCl₆- and MoCl₅-based catalysts. The \bar{M}_w of polymer reached 1x10⁶, although that of poly(phenylacetylene) generally remains below 1x10⁵. This difference is due to the steric effect of the ortho-substituent. The propagating species formed from WCl₆- and MoCl₅-cocatalyst were long-lived. The polymer was a purple solid with UV-visible absorption red-shifted relative to poly(phenylacetylene).

Chapter 6 describes monomer 8, which has a bulky substituent on the silyl group of 7. Practically no change was observed in the yield, molecular weight, or UV-visible absorption of the polymer compared with poly(7), despite of the presence of the ortho-substituent bulkier than SiMe₃.

Chapter 7 presents 1-hexynes (9) with bulky silyl groups at the carbon adjacent to the C≡C bond. Monomers 9 gave polymers with \bar{M}_w of 2x10⁵ - 4x10⁵ in the presence of WCl₆ and MoCl₅. The polymers dissolved in various organic solvents, though poly(10), which has an SiMe₃ group at the same position, is partly insoluble in common organic solvents. The polymerization

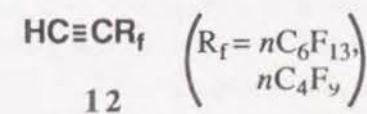
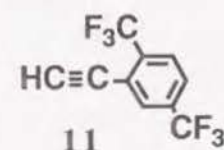


behavior of 9 was similar to that of 10. The WCl₆-cocatalyst and MoCl₅-cocatalyst systems led to long-lived propagating species.

Part III is focused on the polymerization and polymer properties of fluorine-containing acetylenes.

In Chapter 8 was examined the polymerization of a phenylacetylene (11) carrying two CF₃ groups, which is an example of fluorine-containing aromatic acetylene. W, Mo, and Nb catalysts produced polymers from 11 in high yield. The polymers were soluble only in *p*-(CF₃)₂C₆H₄, where the highest intrinsic viscosity was 0.35 dL/g, suggesting that the polymers have higher molecular weights than poly(phenylacetylene). This is probably due to the steric effect of CF₃ groups rather than the electronic effect. The on-set temperature of weight loss in air was relatively high (ca. 300 °C).

Chapter 9 discusses aliphatic monomers 12 as examples of monosubstituted acetylenes with perfluoroalkyl groups. Polymers were obtained in fair yields from 12 with the WCl₆-Ph₄Sn catalyst. They were soluble in hexafluorobenzene (intrinsic viscosity ~0.05 dL/g) and had rather low molecular weight like poly(1-alkynes).



In the present doctoral study, the author synthesized new silicon- and fluorine-containing polyacetylenes and found the remarkable effects of the silicon- and fluorine-containing group on the polymerization and polymer properties, such as gas permeability. It is noteworthy that among the polymers, poly(4)s exhibit very high gas permeabilities. It is desired that novel substituted polyacetylenes will be synthesized further and that the effect of substituent on polymerization and polymer

properties of acetylenes will be clarified for designing new, unique specialty polymers.

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Part I

Polymerization and Polymer Properties of Silicon-Containing Disubstituted Acetylenes

Chapter 1

Polymerization and Polymer Properties of Silicon-Containing Diphenylacetylenes

Abstract

Poly(diphenylacetylene) is thermally very stable, but insoluble in any solvents, whereas polyacetylenes from unsymmetrically disubstituted acetylenes are generally soluble. Hence the synthesis of soluble poly(diphenylacetylenes) was examined by introducing the trimethylsilyl group. 1-Phenyl-2-*p*-(trimethylsilyl)phenylacetylene and 1-phenyl-2-*m*-(trimethylsilyl)phenylacetylene polymerized with TaCl₅-cocatalyst systems to provide new polymers over 70% yields having weight-average molecular weight over 1x10⁶. As cocatalysts, *n*-Bu₄Sn, Et₃SiH, and 9BBN were especially effective. The polymers were yellow solids with the alternating double bond structure, [-CPh=C(C₆H₄-SiMe₃)-]_n. As expected, they completely dissolved in toluene, CHCl₃ etc., and formed free-standing films by solution casting. The temperatures at which their weight loss started in TGA were as high as ca. 400 °C.

Introduction

Various substituted polyacetylenes have recently been synthesized by group 5 and 6 transition-metal catalysts.¹ Among these polymers, poly(diphenylacetylene) [poly(DPA)] is obtained in good yields with TaCl₅-cocatalyst systems, and exhibits the highest thermal stability among substituted polyacetylenes (the temperature at which its weight loss starts in air is ~500 °C).² This polymer, however, does not dissolve in any solvents. In general, polymers from symmetrically disubstituted acetylenes tends to be insoluble in solvents. For instance, poly(2-octyne) and poly(3-octyne) are soluble in common organic solvents, whereas poly(4-octyne) is not.³ Hence, if a bulky substituent is introduced into one phenyl group of diphenylacetylene (DPA), a soluble polymer is anticipated to form.

Among many unique properties of substituted polyacetylenes, the most striking one is their high gas permeability. Especially, silicon-containing polyacetylenes are likely to show high gas permeability.⁴ As an extreme example, the permeability of poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] to oxygen is higher than any other existing polymers, and has recently been under intensive research.⁵

From the viewpoints stated above, it is expected that poly(DPA)s having a trimethylsilyl group on one phenyl group will be soluble in organic solvents, and will exhibit high thermal stability and high gas permeability. Further, it is of interest to examine the influence of the trimethylsilyl group on polymerization behavior. To clarify these points, the polymerization and polymer properties of 1-phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene (*p*-Me₃SiDPA) and 1-phenyl-2-[*m*-(trimethylsilyl)phenyl]acetylene (*m*-Me₃SiDPA) have been investigated in this chapter.

Results and Discussion

Polymerization by Various Catalysts

Polymerization of *p*-Me₃SiDPA was studied by using group 5 and 6 transition metal catalysts which are effective in the polymerization of various substituted acetylenes (Table I). Though *p*-Me₃SiDPA was consumed to some extent with TaCl₅ alone, no methanol-insoluble polymer was produced. On the other hand, polymers were obtained when organometallic cocatalysts that are effective in the polymerization of DPA were added in a two-fold excess to TaCl₅. Especially, *n*-Bu₄Sn, Et₃SiH, and 9BBN achieved almost quantitative monomer conversions,

Table I
Polymerization of *p*-Me₃SiDPA by Various Catalysts^a

no.	Catalyst	Monomer convn, %	Polymer ^b		
			yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
1	TaCl ₅	31	0		
2	TaCl ₅ - <i>n</i> -Bu ₄ Sn	95	85	2200	750
3	TaCl ₅ -Et ₃ SiH	100	71	2100	570
4	TaCl ₅ -9BBN ^d	100	91	2300	720
5	TaCl ₅ - <i>n</i> -BuLi	72	60	2100	530
6	TaCl ₅ -vitride ^e	31	25	1100	320
7	NbCl ₅ - <i>n</i> -Bu ₄ Sn	34	0		
8	WCl ₆ - <i>n</i> -Bu ₄ Sn	19	0		
9	MoCl ₅ - <i>n</i> -Bu ₄ Sn	18	0		

a Polymerized in toluene at 80 °C for 24 h; [M]₀ = 0.50 M, [cat] = 20 mM, [cocat] = 40 mM.

b Methanol-insoluble product.

c Determined by GPC.

d 9BBN: 9-borabicyclo[3.3.1]nonane.

e Vitride: sodium bis(2-methoxy)aluminum hydride.

and polymers were obtained in over 70% yields. When *n*-BuLi and vitride were used as cocatalysts, on the contrary, the monomer did not react so much, and the polymer yields remained low. These cocatalysts, which are weak reducing agents, are considered to help initiation reaction and to modify the propagating species. All the polymers produced were soluble in toluene and CHCl₃ unlike poly(DPA). Many of the weight-average molecular weights (\bar{M}_w) of polymers exceeded 2×10^6 according to gel permeation chromatography (GPC; a polystyrene calibration).

No polymer was obtained from *p*-Me₃SiDPA with NbCl₅-*n*-Bu₄Sn (see Table I), though this catalyst is effective in the polymerization of disubstituted acetylenes like 1-phenyl-1-propyne and 1-(trimethylsilyl)-1-propyne. WCl₆-*n*-Bu₄Sn and MoCl₅-*n*-Bu₄Sn, which polymerize various substituted acetylenes,¹ gave no polymer, either. The methanol-soluble products (differences between the monomer conversions and the polymer yield in Table I) were all linear oligomers according to GPC (several sequential peaks below molecular weight 1000).

The polymerization of *m*-Me₃SiDPA was examined using various catalysts (Table II). When TaCl₅ was employed in conjunction with suitable cocatalysts such as *n*-Bu₄Sn, Et₃SiH, and 9BBN, the yields of methanol-insoluble polymers exceeded 70%. The \bar{M}_w values of the polymers were 1×10^6 and above. *n*-BuLi and vitride were less effective as cocatalysts, as is judged from the polymer yields and molecular weights. Further, none of TaCl₅ alone, NbCl₅-*n*-Bu₄Sn, WCl₆-*n*-Bu₄Sn, and MoCl₅-*n*-Bu₄Sn catalysts produced any methanol-insoluble polymer. Thus, *m*-Me₃SiDPA behaves in polymerization similarly to *p*-Me₃SiDPA and DPA, although the molecular weight of poly(*m*-Me₃SiDPA) is somewhat lower than that of poly(*p*-Me₃SiDPA).

Table II
Polymerization of *m*-Me₃SiDPA by Various Catalysts^a

no.	Catalyst	Monomer convn, %	Polymer ^b		
			yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
1	TaCl ₅	21	0		
2	TaCl ₅ - <i>n</i> -Bu ₄ Sn	100	87	1400	250
3	TaCl ₅ -Et ₃ SiH	100	93	1000	210
4	TaCl ₅ -9BBN ^d	100	73	1300	280
5	TaCl ₅ - <i>n</i> -BuLi	66	44	970	180
6	TaCl ₅ -vitride ^e	43	31	460	32
7	NbCl ₅ - <i>n</i> -Bu ₄ Sn	25	0		
8	WCl ₆ - <i>n</i> -Bu ₄ Sn	10	0		
9	MoCl ₅ - <i>n</i> -Bu ₄ Sn	18	0		

a Polymerized in toluene at 80 °C for 24 h; [M]₀ = 0.50 M, [cat] = 20 mM, [cocat] = 40 mM.

b Methanol-insoluble product.

c Determined by GPC.

d 9BBN: 9-borabicyclo[3.3.1]nonane.

e Vitride: sodium bis(2-methoxy)aluminum hydride.

Polymerization with TaCl₅-*n*-Bu₄Sn

Effects of polymerization conditions were studied by using TaCl₅-*n*-Bu₄Sn which proved to be one of the most effective catalysts in the polymerization of *p*-Me₃SiDPA and *m*-Me₃SiDPA.

Solvent effect on the polymerization of *p*-Me₃SiDPA and *m*-Me₃SiDPA by TaCl₅-*n*-Bu₄Sn was studied (Table III). The polymerization of both monomers proceeded in heptane and chlorine-containing solvents [PhCl and (CH₂Cl)₂] as well as in toluene, and polymers were formed in good yields. The \bar{M}_w values of the polymers formed were similar. On the other hand, no polymerization occurred in anisole, which is a useful solvent to prepare all-cis poly(*tert*-butylacetylene).^{1b}

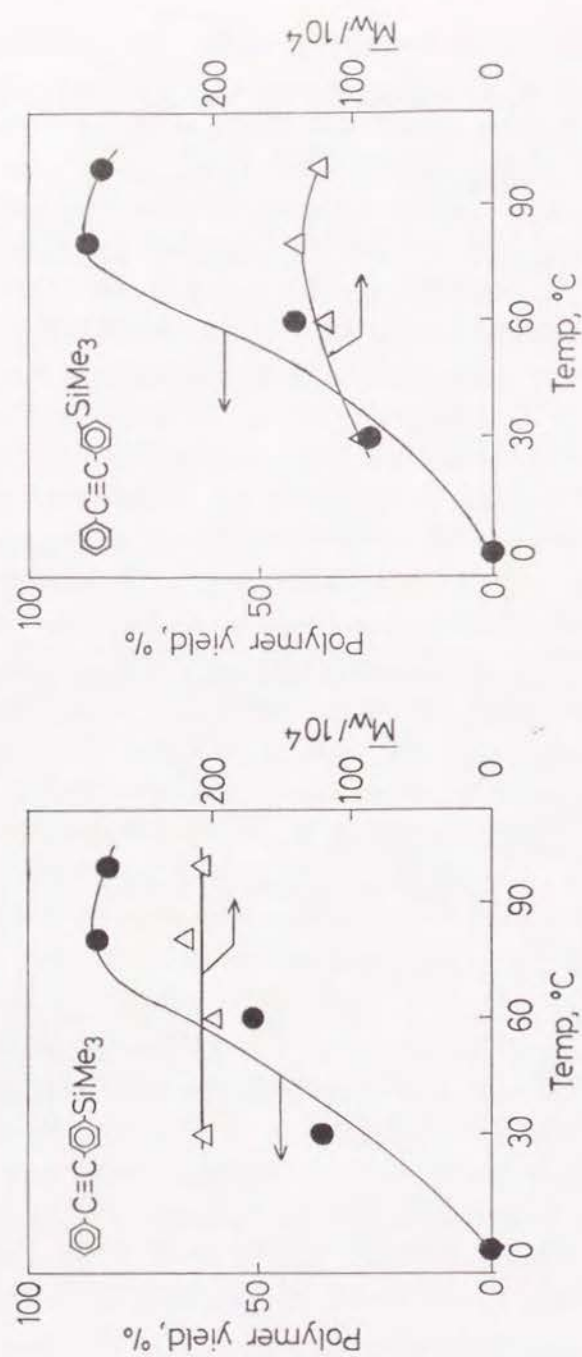


Figure 1. Effects of temperature on the polymerization of *p*-Me₃SiDPA and *m*-Me₃SiDPA by TaCl₅-*n*-Bu₄Sn (in toluene, 24 h, [M]₀ = 0.50 M, [TaCl₅] = 20 mM, [*n*-Bu₄Sn] = 40 mM).

Table III
Solvent Effects on the Polymerization of *p*-Me₃SiDPA and *m*-Me₃SiDPA by TaCl₅-*n*-Bu₄Sn (1:2)^a

Solvent	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
monomer: <i>p</i> -Me ₃ SiDPA				
toluene	95	85	2200	750
heptane	100	79	2100	810
PhCl	81	72	2000	680
(CH ₂ Cl) ₂	81	68	1800	580
PhOMe	0	0		
monomer: <i>m</i> -Me ₃ SiDPA				
toluene	100	87	1400	250
heptane	70	53	1300	210
PhCl	81	70	1100	230
(CH ₂ Cl) ₂	75	52	910	150
PhOMe	0	0		

a Polymerized at 80 °C for 24 h; [M]₀ = 0.50 M, [TaCl₅] = 20 mM.

b Methanol-insoluble product.

c Determined by GPC.

Figure 1 shows the effect of temperature on the polymerization of *p*-Me₃SiDPA and *m*-Me₃SiDPA. Polymers were obtained at 30 °C and above from both monomers. The polymer yields increased with increasing temperature, and leveled off at 80 °C and above. The molecular weights of polymers hardly changed in this temperature range, being ca. 2x10⁶ with poly(*p*-Me₃SiDPA) and 1x10⁶ with poly(*m*-Me₃SiDPA). Thus, it can be said that 80 °C is favorable to obtain the present polymers in good yields.

As seen in Figure 2, the polymerization of *p*-Me₃SiDPA was completed within 15 min, while that of *m*-Me₃SiDPA in 90 min.

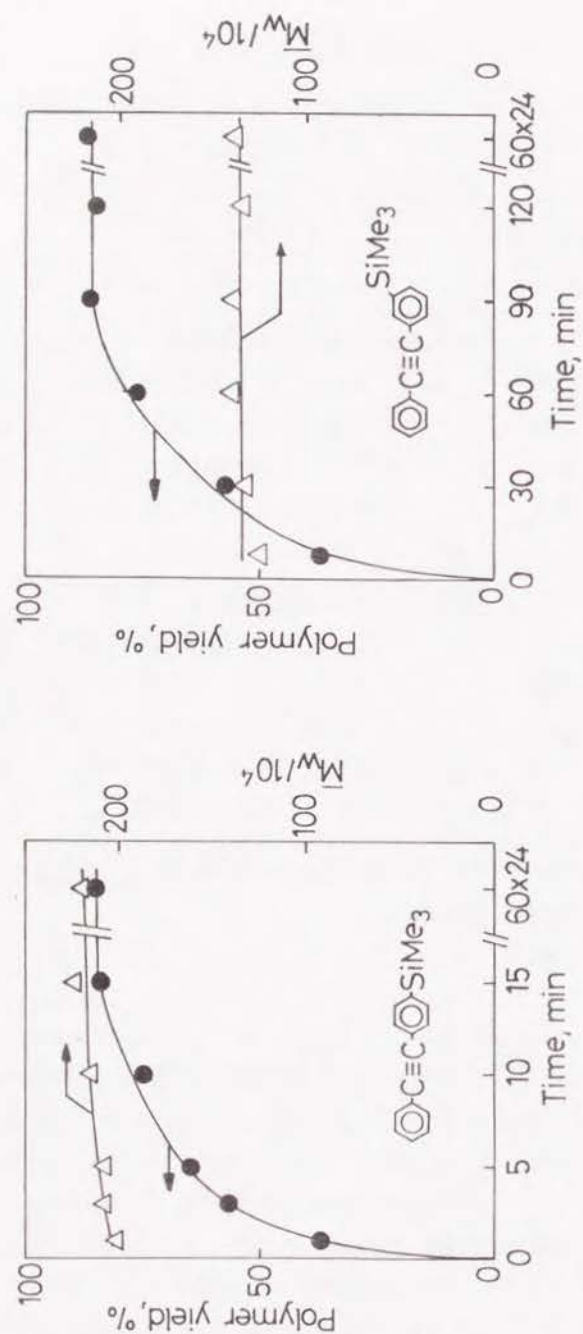


Figure 2. Time profiles of the polymerization of *p*-Me₃SiDPA and *m*-Me₃SiDPA by TaCl₅-*n*-Bu₄Sn (in toluene, 80 °C, [M]₀ = 0.50 M, [TaCl₅] = 20 mM, [*n*-Bu₄Sn] = 40 mM).

Thus, both polymerizations are fairly quick. The fact that the polymerization of *m*-Me₃SiDPA is slower is probably due to the steric hindrance of the meta-SiMe₃ group. The molecular weights of both polymers are independent of monomer conversion, which indicates that a stationary state is held. No changes in polymer molecular weight were observed, even though the polymerization systems were left over 24 h. This is indicative of the absence of polymer degradation after completion of polymerization which is seen in the polymerization of 1-phenyl-1-propyne.⁶

To clarify the influence of trimethylsilyl group on the monomer reactivity, copolymerization of *p*-Me₃SiDPA with DPA was attempted with TaCl₅-*n*-Bu₄Sn catalyst in toluene (Figure 3). *p*-Me₃SiDPA was consumed faster than DPA, which indicates higher relative reactivity of the former monomer. The relative

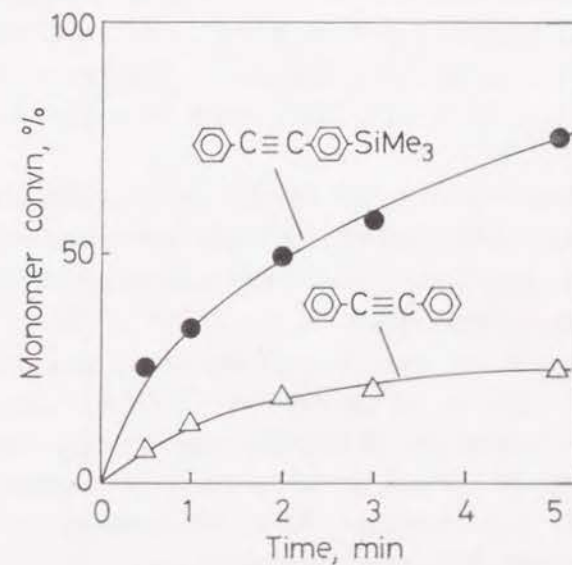


Figure 3. Copolymerization of *p*-Me₃SiDPA with DPA by TaCl₅-*n*-Bu₄Sn (in toluene, 80 °C, [M]₁₀ = [M]₂₀ = 0.25 M, [TaCl₅] = 20 mM, [*n*-Bu₄Sn] = 40 mM).

monomer reactivity in the copolymerization of substituted acetylenes is, in general, governed by both steric and electronic effects of substituent; i.e., the monomer reactivity decreases with increasing bulkiness of substituent and/or with decreasing electron-donating ability of substituent. Since *p*-Me₃SiDPA should be similar in the steric effect to DPA, the observed difference in relative reactivity seems to originate from the electron-donating property of trimethylsilyl group.

Polymer Structure

The structure of poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) did not depend on the polymerization conditions. The data described below have been obtained with the polymer samples obtained with TaCl₅-*n*-Bu₄Sn in toluene (Table I, no. 2 and Table II, no. 2).

The elemental analysis data of poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) agreed well with their calculated values: Calcd for (C₁₇H₁₈Si)_n: C, 81.6; H, 7.2; Si, 11.2. Found for poly(*p*-Me₃SiDPA): C, 81.1; H, 8.0; Si, 10.9. Found for poly(*m*-Me₃SiDPA): C, 81.1; H, 7.7; Si, 11.2.

As seen from Figure 4, the IR spectra of poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) do not show an absorption due to C≡C stretching which was observed at 2100 cm⁻¹ with the monomers. Strong absorptions characteristic of the SiC-H (1250 cm⁻¹) and Si-C (840 cm⁻¹) bonds are seen in both monomers and polymers.

¹H NMR spectra of poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) exhibited broad signals due to the olefinic and aromatic protons (δ 7.5 - 5.5) and a sharp one due to the methyl protons (δ -0.2). No unassignable signals were seen. The ¹³C NMR spectra of the polymers exhibited signals of sp² carbons (δ 150 - 125) and of methyl carbons (δ 1) but showed no signals of sp carbons which were observed in both monomers at δ 89.7 and 89.3.

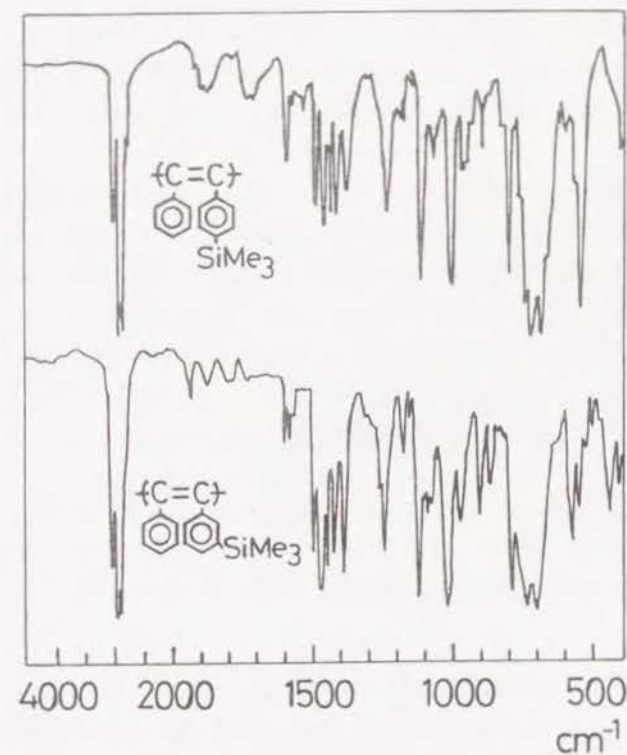


Figure 4. IR spectra of poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) (film; samples from Table I, no. 2 and Table II, no. 2).

It is concluded from the data described above that the present polymers possess alternating double bonds in the main chain. No information was, however, obtained regarding regiospecificity (head-to-tail and other structures) and geometric structure from IR and NMR spectra.

As seen in Figure 5, both polymers have two absorption maxima: poly(*p*-Me₃SiDPA) λ_{max} 375 nm (ε_{max} 4300 M⁻¹·cm⁻¹) and 430 nm (4800); poly(*m*-Me₃SiDPA) 380 nm (3200) and 440

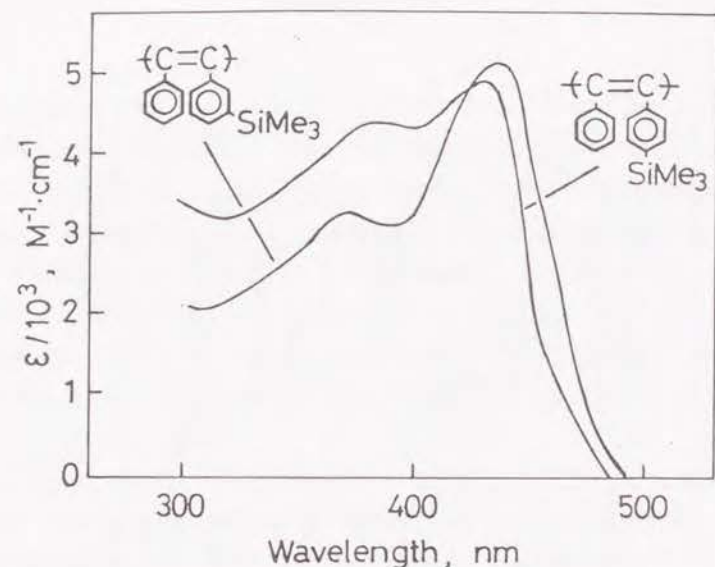


Figure 5. UV-visible spectra of poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) (measured in tetrahydrofuran; samples from Table I, no. 2 and Table II, no. 2).

nm (5100). The absorptions continue up to ca. 500 nm, which is in contrast to the absence of absorption in the visible region with the polymers from aliphatic disubstituted acetylenes.^{1b} Since the present polymers appeared fluorescence, their emission spectra were measured under excitation with the light of 430 nm. Poly(*p*-Me₃SiDPA) showed an emission at 520 nm, while poly(*m*-Me₃SiDPA) at 550 nm. The emission of the former polymer was about ten times more intense than that of the latter, though the reason is not clear at present.

The X-ray diffraction data obtained with Cu K α radiation is as follows: poly(*p*-Me₃SiDPA) $2\theta = 6.3^\circ$ ($\Delta 2\theta/2\theta = 0.297$), 14.3° (0.248); poly(*m*-Me₃SiDPA) 6.0° (0.280), 15.4° (0.461). As seen from the ratios of half-height width to diffraction angle ($\Delta 2\theta/2\theta$), the peaks are rather broad. Hence it can be concluded that all these polymers are amorphous. Further, the insolubility of poly(DPA) should, eventually, be due to some reasons other than crystallinity.

Polymer Properties

Properties of the present polymers were hardly affected by polymerization conditions. Hence, properties were studied in detail using the same samples as employed for structural analysis.

Poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) were both yellow solids like poly(DPA). Poly(*p*-Me₃SiDPA) dissolved in benzene, toluene, cyclohexane, CCl₄, CHCl₃, tetrahydrofuran, anisole, diethyl ether, and triethylamine, and partly dissolved in hexane, 1,4-dioxane, (CH₂Cl)₂, and ethyl acetate. Its nonsolvents include acetone, acetophenone, methyl benzoate, acetonitrile, N,N-dimethylformamide, dimethyl sulfoxide. Though the solubility property of poly(*m*-Me₃SiDPA) was similar, it was soluble in hexane. Since poly(DPA) is insoluble in any of the above-stated

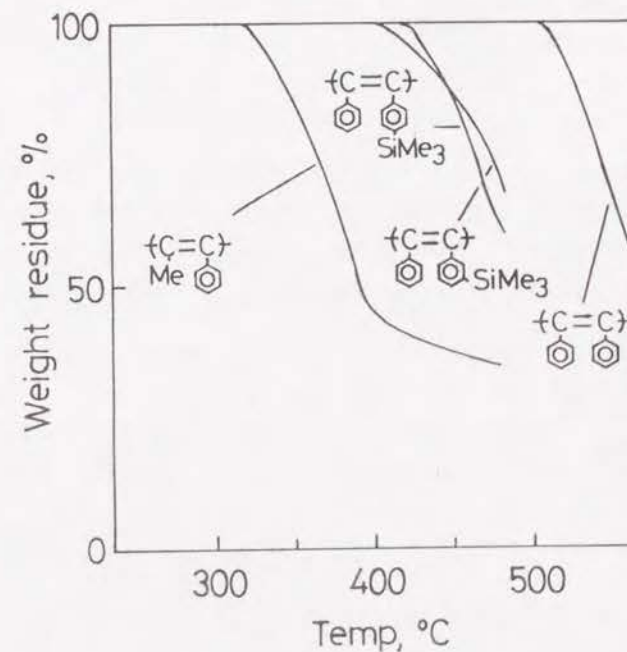


Figure 6. TGA curves of disubstituted acetylene polymers (in air, heating rate 10 °C/min; samples from Table I, no. 2 and Table II, no. 2).

solvents, introduction of a trimethylsilyl group is obviously effective in solubilizing poly(DPA). Free-standing films could be fabricated by casting the present polymers from toluene solution.

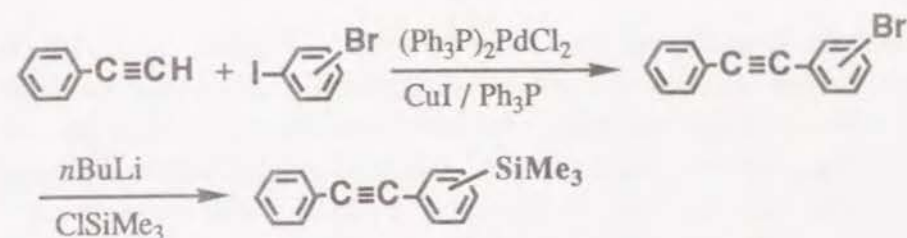
The weight loss of poly(DPA) does not occur below 500 °C in TGA, demonstrating that it is more stable than any other substituted polyacetylenes.² The temperatures at which the weight loss of poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) started in air were 420 °C and 400°C, respectively (Figure 6). These temperatures are lower than that of poly(DPA) but higher than those of most substituted polyacetylenes. Further, even when the polymers in the present study were left in air either at 120 °C for 20 h or at room temperature for one month, their molecular weights did not decrease. These results show that both of the present polymers possess high thermal stability.

The tensile properties of poly(*p*-Me₃SiDPA) and poly(*m*-Me₃SiDPA) measured at 25 °C are as follows:⁷ Poly(*p*-Me₃SiDPA): Young's modulus (*E*) = 1460 MPa, tensile strength (σ_B) = 19 MPa, elongation at break (γ_B) = 1.5%. Poly(*m*-Me₃SiDPA): *E* = 800 MPa, σ_B = 14 MPa, γ_B = 2.1%. Thus both polymers are hard and brittle, and the position of trimethylsilyl group does not greatly affect the tensile properties. The glass transition temperatures of the polymers were above 200 °C according to dynamic viscoelastic measurements.⁷

Experimental

Materials

The monomers (new compounds) were synthesized according to the following scheme with reference to the literature methods for ethynylation⁸ and silylation.⁹



The procedure for preparing *p*-Me₃SiDPA is described below as an example.

1-(*p*-Bromophenyl)-2-phenylacetylene: A 1-L, three-necked, round-bottomed flask was equipped with a reflux condenser, a three-way stopcock and a magnetic stirring bar, and was then flushed with dry nitrogen. Triethylamine (300 mL), (Ph₃P)₂PdCl₂ (0.56 g, 0.80 mmol), CuI (0.91 g, 4.8 mmol), Ph₃P (0.84 g, 3.2 mmol), and phenylacetylene (22.0 mL, 0.20 mol) were placed in the flask, and the mixture was stirred for 1 h. Then, *p*-bromiodobenzene (56.6 g, 0.20 mol) in triethylamine (300 mL) was added dropwise, and stirring was continued for an additional 1 h. After the completion of the reaction was confirmed by gas chromatography (GC), triethylamine was evaporated. Diethyl ether (ca. 400 mL) was added, and insoluble salts were removed by filtration. The solution was washed with 5% hydrochloric acid and water. The organic phase was dried over anhydrous sodium sulfate overnight, and diethyl ether was evaporated. The product was used for the next step without further purification: yield 55%, purity 99% (GC).

***p*-Me₃SiDPA:** A 200 mL, three-necked, round-bottomed flask was equipped with a three-way stopcock, a dropping funnel, and a magnetic stirring bar. After flushed with nitrogen, a hexane solution of *n*-butyllithium (63 mL, 1.6 M, 0.10 mol) was placed in the flask, and the hexane (ca. 40 mL) was evaporated with an aspirator under magnetic stirring. Diethyl ether (40 mL; dried over sodium) was gradually added at -20 °C. At the same temperature, a solution of 1-(*p*-bromophenyl)-2-phenylacetylene (25.7 g, 0.10 mol) in diethyl ether (50 mL) was added dropwise,

and the reaction mixture was left for 30 min. At $-20\text{ }^{\circ}\text{C}$ trimethylchlorosilane (13.9 mL, 0.11 mol) was added dropwise and stirring was continued for an additional 1 h. After the completion of the reaction was confirmed by GC, ice water (20 mL) was added. The product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate overnight. Diethyl ether was evaporated, and the product was purified by flush column chromatography (Nakarai Tesque Co., silica gel 60; eluent, hexane); yield 70%, purity >99% (GC), d^{20} 1.051.

m-Me₃SiDPA was prepared in the same way from *m*-bromiodobenzene. Overall yield 30%, purity >99% (GC), d^{20} 1.022.

Transition-metal catalysts and organometallic cocatalysts were all commercially obtained, and used without purification with care being taken not to be decomposed by moisture and/or air. Polymerization solvents were purified by the standard methods.

Polymerization

A typical procedure for the polymerization of *p*-Me₃SiDPA (cf. Table I, no. 2) is described below. The manipulation and reaction were carried out under dry nitrogen.

A monomer solution (2.4 mL) was prepared in a Schlenk tube by mixing *p*-Me₃SiDPA (0.71 mL, 0.75 g, 3.0 mmol), eicosane (0.50 mL; internal standard of GC), and toluene (1.19 mL). Another Schlenk tube was charged with TaCl₅ (35.8 mg, 0.10 mmol), *n*-Bu₄Sn (65.6 μ L, 69.4 mg, 0.20 mmol), and toluene (3.0 mL); this catalyst solution was aged at $80\text{ }^{\circ}\text{C}$ for 15 min. Then 2.0 mL of monomer solution was added to the catalyst solution. Polymerization was carried out at $80\text{ }^{\circ}\text{C}$ for 24 h, and was quenched with a mixture of toluene and methanol (1 mL, volume ratio 4:1). After monomer conversion was determined by GC (Silicon DC 550, 0.5 m, $180\text{ }^{\circ}\text{C}$), the polymerization mixture was

diluted with toluene (300 mL) and was poured into methanol (4L) under stirring to precipitate the formed polymer. The polymer was isolated by filtration and dried. The polymer yield was determined by gravimetry.

Characterization

The molecular weights of polymers were determined by gel permeation chromatography (GPC) with use of a polystyrene calibration. GPC curves were observed with a Shimadzu LC-9A liquid chromatograph [eluent, CHCl₃; columns Shodex A805, A806, and A807 polystyrene gels (Showa Denko, Co., Japan)]. Monodisperse polystyrene samples with \bar{M}_n 's of 1.0×10^5 , 3.0×10^5 , 6.5×10^5 , 1.8×10^6 , 2.0×10^6 , 3.8×10^6 , and 2.0×10^7 were used to make a calibration curve.

IR and UV-visible spectra were recorded with Shimadzu FTIR-8100 and Shimadzu UV190 spectrophotometers, respectively. TGA was conducted with a Shimadzu 20B thermal analyzer (in air, heating rate $10\text{ }^{\circ}\text{C}/\text{min}$).

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Chapter 2

Polymerization and Polymer Properties of Diphenylacetylenes with Bulky Silyl Groups

Abstract

Polymerization and polymer properties of diphenylacetylenes with bulky silyl groups (SiMe_2iPr , SiMe_2tBu , SiMe_2Ph , SiEt_3) at para or meta position were examined. These monomers polymerized in good yields with TaCl_5 -cocatalysts to form high-molecular-weight polymers ($\bar{M}_w > 4 \times 10^5$). The polymer yields for meta-substituted monomers were lower than that for the monomer having SiMe_3 group, whereas no decrease was observed in the case of para-substituted monomers. Many of the polymers were soluble in common organic solvents, though the polymers with SiMe_2Ph and SiMe_2tBu groups at para position were partly insoluble. The UV-visible absorption property and thermal stability of these polymers were similar to those of poly(diphenylacetylenes) having SiMe_3 group obtained in Chapter 1.

Introduction

Many substituted polyacetylenes have been synthesized by using group 5 and 6 transition-metal catalysts.¹ Among these polymers, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] possesses higher gas permeability than any other synthetic polymers,² and its gas permeation behavior has been intensively studied.³ When a bulkier silyl group (e.g., SiMe₂-*n*-C₆H₁₃, SiMe₂Ph, SiEt₃) is introduced to poly(TMSP) instead of SiMe₃ group, i) the yield and molecular weight of polymer decrease, and ii) the gas permeability of polymer decreases.⁴ It is, however, not known whether these characteristics are seen in other polymers than poly(TMSP).

In Chapter 1, the author synthesized poly[1-phenyl-2-*p*-(trimethylsilyl)phenylacetylene] and poly[1-phenyl-2-*m*-(trimethylsilyl)phenylacetylene] [poly(*para*-1) and poly(*meta*-1), respectively]. These polymers were soluble in various organic solvents, and their weight-average molecular weight (\bar{M}_w) reached over 1×10^6 . The polymers were thermally fairly stable (the temperature at which weight loss starts is ~ 400 °C), and its gas permeability is about 1/4 that of poly(TMSP), being very high. It is of interest how the polymer yield, molecular weight, and properties change when the SiMe₃ group of poly(*para*-1) and poly(*meta*-1) is substituted by bulkier silyl groups.

In this chapter, the polymerization and polymer properties of diphenylacetylenes carrying bulky silyl groups (SiMe₂*i*Pr, SiMe₂*t*Bu, SiMe₂Ph, SiEt₃) by TaCl₅-based catalysts are described. The results are compared with those of *para*-1 and *meta*-1 to clarify the effects of bulky silyl groups.

Results and Discussion

Polymerization

Para-1 and *meta*-1 polymerize with TaCl₅-*n*-Bu₄Sn in good yields to produce high polymers whose \bar{M}_w 's reach over 1×10^6 . Hence, polymerization of diphenylacetylenes with bulky silyl groups was studied by using this catalyst.

Table I shows the polymerization of *para*-substituted diphenylacetylenes. When polymerized for 24 h, the monomers were consumed virtually quantitatively, and polymers were formed in high yields. Polymer yield decreased with increasing bulkiness of the silyl group. Soluble polymers were obtained from the monomers carrying relatively small silyl groups such as SiMe₂*i*Pr and SiEt₃. The \bar{M}_w 's of these polymers were ca. 160×10^4 being relatively close to that of *para*-1. On the other hand, the polymers with very bulky silyl groups like SiMe₂Ph

Table I

Polymerization of  by TaCl₅-*n*-Bu₄Sn^a

Monomer SiR¹R²R³	Monomer convn, %	Polymer ^b	
		yield, %	$\bar{M}_w/10^4$ ^c
SiMe ₃	95	85	220
SiMe ₂ Ph	100	63 ^d	
SiMe ₂ <i>i</i> Pr	100	74	160
SiMe ₂ <i>t</i> Bu	95	61 ^d	
SiEt ₃	100	84	160

a Polymerized in toluene at 80 °C for 24 h; [M]₀ = 0.50 M, [TaCl₅] = 20 mM, [*n*Bu₄Sn] = 40 mM.

b Methanol-insoluble product.

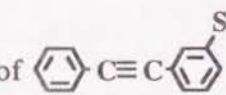
c Determined by GPC.

d Partly insoluble in CHCl₃.

and SiMe_2tBu were partly insoluble in toluene and CHCl_3 . Thus, introduction of bulky silyl groups into the para position of diphenylacetylene did not greatly change the yield and molecular weight of polymers as compared with *para*-1. This indicates that bulky substituents at para position hardly affects polymerization behavior, while very bulky one reduces yield and solubility of the polymer.

Meta-substituents are expected to exert a larger steric effect than do para-substituents. Thus, the polymerization of monomers having bulky meta-silyl groups was examined (Table II). *Meta*-1 reacts quantitatively with TaCl_5 -*n*- Bu_4Sn to give in high yield a polymer having \bar{M}_w of 1×10^6 . In the polymerization of monomers with bulkier groups, on the other hand, the monomer conversions did not reach 100% after 24 h, and the polymer yields were lower than that of *meta*-1. Polymer yield decreased with increasing bulkiness of the silyl group. All of the

Table II

Polymerization of  by TaCl_5 -*n*- Bu_4Sn ^a

Monomer	Monomer convn, %	Polymer ^b	
		yield, %	$\bar{M}_w/10^4$ ^c
SiMe_3	100	87	140
SiMe_2Ph	60	42	45
SiMe_2iPr	82	71	105
SiMe_2tBu	75	51	50
SiEt_3	81	63	54

a Polymerized in toluene at 80 °C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{TaCl}_5] = 20 \text{ mM}$, $[n\text{Bu}_4\text{Sn}] = 40 \text{ mM}$.

b Methanol-insoluble product.

c Determined by GPC.

produced polymers were soluble in various organic solvents, and their \bar{M}_w 's were as high as $5 \times 10^5 - 10 \times 10^5$.

As described above, the polymer yields for meta-substituted monomers were lower than that for *meta*-1, whereas no decrease was observed in the case of para-substituted monomers. If a substituent of a disubstituted acetylene is too bulky, the yield and molecular weight of the polymer tend to decrease. For instance, when a bulky substituent is introduced onto the silicon of $\text{MeC}\equiv\text{CSiMe}_3$, the yield and molecular weight of polymer becomes lower than those of $\text{MeC}\equiv\text{CSiMe}_3$.⁴ These facts suggest that decreases in the polymer yield and molecular weight of meta-substituted poly(diphenylacetylenes) are due to the

Table III

Cocatalyst Effects on the Polymerization of *Para*-2 by TaCl_5 ^a

Cocatalyst	Monomer convn, %	Polymer ^b	
		yield, %	$\bar{M}_w/10^4$ ^c
none	0	0	
<i>n</i> - Bu_4Sn	100	74	160
Et_3SiH	100	78	170
9BBN	100	70	161
Ph_4Sn	35	15	108

a Polymerized in toluene at 80 °C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{TaCl}_5] = 20 \text{ mM}$, $[\text{cocat}] = 40 \text{ mM}$.

b Methanol-insoluble product.

c Determined by GPC.

steric effect of meta-substituents. The differences between monomer conversion and polymer yield were due to the formation of linear oligomers with both para and meta isomers.

Cocatalyst effect on the polymerization was examined by using monomers with SiMe_2iPr group which formed soluble polymers from both para and meta isomers (*para-2* and *meta-2*, respectively). Table III shows the effect of cocatalysts on the polymerization of *para-2*. No polymer was obtained with TaCl_5 alone. Polymers formed when $n\text{-Bu}_4\text{Sn}$, Et_3SiH , and 9BBN, which are effective in the polymerization of *para-1*, were used as cocatalyst. The yield and molecular weight of polymer hardly changed with these cocatalysts. On the other hand, when Ph_4Sn was used as cocatalyst, polymer yield was greatly lower than the case of other cocatalysts, though no decrease was observed for molecular weight of the polymer.

Polymerization of *meta-2* was attempted by using various cocatalysts (Table IV). TaCl_5 alone was ineffective again, while

Table IV

Cocatalyst Effects on the Polymerization of *Meta-2* by TaCl_5^a

Cocatalyst	Monomer convn, %	Polymer ^b	
		yield, %	$\bar{M}_w/10^4$ ^c
none	0	0	
$n\text{-Bu}_4\text{Sn}$	82	71	105
Et_3SiH	80	68	110
9BBN	88	72	112
Ph_4Sn	41	20	108

a Polymerized in toluene at 80 °C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{TaCl}_5] = 20 \text{ mM}$, $[\text{cocat}] = 40 \text{ mM}$.

b Methanol-insoluble product.

c Determined by GPC.

use of suitable cocatalysts provided polymers. Effective cocatalysts were common in both *para-2* and *meta-2* and these cocatalysts gave polymers having \bar{M}_w 's over 1×10^6 in about 60% yields.

Figure 1 shows time dependences of the polymerization with $\text{TaCl}_5\text{-}n\text{-Bu}_4\text{Sn}$. Under the conditions shown in Figure 1, polymerization of *para-2* was completed rapidly (<15 min), whereas *meta-2* was consumed completely more slowly (quantitative after 60 min). A similar difference in polymerization rate was observed between *para-1* and *meta-1*. This is attributable to the steric effect of bulky meta-substituents. The molecular weight of polymer was independent of polymerization time, being over 1.5×10^6 and about 1.0×10^6 for

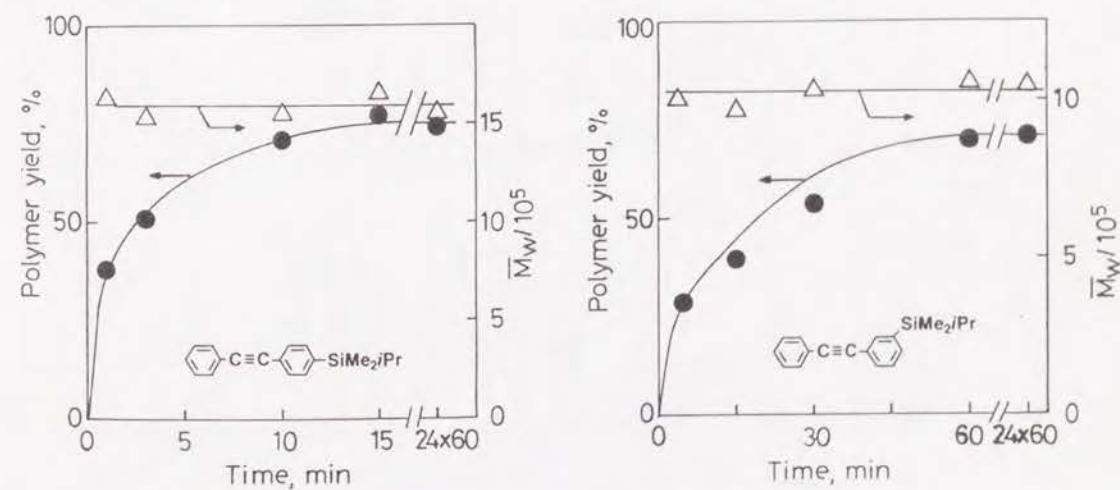


Figure 1. Time profiles of the polymerization of *para-2* and *meta-2* by $\text{TaCl}_5\text{-}n\text{-Bu}_4\text{Sn}$ (in toluene, 80 °C, $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{TaCl}_5] = 20 \text{ mM}$, $[n\text{-Bu}_4\text{Sn}] = 40 \text{ mM}$).

para-2 and *meta*-2, respectively.

Structure and Properties of Polymers

Polymer structure was studied by using the poly(*para*-2) and poly(*meta*-2) samples obtained in Table I. The elemental analysis values for the polymers agreed well with the ones calculated for the polymerization products; Anal Calcd for $(C_{19}H_{22}Si)_n$: C, 82.0; H, 7.9; Si, 10.1. Found for poly(*para*-2): C, 81.7; H, 8.1; Si, 10.2. Found for poly(*meta*-2): C, 81.5; H, 8.2; Si, 10.3.

Figure 2 shows IR spectra of poly(*para*-2) and poly(*meta*-2). In the spectra of these polymers the signals characteristic of

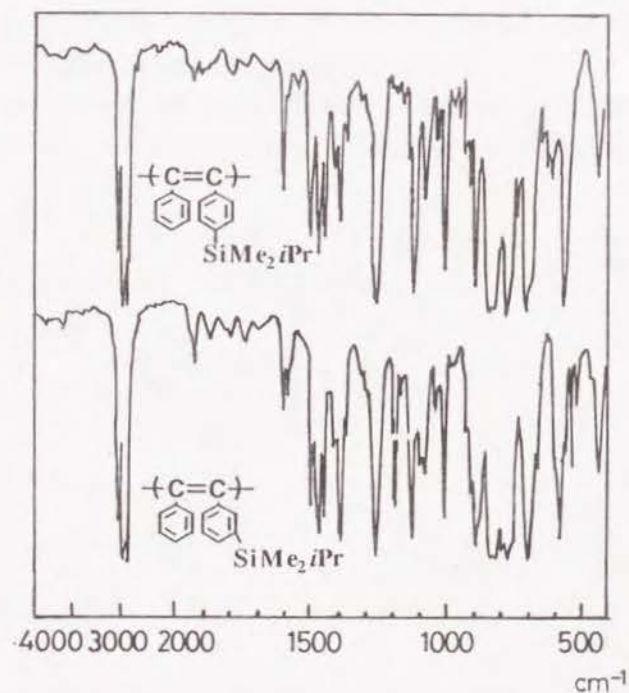


Figure 2. IR spectra of poly(*para*-2) and poly(*meta*-2)

the $\equiv C-H$ (3290 cm^{-1}) and $C\equiv C$ (2200 cm^{-1}) bonds, which are seen in the monomer, have disappeared. The absorptions assignable to the SiC-H and Si-C bonds were observed in the spectra of both monomers and polymers. These analytical and spectral data supports that these polymers have the structure containing alternating double bonds in the main chain as shown in Figure 2.

Polymers obtained in this chapter are novel polymers with the form of yellow solid like poly(*para*-1) and poly(*meta*-1). The polymers with $SiMe_2Ph$ and $SiMe_2tBu$ groups, which are very bulky silyl groups, at *para* position were partly insoluble in common organic solvents such as toluene and $CHCl_3$. Other polymers provided in this chapter were soluble in various organic solvents like toluene and $CHCl_3$. Table V summarizes solubility of some silicon-containing poly(diphenylacetylenes). Which solvent dissolves a polymer depends on the kind of silyl group in the polymer. The solvents in which poly(*para*-1) and

Table V
Solubility of Silicon-containing Poly(diphenylacetylenes)^a

	<i>p</i> -SiMe ₂ R			<i>m</i> -SiMe ₂ R		
	Me	<i>i</i> Pr	Ph	Me	<i>i</i> Pr	Ph
toluene	+	+	±	+	+	+
cyclohexane	+	+	±	+	+	+
CCl ₄	+	+	±	+	+	+
CHCl ₃	+	+	±	+	+	+
anisole	+	±	±	+	±	±
1,4-dioxane	±	±	±	±	±	±

a + : soluble ± : partly insoluble.

poly(*meta*-1) are partly insoluble did not completely dissolve the present polymers. Further, all of the polymers having bulky silyl group were partly insoluble in anisole, whereas poly(*para*-1) and poly(*meta*-1) are soluble. These results indicate that the solubility of the present polymers is lower than that of poly(*para*-1) and poly(*meta*-1). This is probably due to the lack of flexibility of the bulky silyl groups. A self-standing film could be obtained by casting the soluble polymers.

Figure 3 shows UV-visible spectra of polymers with silyl groups at meta position. The absorption of poly(*meta*-1) has maxima at around 380 and 430 nm, and extends up to ~500 nm. The poly(diphenylacetylenes) carrying bulky silyl groups at meta position showed similar absorption bands and maxima, no large differences being observed with the kind of silyl group. In

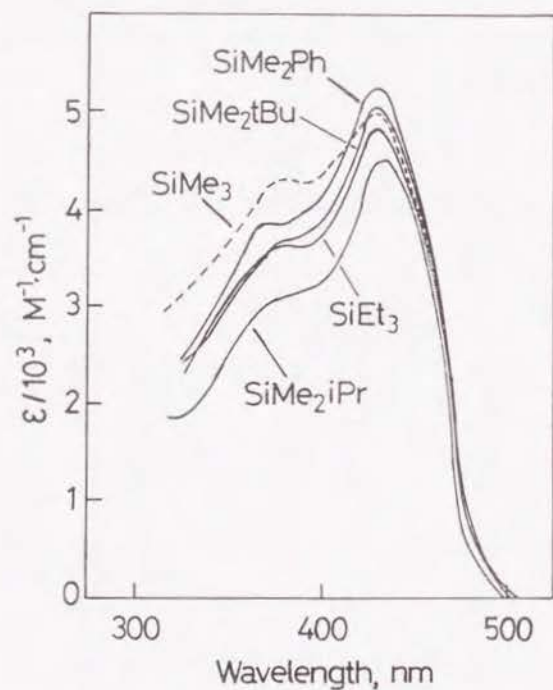


Figure 3. UV-visible spectra of meta-substituted poly(diphenylacetylenes) (measured in tetrahydrofuran).

general, the absorption of substituted polyacetylenes tends to show a blue shift with increasing bulkiness of substituent, because bulky substituents twist the main chain to narrow the conjugation. Silyl groups at meta position, however, hardly affected the absorption. Thus, conjugation of the main chain appears to be hardly affected by the bulkiness of meta-substituent. These absorptions correspond to the yellow color of these polymers.

Generally, the thermal stability of substituted polyacetylenes increases with increasing bulkiness of substituents, because bulky substituents twist the main chain making the radical formation difficult and further preclude the reaction of the radical with oxygen. Thus, the thermal stability of poly(diphenylacetylenes) with bulky silyl groups were studied

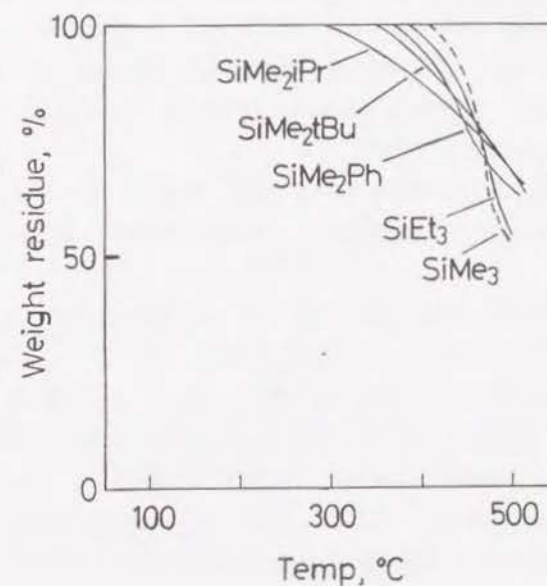


Figure 4. TGA curves of meta-substituted poly(diphenylacetylenes) (in air, heating rate 10 °C/min).

(Figure 4). In the thermogravimetric analysis (TGA) of poly(diphenylacetylene) in air, no weight loss is observed up to 500 °C, indicating that the polymer possesses the highest thermal stability among substituted polyacetylenes. The temperature at which weight loss starts in air is ~400°C for both poly(*para*-1) and poly(*meta*-1), being fairly high. The polymers obtained in this chapter began to lose weight at around 350 °C. Thus, the thermal stability of these polymers is relatively high among substituted polyacetylenes, though slightly lower than those of poly(*para*-1) and poly(*meta*-1).

Experimental

Monomers (new compounds) were prepared with reference to the method for *para*-1 and *meta*-1 described in Chapter 1 using $\text{ClSiR}^1\text{R}^2\text{R}^3$ instead of ClSiMe_3 . The crude product was purified by flush column chromatography (Nakarai Tesque Co., silica gel 60; eluent, hexane).

Transition metal chlorides and organometallic compounds were commercially obtained and used without further purification.

Polymerization was carried out as described in Chapter 1. Monomer conversions were determined by GC, and molecular weights of polymers were determined by gel permeation chromatography (GPC; eluent, CHCl_3 , polystyrene calibration).

UV-visible spectra were recorded with a Shimadzu UV-2200 spectrophotometer. TGA was performed with a Shimadzu 20B thermal analyzer (heating rate 10 °C/min).

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Chapter 3

Polymerization and Polymer Properties of 1-[*m*-(Trimethylsilyl)phenyl]-1-propyne

Abstract

1-[*m*-(Trimethylsilyl)phenyl]-1-propyne polymerized in good yields in the presence of NbCl₅- and TaCl₅-based catalysts to give a new polymer ($\bar{M}_w \sim 5 \times 10^5$). When 1-phenyl-1-propyne is polymerized with NbCl₅ and TaCl₅ alone, its polymer molecular weight decreases after the complete consumption of monomer. Such a phenomenon was not observed with the present monomer. The product polymer possessed the structure, [-CMe=C(C₆H₄-*m*-SiMe₃)-]. The polymer was in the form of a white solid, completely soluble in common organic solvents (e.g., toluene, CHCl₃), formed a self-standing film by solution casting.

Introduction

Silicon-containing polyacetylenes often exhibit unique properties, especially high gas permeability.^{1,2} For example, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] shows the highest gas permeability among all the synthetic polymers,³ and has recently been under intensive research.^{4,5} Therefore, it is of interest to introduce trimethylsilyl group into the side chain of various polyacetylenes.

Disubstituted acetylenes are known to undergo metathesis polymerization with Nb and Ta catalysts. Among them, 1-phenyl-1-propyne⁶ ($\text{MeC}\equiv\text{CPh}$; PhP) affords a polymer having a weight-average molecular weight (\bar{M}_w) over 1×10^6 . The polymer [poly(PhP)] is a white solid, which is soluble in many organic solvents and thermally fairly stable. It is one of the least gas-permeable polyacetylenes.

In Chapter 1, the author discovered that diphenylacetylenes having SiMe_3 group at meta position on one phenyl group ($\text{PhC}\equiv\text{CC}_6\text{H}_4\text{-}m\text{-SiMe}_3$; $m\text{-Me}_3\text{SiDPA}$) polymerizes in good yield with TaCl_5 -cocatalyst to form high polymer whose \bar{M}_w reaches over 1×10^6 . The polymer dissolved in various organic solvents and more stable than poly(PhP). It is of interest to examine how polymerization behavior and polymer properties change if one phenyl group of $m\text{-Me}_3\text{SiDPA}$ is replaced by methyl group.

This chapter reports on the polymerization of 1-[m -(trimethylsilyl)phenyl]-1-propyne ($\text{MeC}\equiv\text{CC}_6\text{H}_4\text{-}m\text{-SiMe}_3$; $m\text{-Me}_3\text{SiPhP}$), a silicon-containing PhP, and properties of the product polymer. The author anticipated that the o -trimethylsilyl substituted PhP would not polymerize owing to too large a steric hindrance. Hence, the meta derivative, for which an appropriate steric effect is expected, was chosen as monomer. $m\text{-Me}_3\text{SiPhP}$ polymerized with NbCl_5 to give a new, high molecular weight polymer in high yield. The polymerization behavior and polymer properties of $m\text{-Me}_3\text{SiPhP}$ are compared with those of PhP.

Results and Discussion

Polymerization

Table I shows results for the polymerization of $m\text{-Me}_3\text{SiPhP}$ by TaCl_5 - and NbCl_5 -based catalysts. When $m\text{-Me}_3\text{SiPhP}$ was polymerized with NbCl_5 alone, this monomer was completely consumed to give a methanol-insoluble polymer in high yield. The weight-average molecular weight (\bar{M}_w) of the polymer reached 680×10^3 , but the molecular weight distribution was broad. When organometallic cocatalysts, which are effective for the polymerization of PhP, were used in conjunction with NbCl_5 , polymers were formed in high yields as well. The polymers were, however, partly insoluble in CHCl_3 . The tendency that NbCl_5 -cocatalyst systems produce insoluble polymers has been observed with 1-(trimethylsilyl)-1-propyne as well.⁷ This is probably because NbCl_5 provide polymers having relatively high stereoregularity⁸ and further the use of a cocatalyst increases its molecular weight.

When TaCl_5 alone was used as catalyst, the monomer conversion did not reach 100%, and the polymer yield was considerably lower than that for NbCl_5 . Use of cocatalyst for TaCl_5 was more or less effective in the increase of yield and \bar{M}_w of polymer. NbCl_5 alone, however, achieves a higher polymer yield than do these TaCl_5 -cocatalyst systems. The differences between monomer conversion and polymer yield were due to the formation of cyclotrimers.

As described above, not only TaCl_5 - but also NbCl_5 -based catalysts produce polymer from $m\text{-Me}_3\text{SiPhP}$, whereas $m\text{-Me}_3\text{SiDPA}$ polymerizes only with TaCl_5 -cocatalysts. This difference is probably due to steric effect of bulky pendant group of $m\text{-Me}_3\text{SiDPA}$.

When PhP is polymerized with NbCl_5 or TaCl_5 alone, the molecular weight of the polymer formed decreases after complete consumption of monomer.⁶ It is interesting whether

Table I
Polymerization of *m*-Me₃SiPhP by Various Nb and Ta Catalysts^a

Cocatalyst	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
NbCl ₅ -cocatalyst				
none	100	89	680	72
<i>n</i> -Bu ₄ Sn	100	91 ^d		
Ph ₄ Sn	100	93 ^d		
Et ₃ SiH	100	83 ^d		
Ph ₃ SiH	100	85 ^d		
Ph ₃ Sb	100	100 ^d		
Ph ₃ Bi	100	97 ^d		
TaCl ₅ -cocatalyst				
none	53	23	140	42
<i>n</i> -Bu ₄ Sn	100	68 ^d		
Ph ₄ Sn	100	49	1000	170
Et ₃ SiH	79	52	220	56
Ph ₃ SiH	100	46	120	18
Ph ₃ Sb	60	38	350	170
Ph ₃ Bi	71	42	890	260

a Polymerized in toluene at 80 °C for 24 h; [M]₀ = 0.50 M, [cat] = [cocat] = 10 mM.

b Methanol-insoluble product.

c Determined by GPC.

d Partly insoluble in CHCl₃.

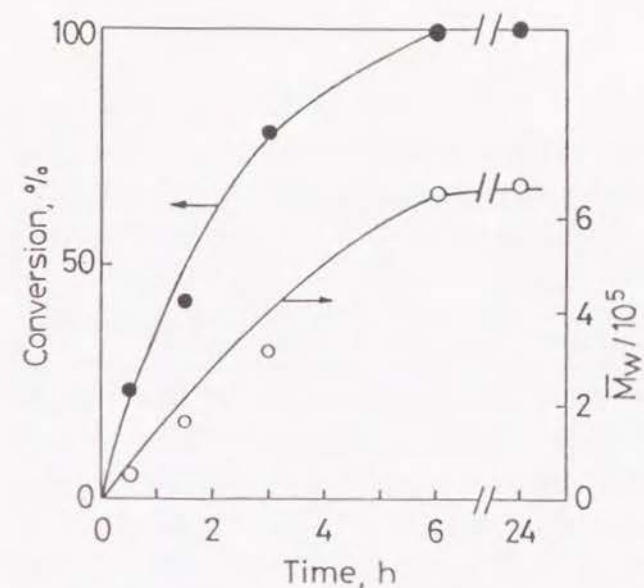


Figure 1. Time course of the polymerization of *m*-Me₃SiPhP by NbCl₅ (in toluene, 80 °C, [M]₀ = 0.50 M, [NbCl₅] = 10 mM).

this molecular weight decrease is prevented by the introduction of the bulky trimethylsilyl group into meta position. Thus, time course of the polymerization was studied using the NbCl₅ catalyst which achieves a high polymer yield (Figure 1). The monomer conversion reached 100% after 6 h. The reaction rate is smaller than that of PhP (the polymerization of PhP proceeded completely within 2 h). The \bar{M}_w of polymer was $\sim 600 \times 10^3$ after 6 h, which was maintained even after 24 h. Thus, it is possible to restrain the decrease of molecular weight by increasing bulkiness of the substituent.

As seen in Figure 1, the \bar{M}_w of polymer increased approximately in proportion to monomer conversion. This indicates the presence of a long-lived propagating species. Such a tendency was seen also in the polymerization of 1-phenyl-1-alkynes by NbCl₅ and TaCl₅.⁶

Solvent effects on the polymerization by NbCl₅ were studied (Table II). High-molecular-weight polymers were obtained in

Table II

Solvent Effects on the Polymerization of *m*-Me₃SiPhP by NbCl₅^a

Solvent	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
toluene	100	89	680	72
heptane	100	75 ^d		
CCl ₄	66	37	100	30
(CH ₂ Cl) ₂	100	73	440	93
PhOMe	100	72	360	88

a Polymerized at 80 °C for 24 h; [M]₀ = 0.50 M, [NbCl₅] = 10 mM.

b Methanol-insoluble product.

c Determined by GPC.

d Partly insoluble in CHCl₃.

good yields not only in hydrocarbon solvents (toluene, heptane) but also in chlorine-containing solvents [CCl₄, (CH₂Cl)₂] and anisole.

In order to know the relative monomer reactivity in the propagation reaction, copolymerization of *m*-Me₃SiPhP with PhP was attempted in toluene solution at 80 °C; [M₁]₀ = [M₂]₀ = 0.25 M, [NbCl₅] = 20 mM. Both monomers reacted virtually at the same rate (relative rate, *m*-Me₃SiPhP:PhP = 0.9:1). Further, *m*-Me₃SiPhP was more reactive than 1-(*m*-bromophenyl)-1-propyne (*m*-BrPhP) in their copolymerization (relative rate, *m*-Me₃SiPhP:*m*-BrPhP = 2:1). In general, the relative monomer reactivity in copolymerization is determined by steric and electronic effects; i.e., it increases with decreasing bulkiness of substituent and with increasing electron-donating ability of substituent.^{9,10} Consequently, the similar reactivity of PhP and *m*-Me₃SiPhP are attributable to compensation of the steric and electronic effects in the latter monomer.

Structure and Properties of the Polymer

The structure and properties were studied by using the poly(*m*-Me₃SiPhP) obtained with NbCl₅ alone in Table I.

The elemental analysis values for the polymers agreed well with the ones calculated for the polymerization products; Anal Calcd for (C₁₂H₁₆Si)_n: C, 76.6; H, 8.5; Si, 14.9. Found: C, 76.9; H, 8.3; Si, 14.9.

The IR spectrum of poly(*m*-Me₃SiPhP) showed no signal characteristic of the C≡C stretching (2200 cm⁻¹) seen in the monomer. Instead, an absorption assignable to the C=C stretching appeared at ~1580 cm⁻¹ (w). Furthermore, no signals due to acetylenic carbons were observed in the ¹³C NMR spectrum of poly(*m*-Me₃SiPhP). These analytical and spectral data are compatible with the polymer structure of -(CMe=CC₆H₄-*m*-SiMe₃)-.

Poly(*m*-Me₃SiPhP) is a novel polymer with the form of

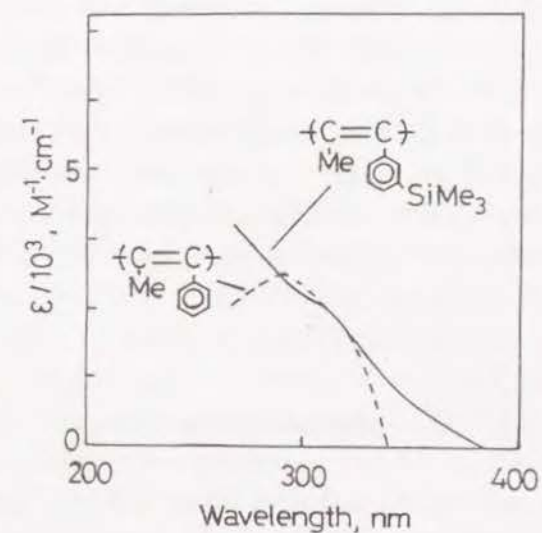


Figure 2. UV-visible spectra of poly(1-phenyl-1-propynes) (measured in cyclohexane).

white solid. The solubility of the polymer is as follows: completely soluble in toluene, cyclohexane, CCl_4 , CHCl_3 , and anisole; partly soluble in *n*-hexane, diethyl ether, and tetrahydrofuran; and insoluble in $(\text{CH}_2\text{Cl})_2$, 1,4-dioxane, acetone, acetophenone, ethyl acetate, methyl benzoate, nitrobenzene, and acetonitrile. A free-standing film could be obtained by casting the polymer from toluene solution.

Figure 2 shows UV-visible spectra of poly(*m*- Me_3SiPhP) and poly(PhP). The absorption of poly(*m*- Me_3SiPhP) appears only below 400 nm; i.e., in the ultraviolet region, which corresponds to the fact that poly(*m*- Me_3SiPhP) is a white solid. The absorption pattern resemble that of poly(PhP), although a minor difference is seen in the 350 - 400 nm region. The absorption of poly(*m*- Me_3SiPhP) exists in shorter wavelength region than that of poly(*m*- Me_3SiDPA).

In the TGA measurement in air, poly(*m*- Me_3SiPhP) began to lose weight at 310 °C, whereas poly(PhP) did at 280 °C; i.e., introduction of trimethylsilyl group somewhat increased thermal stability. Even after the poly(*m*- Me_3SiPhP) had been heated at 120 °C for 20 h in air, no molecular-weight change was observed. Thus, poly(*m*- Me_3SiPhP) turns out thermally fairly stable among substituted polyacetylenes, though thermal stability of poly(*m*- Me_3SiPhP) is lower than that of poly(*m*- Me_3SiDPA) (weight loss of poly(*m*- Me_3SiDPA) starts at 400 °C).

Comparison with PhP

In Table III, the polymerization behavior and polymer properties of *m*- Me_3SiPhP are compared with those of PhP.

i) In the polymerization of PhP by NbCl_5 and TaCl_5 , the molecular weight of polymer decreases after the monomer has been completely consumed. In contrast, no decrease in molecular weight occurred in the case of *m*- Me_3SiPhP . This is explained by an idea that the bulky trimethylsilyl group inhibits the attack of the main chain.

Table III
Comparison of Poly(*m*- Me_3SiPhP) with Poly(PhP)^a

	$\begin{array}{c} \text{+C=C+} \\ \quad \\ \text{Me} \quad \text{C}_6\text{H}_4 \quad \text{SiMe}_3 \end{array}$	$\begin{array}{c} \text{+C=C+} \\ \quad \\ \text{Me} \quad \text{C}_6\text{H}_5 \end{array}$
Polymer	no	yes
Degradn ^b		
$\bar{M}_w/10^3$	1000	1800
$T_0, ^\circ\text{C}^c$	310	280

a Data from ref. 6.

b Molecular weight decrease after the polymerization by NbCl_5 and TaCl_5 is completed.

c Temperature at which weight loss starts in air.

ii) The molecular weight of poly(*m*- Me_3SiPhP) reached 1×10^6 , which is slightly lower than that of poly(PhP). Thus, trimethylsilyl group at meta position of PhP does not affect very much the molecular weight of the polymer formed.

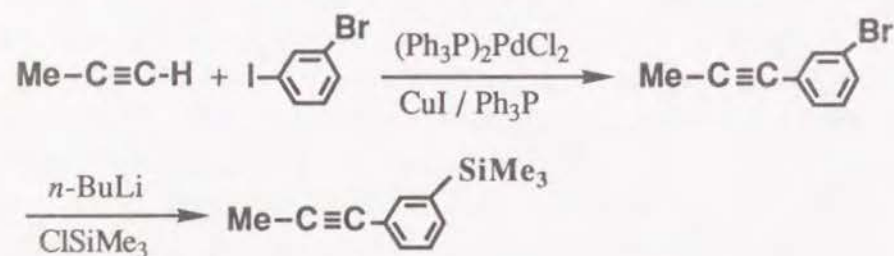
iii) Though poly(*m*- Me_3SiPhP)s obtained with NbCl_5 alone and TaCl_5 -cocatalyst systems were soluble in various organic solvents, the polymers formed with NbCl_5 -cocatalyst systems were insoluble. In contrast, poly(PhP) is soluble in many organic solvents irrespective of the kind of catalyst. This difference seems due to the lower flexibility of the more sterically crowded poly(*m*- Me_3SiPhP).

iv) The thermal stability of poly(*m*- Me_3SiPhP) did not greatly differ from that of poly(PhP). It is, however, noted that these polymers are thermally more stable than sterically less crowded polymers such as poly(2-alkynes).

Experimental

Materials

The monomer, *m*-Me₃SiPhP, was prepared according to the following scheme with reference to the literature method.¹¹



1-(*m*-Bromophenyl)-1-propyne (**1**): After flushed with dry nitrogen, a 500 mL flask was charged with triethylamine (150 mL), (Ph₃P)₂PdCl₂ (0.84 g, 1.2 mmol), CuI (1.4 g, 7.2 mmol), Ph₃P (1.3 g, 4.8 mmol), and *m*-bromiodobenzene (15.3 mL, 0.12 mol). Then, propyne (4.5 mL, 0.24 mol) was bubbled for 5 min into the mixture at 10 °C, and the mixture was stirred for 1 h at room temperature. The completion of the reaction was confirmed by gas chromatography (GC), triethylamine was evaporated. Diethyl ether (200 mL) was added, and insoluble salts were filtered off. The solution was washed with 5% hydrochloric acid and water. The organic phase was dried over anhydrous sodium sulfate overnight, and diethyl ether was evaporated. The product (**1**) was distilled at reduced pressure; bp 90 - 92 °C/3 mmHg, yield 60%, *d*²⁰ 1.384.

m-Me₃SiPhP: A 200 mL flask was flushed with dry nitrogen, and charged with a hexane solution of *n*-butyllithium (63 mL, 1.6 M, 0.10 mol). Part of the hexane (ca. 40 mL) was evaporated with an aspirator under magnetic stirring. After the flask was cooled at -20 °C, diethyl ether (30 mL; dried over sodium) was gradually added at the same temperature, a solution of **1** (14.1 mL, 0.10 mol) in diethyl ether (10 mL) was added

dropwise, and the reaction mixture was left for 30 min. At -20 °C trimethylchlorosilane (12.7 mL, 0.10 mol) was added dropwise and the mixture was allowed to stand at room temperature for 1 h. After the completion of the reaction was confirmed by GC, ice water (50 mL) was added. The product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate overnight. Diethyl ether was evaporated, and the product was distilled twice at reduced pressure from calcium hydride; bp 95 °C/3 mmHg, yield 45%, *d*²⁰ 0.899.

Transition-metal chlorides and organometallic cocatalysts were all commercially obtained, and used without further purification. Polymerization solvents were purified by the standard methods.

Procedure

Polymerization was carried out as described in Chapter 1. The molecular weights of polymers were determined by gel permeation chromatography (GPC) with use of a polystyrene calibration. IR and UV-visible spectra were recorded with Shimadzu FTIR-8100 and Shimadzu UV 190 spectrophotometers, respectively. TGA was conducted with a Shimadzu 20B thermal analyzer (in air, heating rate 10 °C/min).

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Chapter 4

Gas Permeability of Silicon-Containing Polyacetylenes

Abstract

The gas permeability of silicon-containing polyacetylenes produced in Chapters 1 - 3 and 5 - 7 was examined, and the results were compared with the data previously obtained. The P_{O_2} values of poly(diphenylacetylenes) having $SiMe_3$ group at para and meta position, which were provided in Chapter 1, were $1.1 \times 10^{-7} \text{ cm}^3(\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$ and 1.2×10^{-7} , respectively, being very high. The gas permeability of polymers having $SiMe_3$ group varied remarkably depending on the kind of substituents. Introduction of $SiMe_3$ group into hydrocarbon polyacetylenes enhanced gas permeability. If bulkier silyl group was introduced instead of $SiMe_3$ group, gas permeability of polymer decreased.

Introduction

Recently, gas-permeable membranes have been studied intensively.¹ Such membranes are expected to be applicable to oxygen enrichment of air, artificial lungs, contact lenses, and so on. Investigation on gas-permeable membranes includes development of new membrane materials, study of permeation mechanism, fabrication of membrane modules, etc. Among them, it is very important to create polymers which show high gas permeability and permselectivity.

Various substituted polyacetylenes have been newly synthesized, and their unique properties have been clarified.² One of the most salient features is high gas permeability. Though the gas permeability of substituted polyacetylenes depends on the kind of pendant groups, it is generally high. This is noteworthy particularly because these polymers are in the glass state at room temperature. Especially silicon-containing polyacetylenes tend to show high gas permeability. For instance, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] shows the highest gas permeability among synthetic polymers.³ The oxygen permeability coefficient (P_{O_2}) of the polymer is ca. 4×10^{-7} $\text{cm}^3(\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$, which is 10 times that of poly(dimethylsiloxane). Its permeability mechanism⁴ and applications⁵ have recently been studied extensively.

In Chapters 1 - 3 and 5 - 7 in this thesis, the author described the synthesis of various silicon-containing polyacetylenes. From the viewpoints stated above, it is of great interest to examine the gas permeability of these polymers. Further, studies on the effect of silyl group on gas permeability will help to clarify the relationship between polymer structure and gas permeability. In this chapter, the gas permeability of silicon-containing polyacetylenes obtained in other chapters is described and the results are compared with the data previously obtained. It has been found that the polymers synthesized in

Chapter 1 show very high gas permeabilities reaching ca. 1/4 those of poly(TMSP).

Results and Discussion

Silicon-containing Poly(diphenylacetylenes)

The P_{O_2} values were calculated from the increase of pressure in a downstream side when the permeate gas filled at about 1 atom in an upstream side. Figure 1 illustrates the time dependence of O_2 pressure in a downstream side of poly(diphenylacetylenes) having SiMe_3 group at para position [poly(*para*-1)]. The permeation rate was independent of the pressure of downstream side in the steady state. From the slope of this line, the P_{O_2} value of poly(*para*-1) can be calculated.⁶

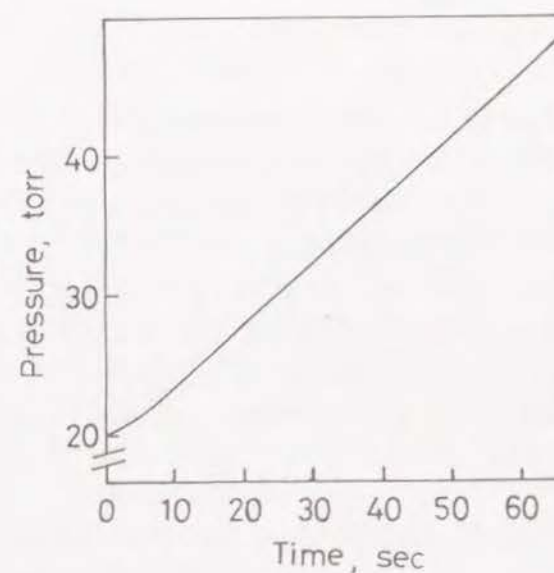


Figure 1. Time course of the pressure in a downstream side of poly(*para*-1).

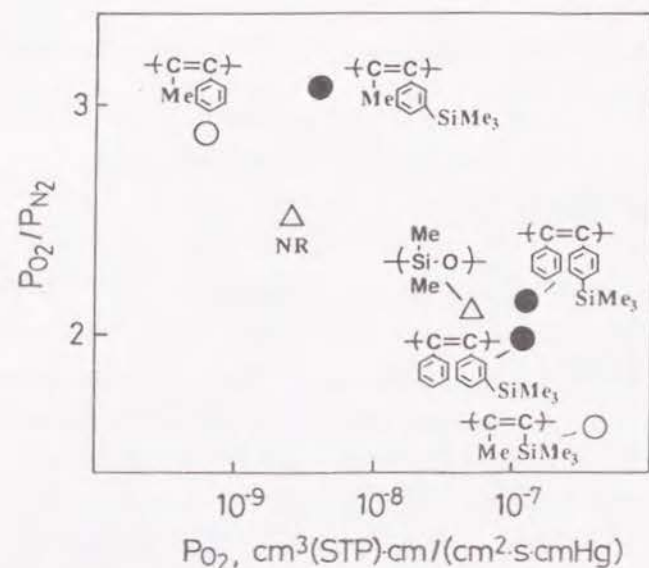


Figure 2. P_{O_2} vs P_{O_2}/P_{N_2} of disubstituted acetylene polymers. (25 °C)

The P_{O_2} values of poly(diphenylacetylenes) having $SiMe_3$ group, poly(*para*-1) and poly(*meta*-1), which were obtained in Chapter 1, were $1.1 \times 10^{-7} \text{ cm}^3(\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$ (units will be omitted below for simplicity) and 1.2×10^{-7} , respectively (Figure 2). These values are about 1/4 that of poly(TMSP) which is the most gas-permeable among all the existing polymers, and correspond to about twice that of poly(dimethylsiloxane), which is popular as the most gas-permeable rubbery polymer. Thus poly(*para*-1) and poly(*meta*-1) proved to be highly gas-permeable. Their separation factors between oxygen and nitrogen were about 2.0, being larger than that of poly(TMSP).

Table I shows the permeability coefficients (P) of silicon-containing poly(diphenylacetylenes) and poly(TMSP) to six gases. No large differences in P are seen between poly(*para*-1) and

Table I
Gas Permeability of Silicon-Containing Polyacetylenes

Polymer	P^a						$\frac{P_{O_2}}{P_{N_2}}$
	He	H ₂	O ₂	N ₂	CO ₂	CH ₄	
poly(<i>para</i> -1)	1000	2100	1100	520	4700	1500	2.1
poly(<i>meta</i> -1)	1000	2100	1200	610	4000	1500	2.0
poly(TMSP)	3300	7800	4500	2700	29000	6500	1.7

a Gas permeability coefficients at 25 °C in the units of $1 \times 10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$ (= barrer).

poly(*meta*-1) for all the gases, which indicates that the position of $SiMe_3$ group hardly affect their gas permeability. Further, the permeability of these polymers were 1/3 - 1/6 the values of poly(TMSP) irrespective of the kind of gases. Thus, it can be said that through all these polymers gases permeate by the same mechanism which is called "dual-mode sorption model".^{4b}

Figure 3 plots the P_{O_2} vs P_{O_2}/P_{N_2} of poly(diphenylacetylenes) with bulky substituents on silicon atom which were obtained in Chapter 2. The P_{O_2} values of these polymers are in the order of 10^{-9} - 10^{-8} , being 1/10 - 1/100 those of poly(*para*-1) and poly(*meta*-1). P_{O_2}/P_{N_2} are ca. 2.5 being larger than those of poly(*para*-1) and poly(*meta*-1). Interestingly, introduction of bulky substituents onto silicon atom reduces the gas permeability of these polymers.

Figure 4 shows the permeability coefficients of poly(diphenylacetylenes) carrying *m*- $SiEt_3$ or *m*- $SiMe_2iPr$ group to six gases along with those of other polymers. It is clear that the gas permeability of substituted polyacetylenes greatly

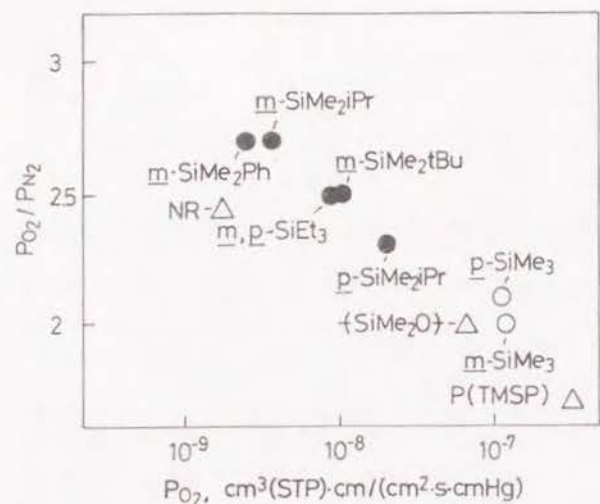


Figure 3. P_{O_2} vs P_{O_2}/P_{N_2} of silicon-containing poly(diphenylacetylenes). (25 °C)

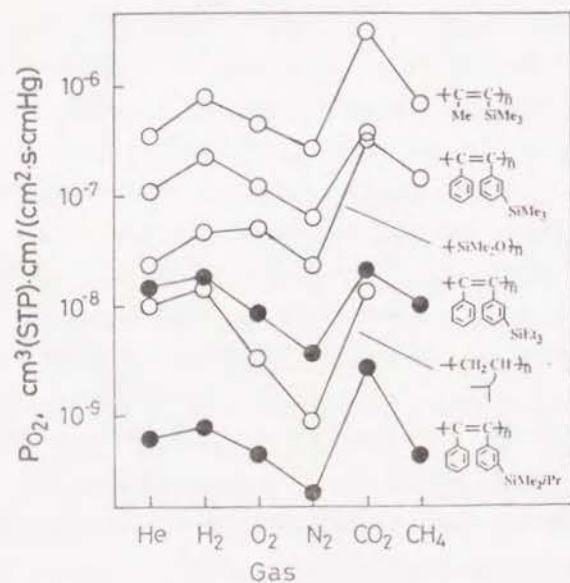


Figure 4. Gas permeability coefficients of polymers. (25 °C)

depends on the kind of substituents. However, their tendencies on the permeability to various gases resemble one another irrespective of the substituents.

Gas Permeability of Various Silicon-containing Polyacetylenes

Poly[1-*m*-(trimethylsilyl)phenyl]-1-propyne [poly(2)] obtained in Chapter 3 is regarded as the polymer that has methyl group instead of phenyl group in poly(*meta*-1). The P_{O_2} value of poly(2) was about 1/30 that of poly(*meta*-1), being small (Figure 2). Interestingly, which of phenyl and methyl is a pendant generates a great difference in the gas permeability. The P_{O_2} value of poly(1-phenyl-1-propyne) is smaller than that of poly(2). This manifests that introduction of $SiMe_3$ group

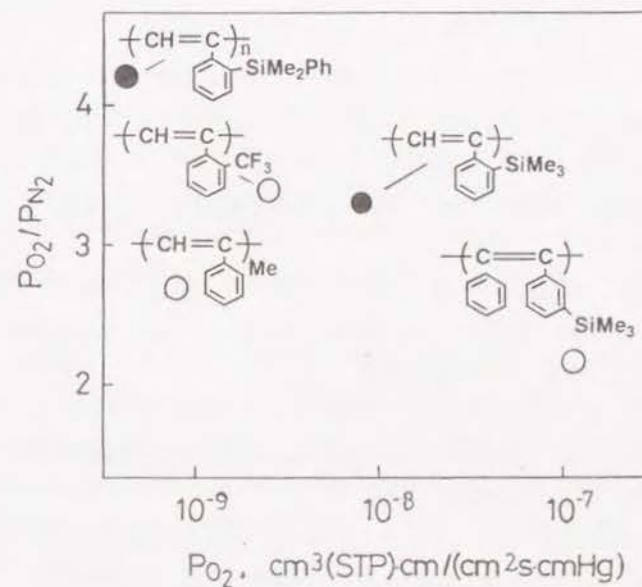


Figure 5. P_{O_2} vs P_{O_2}/P_{N_2} of substituted polyacetylenes. (25 °C)

increases gas permeability. The P_{O_2}/P_{N_2} of poly(2) was ca. 3, being relatively large.

The gas permeability of ortho-substituted poly(phenylacetylenes), which belong to monosubstituted acetylene polymers, was studied (Figure 5). The P_{O_2} value of poly[*o*-(trimethylsilyl)phenylacetylene] [poly(3)] obtained in Chapter 5 was 8×10^{-9} . Though smaller than those of poly(*para*-1) and poly(*meta*-1), this value is the highest among the ortho-substituted poly(phenylacetylenes) synthesized so far. As seen in Figure 5, the gas permeability of an ortho-substituted poly(phenylacetylene) tends to increase with increasing bulkiness of its ortho substituent. On the other hand, the P_{O_2} value of poly[*o*-(dimethylphenylsilyl)phenylacetylene] [poly(4)] obtained in Chapter 6 was 4×10^{-10} , being much smaller than that of poly(3). This result does not necessarily correspond to the tendency described above. The P_{O_2}/P_{N_2} values of poly(3) and poly(4) were as large as 3.3 and 4.0, respectively.

P_{O_2} values of poly[3-(dimethyl-*n*-hexylsilyl)-1-hexyne] and poly[3-(dimethylphenylsilyl)-1-hexyne] obtained in Chapter 7 were 1.9×10^{-9} and 9.5×10^{-10} , respectively. These values are slightly smaller than that of poly[3-(trimethylsilyl)-1-octyne] ($P_{O_2} = 2.7 \times 10^{-9}$).

Table II summarizes P_{O_2} values of silicon-containing polyacetylenes. The following characteristics are observed in gas permeability of these polymers.

- i) Among polyacetylenes having SiMe_3 group, the gas permeability of polymer varies remarkably depending on the kind of its substituents.
- ii) Gas permeability of polyacetylenes increases with increasing bulkiness of substituent. This is probably because polyacetylenes carrying bulky substituent have large space between main chains due to their bulkiness of substituent and/or the stiffness of their main chain.

Table II
Oxygen Permeability Coefficient (P_{O_2}) of Silicon-Containing Polyacetylenes^a

X	$\begin{array}{c} \text{-(C=C)-} \\ \\ \text{Me} \quad \text{X} \end{array}$	$\begin{array}{c} \text{-(C=C)-} \\ \\ \text{Me} \quad \text{C}_6\text{H}_4 \\ \\ \text{X} \end{array}$	$\begin{array}{c} \text{-(C=C)-} \\ \\ \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \\ \\ \text{X} \end{array}$	$\begin{array}{c} \text{-(C=C)-} \\ \\ \text{H} \quad \text{C}_6\text{H}_4 \\ \\ \text{X} \end{array}$	$\begin{array}{c} \text{-(C=C)-} \\ \\ \text{H} \quad \text{CH-}n\text{R} \\ \\ \text{X} \end{array}$
SiMe_3	4×10^{-7}	4×10^{-9}	1×10^{-7}	8×10^{-9}	3×10^{-9}
SiMe_2nhex	2×10^{-9}				2×10^{-9}
SiMe_2Ph			2×10^{-9}	4×10^{-10}	1×10^{-9}

a Measured at 25 °C in the units of $\text{cm}^3(\text{STP}) \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$.

- iii) Introduction of SiMe_3 group into hydrocarbon polyacetylenes enhances gas permeability. Bulkiness and high mobility of SiMe_3 group can be considered for the reason.
- iv) Bulky substituents on silicon atom reduce gas permeability. The reason is not clear at present, but it can be considered that by such substituents, space between main chains is filled up and/or mobility of silyl group is reduced.

In this chapter, gas permeability of various silicon-containing acetylene polymers was examined, and revealed that poly(*para*-1) and poly(*meta*-1) show very high gas permeability. Further, some relationships between polymer structure and gas permeability were discovered. The author hopes that the relationship will be clarified more and more through investigation of the gas permeability of variously substituted polyacetylenes.

Experimental

Membrane Preparation

All the membranes were obtained by casting toluene solutions of polymers (3 - 5%). The solutions were cast into a flat-bottomed Petri dish, and the solvent was removed slowly by keeping the membranes at room temperature over a few days to give homogeneous membranes with uniform thickness (~50 μm). Membrane thicknesses were measured with a micrometer.

Measurement of Gas Permeability

The gas permeation was observed on a K-315-N gas permeability apparatus (Rikaseiki Co., Japan) equipped with a MKS Baratron detector. High purity gases (He, H₂, O₂, N₂, CO₂, and CH₄; purities all >99.5%; Teisan K. K., Japan) were used. The measuring temperature was ~25 °C. The downstream side of the membrane (7.0 cm³ disc) was evacuated to about 0.1 mmHg, the upstream side was filled with a gas at about 1 atm, and the increase of pressure in a downstream receiving vessel was measured. The P values were calculated from the slopes of time-pressure curves in the steady state where Fick's law held.

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Part II

**Polymerization and
Polymer Properties of
Silicon-Containing Monosubstituted
Acetylenes**

Chapter 5

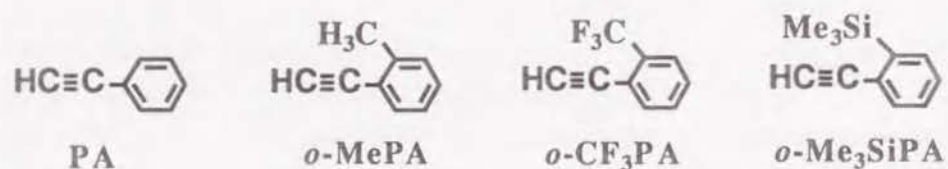
Synthesis and Characterization of Poly[[*o*-(trimethylsilyl)phenyl]acetylene]

Abstract

[*o*-(Trimethylsilyl)phenyl]acetylene quantitatively polymerized in the presence of $\text{WCl}_6\text{-Et}_3\text{SiH}$ (1:1), $\text{W}(\text{CO})_6\text{-hv}$, and $\text{MoCl}_5\text{-Et}_3\text{SiH}$ (1:1) catalysts in toluene or CCl_4 at 30 °C to give a new polymer having weight-average molecular weight over 1×10^6 . Effects of organometallic cocatalysts, solvents, and temperature on the polymerization were studied. The polymer was in the form of a dark purple solid (λ_{max} 542 nm), completely dissolved in common organic solvents such as toluene and CHCl_3 , formed a self-standing film by solution casting, and did not lose weight below 280 °C in air, being fairly thermally stable.

Introduction

It has recently been found that not only phenylacetylene (PA) but also ortho-substituted PA's such as (*o*-methylphenyl)acetylene¹ (*o*-MePA) and [*o*-(trifluoromethyl)phenyl]acetylene² (*o*-CF₃PA) polymerize with W and Mo catalysts. Quite interestingly, poly[*o*-(methylphenyl)acetylene] [poly(*o*-MePA)] and poly[*o*-(trifluoromethyl)phenyl]acetylene] [poly(*o*-CF₃PA)] obtained have higher molecular weights than that of poly(phenylacetylene) [poly(PA)] irrespective of the steric hindrance due to the ortho substituents. Eventually poly(*o*-CF₃PA) provides a strong film by solution casting, whereas poly(PA) is too brittle to form a free-standing film.



So far, a number of substituted polyacetylenes have been synthesized by using transition-metal catalysts.³ Among these polymers are Si-containing polyacetylenes, some of which exhibit unique properties not seen in hydrocarbon polyacetylenes. For example, poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] shows extremely high gas permeability⁴ and ethanol permselectivity in the ethanol/water pervaporation.⁵

It can be considered that PA with bulky ortho-substituent produces high polymer. Further, it is important to know electronic effect of ortho-substituent on polymerization behavior by introducing electron-donating group. [*o*-(Trimethylsilyl)phenyl]acetylene (*o*-Me₃SiPA) is an ortho-substituted PA which has bulky and electron-donating group at ortho position and is a Si-containing acetylene as well. It is of interest to study the polymerizability of this monomer, the molecular weight of

poly[*o*-(trimethylsilyl)phenyl]acetylene] [poly(*o*-Me₃SiPA)], and properties of this novel polymer. In this chapter, the author reports on the polymerization of *o*-Me₃SiPA and on the characterization of poly(*o*-Me₃SiPA).

Results and Discussion

Polymerization by Various Catalysts

It has been found that mixtures of WCl₆ or MoCl₅ (main catalyst) and Ph₄Sn (organometallic cocatalyst) are effective in the polymerization of substituted acetylenes.^{3b} As seen in Table I, WCl₆-Ph₄Sn and MoCl₅-Ph₄Sn gave polymers in ca. 80% yields. The W(CO)₆-hv catalyst polymerized *o*-Me₃SiPA quantitatively, whereas the Mo(CO)₆ counterpart was ineffective.

The \bar{M}_w values of the polymers obtained with WCl₆-Ph₄Sn, W(CO)₆-hv, and MoCl₅-Ph₄Sn exceeded one million according to gel permeation chromatography (GPC; a polystyrene calibration used). It is especially noteworthy that the polymer formed with the W(CO)₆-hv catalyst had a very high molecular weight reaching 3×10⁶. The high molecular weight is supported by its large intrinsic viscosity ([η]).

In the case of group 5 transition-metal (Nb and Ta) chlorides as catalysts, the monomer was totally consumed, but methanol-insoluble polymers were formed only in small amounts. The methanol-soluble main products showed a single peak around the molecular weight of 523 corresponding to a trimer in GPC. Further, their mass spectrum showed virtually selectively three peaks of similar magnitude at 539, 540 and 541; these peaks are assignable to the NH₄⁺ adduct (541) of the trimer and to those in which one or two hydrogens have been eliminated. Therefore, the oligomeric products are thought to be the cyclotrimer [1,2,4- and 1,3,5-[tris(trimethylsilyl)phenyl]benzenes].

Table I
Polymerization of *o*-Me₃SiPA by Various Catalysts^a

Catalyst	Monomer		Polymer ^b	
	convn, %	yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
WCl ₆ -Ph ₄ Sn (1:1)	100	86	1800 ^g	780
MoCl ₅ -Ph ₄ Sn (1:1)	100	76	1600	740
W(CO) ₆ -hv ^d	100	100	3400 ^h	1200
Mo(CO) ₆ -hv ^d	6	0		
NbCl ₅ ^e	100	15	1500	1100
TaCl ₅ ^e	100	3		
[(COD)RhCl] ₂ ^f	0	0		
(Ph ₃ P) ₂ PdCl ₂	0	0		
Fe(acac) ₃ -Et ₃ Al (1:3) ^f	4	0		
Ti(O- <i>n</i> -Bu) ₄ -Et ₃ Al (1:4)	3	0		

a Polymerized in toluene at 30 °C for 24 h; [M]₀ = 1.0 M, [transition metal] = 10 mM.

b Methanol-insoluble product.

c Determined by GPC.

d Polymerized in CCl₄.

e Polymerized at 80 °C.

f Abbreviations: COD, 1,5-cyclooctadiene; acac, acetylacetonate.

g $[\eta] = 1.57$ dL/g (measured in toluene at 30 °C).

h $[\eta] = 2.34$ dL/g.

None of the group 8 transition-metal (Rh, Pd) catalysts and Ziegler-type catalysts produced any polymer from *o*-Me₃SiPA. The Rh and Fe catalysts are known to polymerize PA in high yield. Hence, it is inferred that, unlike W and Mo catalysts, these catalysts are very sensitive to the steric hindrance of the monomer. Consequently, the polymerization by W and Mo catalysts was examined in detail.

Polymerization by W Catalysts

Table II details the effects of organometallic cocatalysts involving group 4 and 5 main-group metals in the polymerization by WCl₆. When Et₃SiH and some other cocatalysts were used, poly(*o*-Me₃SiPA) was obtained quantitatively. In the case of Ph₄Sn and Ph₃SiH, the polymer yields were lower than 100% for some reason. The polymer yield was high enough even without a cocatalyst. This is consistent with the general tendency that addition of a cocatalyst mainly affects the polymerization rate for monosubstituted acetylenes, whereas a cocatalyst is usually indispensable for disubstituted acetylenes to polymerize.^{3b} No large difference in the molecular weight of polymer was observed with changing the kind of cocatalyst. Et₃SiH was adopted as a cocatalyst in the following experiments.

Table II
Cocatalyst Effects on the Polymerization of *o*-Me₃SiPA by WCl₆^a

no.	Cocatalyst	Monomer		Polymer ^b	
		convn, %	yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
1	none	100	91	1500	670
2	Et ₃ SiH	100	100	1600 ^d	670
3	Ph ₃ SiH	100	91	1500	720
4	<i>n</i> -Bu ₄ Sn	100	100	1500	640
5	Ph ₄ Sn	100	86	1800	780
6	Ph ₃ Sb	100	100	1400	510
7	Ph ₃ Bi	100	100	1500	710

a Polymerized in toluene at 30 °C for 24 h; [M]₀ = 1.0 M, [WCl₆] = [cocat] = 10 mM.

b Methanol-insoluble product.

c Determined by GPC.

d $[\eta] = 1.57$ dL/g.

The WCl_6 - Et_3SiH catalyzed polymerization of the present monomer proceeded practically quantitatively in hydrocarbons, halogenated hydrocarbons, and some oxygen-containing solvents (Table III). In contrast, nitrogen-containing compounds do not appear useful as polymerization solvents. The molecular weight of polymer appreciably varied with the kind of polymerization solvents; e.g., the \bar{M}_w in $(CH_2Cl)_2$ reached 3.7×10^6 . It is, however, not clear at present how solvents affect the polymer molecular weight.

Figure 1a illustrates the effect of temperature on the polymerization by WCl_6 - Et_3SiH in toluene. When carried out at 0 °C or above, the polymerization conversion reaches 100%. The \bar{M}_w of polymer shows a maximum around 30 °C and clearly decreases with increasing temperature. Thus about 30 °C seems

Table III

Solvent Effects on the Polymerization of *o*- Me_3SiPA by WCl_6 - Et_3SiH^a

Solvent	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3^c$	$\bar{M}_n/10^3^c$
toluene	100	100	1600	670
cyclohexane	100	100	3200	1600
CCl_4	100	100	2100	680
$(CH_2Cl)_2$	100	96	3700 ^d	1900
PhOMe	100	96	1600	670
PhCOOMe	100	83	1000	390
PhCOMe	3	0		
PhCN	22	8	37	18
PhNO ₂	4	0		

a Polymerized at 30 °C for 24 h; $[M]_0 = 1.0$ M, $[WCl_6] = [Et_3SiH] = 10$ mM.

b Methanol-insoluble product.

c Determined by GPC.

d $[\eta] = 2.39$ dL/g.

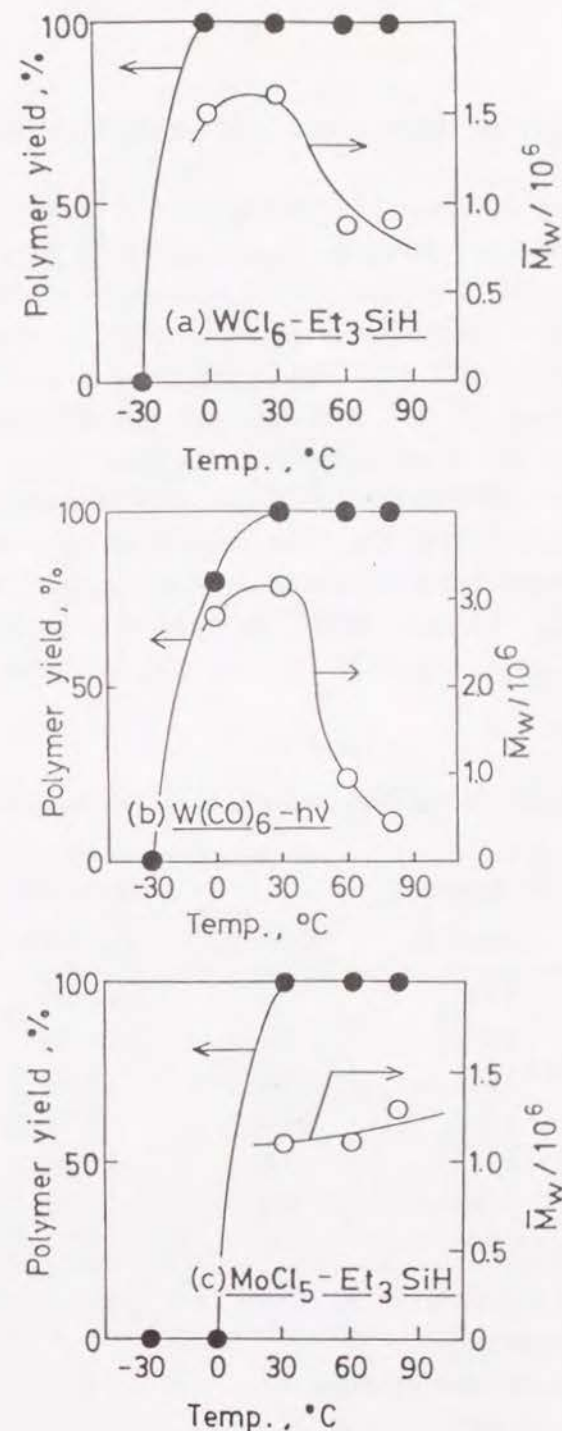


Figure 1. Temperature dependence on the polymerization of *o*- Me_3SiPA (in toluene (a,c) or CCl_4 (b), 24 h; $[M]_0 = 1.0$ M, $[cat] = [Et_3SiH] = 10$ mM).

favorable to keep both yield and molecular weight of the polymer high.

The polymerization by WCl_6-Et_3SiH is completed in 1 h under the conditions shown in Figure 2a, being fairly rapid. The \bar{M}_w of the polymer increases with polymer yield, which suggests the presence of a long-lived propagating species. The high \bar{M}_w of 1.6×10^6 achieved at 1 h is maintained even if the polymerization is continued over 24 h. This indicates that polymer degradation does not occur under the polymerization conditions.

The effect of temperature on the polymerization by $W(CO)_6-h\nu$ is depicted in Figure 1b. This catalyst provides the polymer at 30 °C and above, being somewhat less active than WCl_6-Et_3SiH . The high \bar{M}_w around 3×10^6 is achieved at relatively low temperatures such as 0 and 30 °C. As seen in Figure 2b, the

Table IV

Cocatalyst Effects on the Polymerization of *o*-Me₃SiPA by MoCl₅^a

Cocatalyst	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
none	100	86	1700	780
Et ₃ SiH	100	100	1100 ^d	470
Ph ₃ SiH	100	100	2600	1200
<i>n</i> -Bu ₄ Sn	100	100	570	220
Ph ₄ Sn	100	76	1600	740
Ph ₃ Sb	100	85	840	340
Ph ₃ Bi	28	0		

^a Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 1.0$ M, $[MoCl_5] = [cocat] = 10$ mM.

^b Methanol-insoluble product.

^c Determined by GPC.

^d $[\eta] = 1.16$ dL/g.

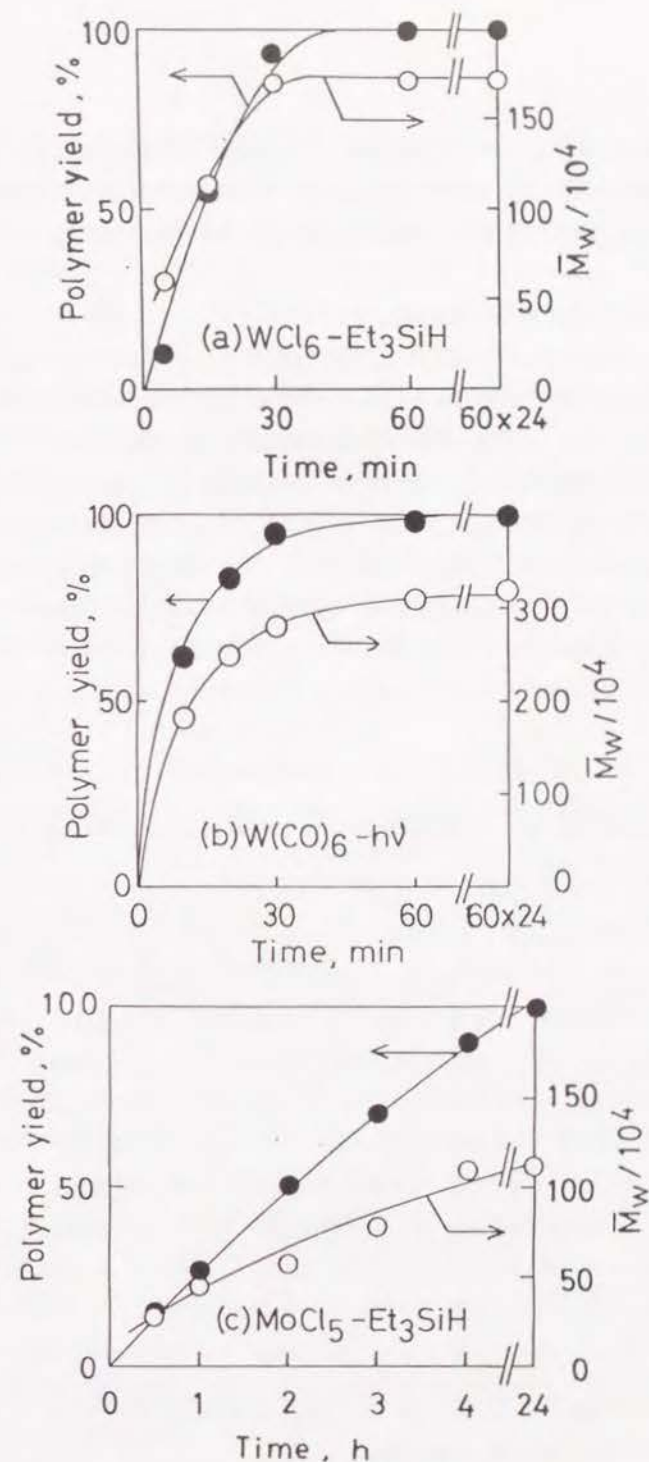


Figure 2. Time courses of the polymerization of *o*-Me₃SiPA [in toluene (a, c) or CCl₄ (b); 30 °C, $[M]_0 = 1.0$ M, $[cat] = [Et_3SiH] = 10$ mM].

polymerization by $W(CO)_6$ -hv reaches 100% in 1 h under the standard conditions. The \bar{M}_w of the polymer increases with polymer yield also in this case to reach 3×10^6 finally.

Polymerization by Mo Catalysts

As seen in Table IV, the polymer yield in the polymerization by $MoCl_5$ was affected by the kind of cocatalysts. For example, the yield was quantitative in the case of Et_3SiH , being higher than that without a cocatalyst. In contrast, Ph_3Bi exhibited an inhibiting effect. The \bar{M}_w of the polymer also varied to some extent with the kind of cocatalysts. The $MoCl_5$ - Et_3SiH catalyst was employed in the following experiments for the sake of comparison with the WCl_6 - Et_3SiH catalyst.

Solvent effects on the polymerization by $MoCl_5$ - Et_3SiH

Table V

Solvent Effects on the Polymerization of *o*- Me_3SiPA by $MoCl_5$ - Et_3SiH ^a

Solvent	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
toluene	100	100	1100	470
cyclohexane	80	76	370	49
CCl_4	100	100	820	190
$(CH_2Cl)_2$	100	87	2300 ^d	1100
PhOMe	100	93	1300	460
PhCOOMe	100	87	680	290
PhCOMe	15	0		
PhCN	10	0		
PhNO ₂	8	0		

a Polymerized at 30 °C for 24 h; $[M]_0 = 1.0$ M, $[MoCl_5] = [Et_3SiH] = 10$ mM.

b Methanol-insoluble product.

c Determined by GPC.

d $[\eta] = 1.69$ dL/g.

resembled those found in the polymerization by WCl_6 - Et_3SiH (see Tables III and V). Namely, high polymer yields were attained in hydrocarbons, halogenated hydrocarbons, and some oxygen-containing solvents.

Regarding the polymerization temperature, the polymer yield with $MoCl_5$ - Et_3SiH reaches 100% at 30 °C and above (Figure 1c). The \bar{M}_w of the polymer hardly changes in the range 30 - 90 °C. The polymerization by $MoCl_5$ - Et_3SiH at 30 °C is completed in ca. 4 h. The \bar{M}_w of the polymer increases virtually in proportion to polymer yield to reach 1.1×10^6 at 100% yield (Figure 2c). Comparison of Figures 1a and 2a with Figures 1c and 2c leads to the conclusion that WCl_6 - Et_3SiH is a more active catalyst for the present monomer than $MoCl_5$ - Et_3SiH is.

Comparison of Polymerization of PA's

PA polymerizes in high yield with W catalysts but does not polymerize in as high a yield with Mo catalysts (yields are lower than 50% even under optimal conditions).^{3b} The polymerization behavior of 1-hexyne is similar. In contrast, *o*- Me_3SiPA , *o*- CF_3PA , and *tert*-butylacetylene polymerize quantitatively with both W and Mo catalysts. Though the reason is not clear, it is of interest that these sterically crowded monosubstituted acetylenes achieve high yields of the polymer with Mo catalysts.

Not only *o*- CF_3PA but also *o*- Me_3SiPA give a polymer whose \bar{M}_w exceeded one million. The \bar{M}_w of poly(PA) is no more than 2×10^5 at the highest and that of poly(*o*- $MePA$) is in between. Thus the bulkiness of the substituent in an acetylenic monomer is a very important factor in determining the molecular weight of the polymer formed. The fact that both *o*- Me_3SiPA and *o*- CF_3PA can give high molecular weight polymers implies that the electronic effect of substituent is not a substantial factor for the high molecular weight.

In order to gain knowledge on the relative reactivity of monomers, copolymerizations of *o*- Me_3SiPA with PA and *o*- CF_3PA

were studied in toluene at 30 °C ($[M_1]_0 = [M_2]_0 = 0.50$ M; $[WCl_6] = 10$ mM). The relative reactivities of PA, *o*-Me₃SiPA, and *o*-CF₃PA, which were determined from their relative initial polymerization rates, were 6.2, 1.0, and 0.50, respectively. Thus, PA is most reactive among these monomers, while *o*-Me₃SiPA and *o*-CF₃PA are close to each other, irrespective of the opposite electronic effects of the ortho substituents. This fact indicates that the steric effects of the substituents affect greatly to relative monomer reactivity.

Polymer Structure

The structure of poly(*o*-Me₃SiPA) did not depend on the polymerization conditions. Hence, the data of the polymer sample from Table II, number 2 will be described.

The combustion analytical data of poly(*o*-Me₃SiPA) are as follows. Calcd for (C₁₁H₁₄Si)_n: C, 75.79; H, 8.09; Si, 16.12. Found: C, 75.78; H, 8.18; Si, 16.81. Thus the polymer possesses just the elemental composition for the polymerization product.

While strong \equiv C-H (3290 cm⁻¹) and weak C \equiv C (2100 cm⁻¹) absorptions are observed in the IR spectrum of the monomer, these bands disappear in the polymer (Figure 3a). Strong absorptions characteristic of the SiC-H and Si-C bonds are seen in both the monomer and the polymer.

In the ¹H NMR spectrum of poly(*o*-Me₃SiPA) appears a broad signal due to the olefinic and aromatic protons (δ 8.0 - 4.5) and a sharp one due to the methyl protons (δ 0.0); the acetylenic proton in the monomer (δ 3.2) and any other unexpected protons are not seen (Figure 3b). The ¹³C NMR spectrum of polymer exhibits signals of sp² carbons in the monomer: δ 85.9 and 80.9. The ¹³C NMR data corresponds well to ¹H NMR data (Figure 3c).

The IR and NMR spectra above support the idea that the polymer possesses alternating double bonds in the main chain as shown in Figure 3. The polymer should have the regular head-to-tail structure because the head-to-head structure seems

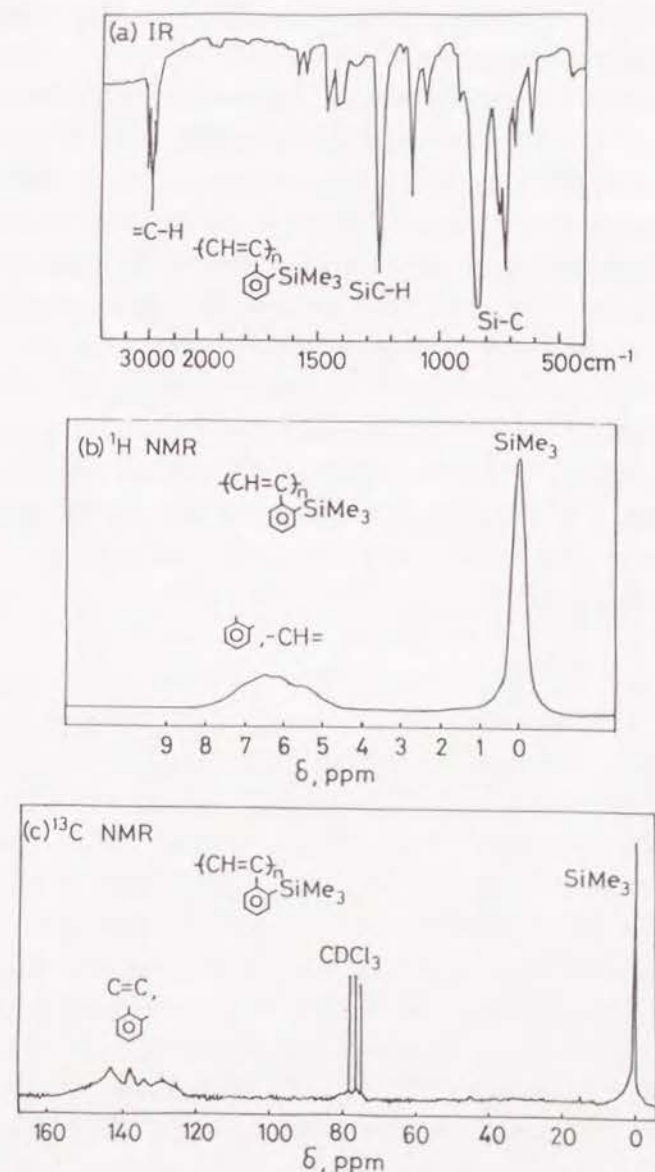


Figure 3. IR, ¹H NMR, and ¹³C NMR spectra of poly(*o*-Me₃SiPA) (sample from Table II, no. 2; IR, KBr pellet; NMR, CDCl₃ solution).

difficult to form. The geometric structure of the main chain, however, remains unsolved.

In general, the UV-visible spectrum of a substituted polyacetylenes gives some information about the conformation. Quite interestingly, poly(*o*-Me₃SiPA) shows a fairly large absorption maximum (ϵ_{\max} 6400 M⁻¹·cm⁻¹) in a very long wavelength region (λ_{\max} 542 nm) (see Figure 4). The absorption extends up to ca. 700 nm. The absorption maximum of poly(*o*-CF₃PA) is at 458 nm, being relatively near that of poly(*o*-Me₃SiPA), while that of poly(PA) is below 300 nm.^{2b} In contrast, most disubstituted acetylene polymers exhibit absorptions only in the UV region.^{3b} The reason why ortho substituents in poly(PA) cause a red shift is, however, not clear at present.

The X-ray diffraction data of poly(*o*-Me₃SiPA) obtained

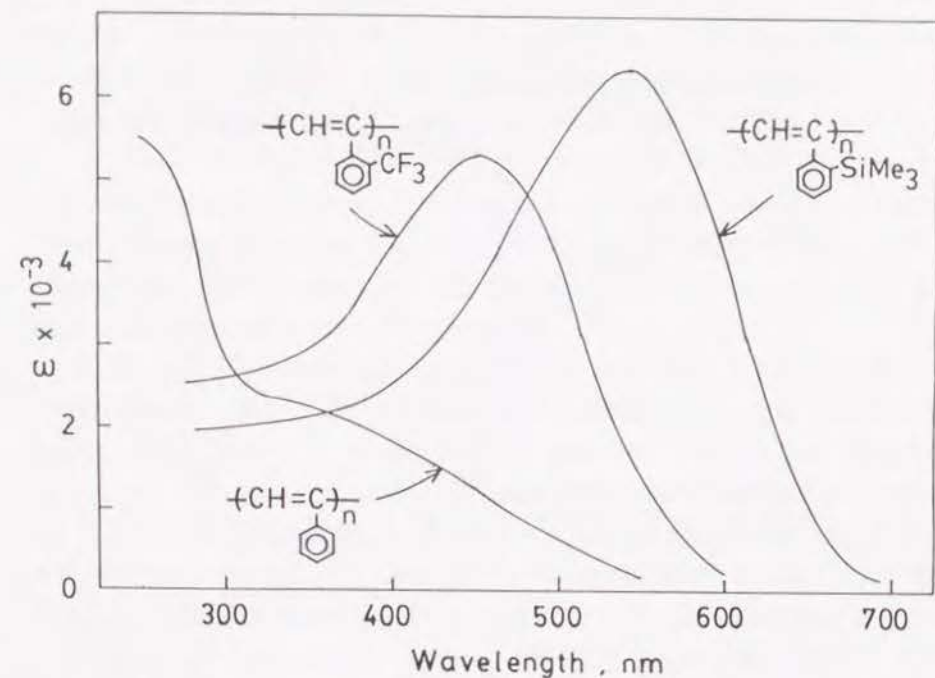


Figure 4. UV-visible spectra of poly(*o*-Me₃SiPA) and related polymers [poly(*o*-Me₃SiPA) sample from Table II, no. 2, measured in tetrahydrofuran; other data from ref 3b].

with Cu K α radiation is as follows [2θ ($\Delta 2\theta/2\theta$)]: 7.6° (0.358); 15.1° (0.202). As seen from the ratios of half-height width to diffraction angle ($\Delta 2\theta/2\theta > 0.20$), the peaks are rather broad; this indicates that the present polymer is amorphous. The 2θ values are in a ratio of 1:2:3, being attributed to the first-, second-, and third-order diffractions, respectively, in the Bragg equation. The 2θ of 7.6 corresponds to the distance of 1.16 nm, suggesting the presence of a certain regular structure within a short range.

Polymer Properties

There were no discernable differences in the properties of poly(*o*-Me₃SiPA) with polymerization conditions. The following properties are of the polymer obtained with WCl₆-Et₃SiH (Table II, number 2).

Poly(*o*-Me₃SiPA) has the form of dark purple solid irrespective of the polymerization conditions. Poly(*o*-CF₃PA) is a dark brown solid, while poly(PA) is brown (W catalysts) or yellow (Mo catalysts). Therefore, it can be said that the ortho-substituted poly(PA)s are more deeply colored than poly(PA).

Poly(*o*-Me₃SiPA) dissolved in benzene, toluene, cyclohexane, CCl₄, CHCl₃, CH₂Cl₂, tetrahydrofuran, and triethylamine, while it was partly insoluble in chlorobenzene, anisole, (CH₂Cl)₂, and diethyl ether. Its nonsolvents include hexane, heptane, 1,4-dioxane, acetone, acetophenone, ethyl acetate, methyl benzoate, nitrobenzene, N,N-dimethylformamide, and acetonitrile. These solubility properties resemble those of poly(PA) and poly(*o*-CF₃PA).

A logarithmic plot of the intrinsic viscosity vs \bar{M}_w of poly(*o*-Me₃SiPA) is shown in Figure 5. The plot can be represented by a good linear relationship, leading to the following equation:

$$[\eta] = K\bar{M}_w^a \quad (K = 2.42 \times 10^{-5} \text{ dL/g}; a = 0.764)$$

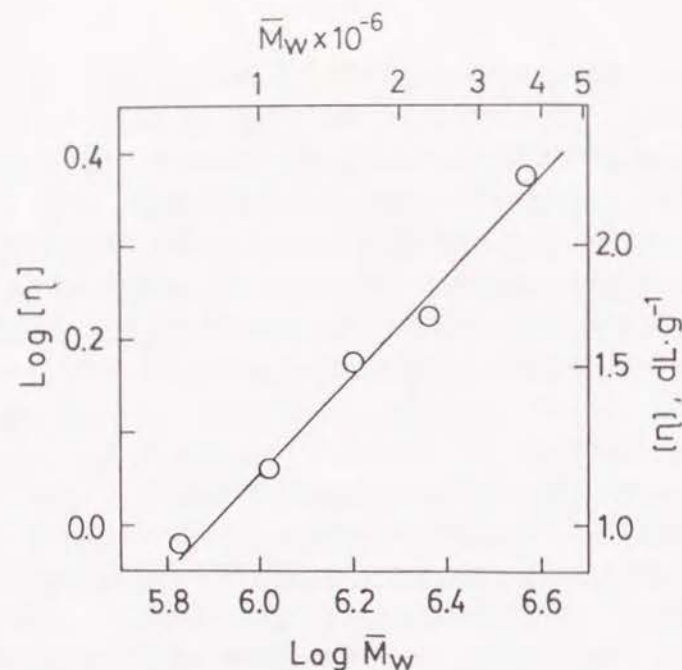


Figure 5. $[\eta]$ vs \bar{M}_w plot for poly(*o*-Me₃SiPA) (the samples with polydispersity ratio of around 2.5 were used; $[\eta]$ measured in toluene at 30 °C, and \bar{M}_w determined by GPC).

The exponent a is 0.76 being close to that of poly(*o*-CF₃PA) ($a = 0.59$).^{2a} These values are not so large as those for disubstituted acetylene polymers [e.g., poly(TMSP), $a = 1.04$; $(-\text{CCl}=\text{CPh}-)_n$, $a = 1.07$].^{3b} Apparently these monosubstituted acetylene polymers assume less expanded conformations in solution than do disubstituted acetylene polymers.

One can prepare a free-standing film by casting poly(*o*-Me₃SiPA) from toluene solution as in the case of poly(*o*-CF₃PA). In contrast, poly(PA) is too brittle to form a film, and the film from poly(*o*-MePA) is rather brittle. The film-forming properties of poly(*o*-Me₃SiPA) and poly(*o*-CF₃PA) are attributable to their high molecular weight. The author believes that the ease of preparation of poly(*o*-Me₃SiPA) film will greatly help find practical applications in the future.

Poly(*o*-Me₃SiPA) began to lose weight at about 280 °C in thermogravimetric analysis (TGA) in air (Figure 6). This

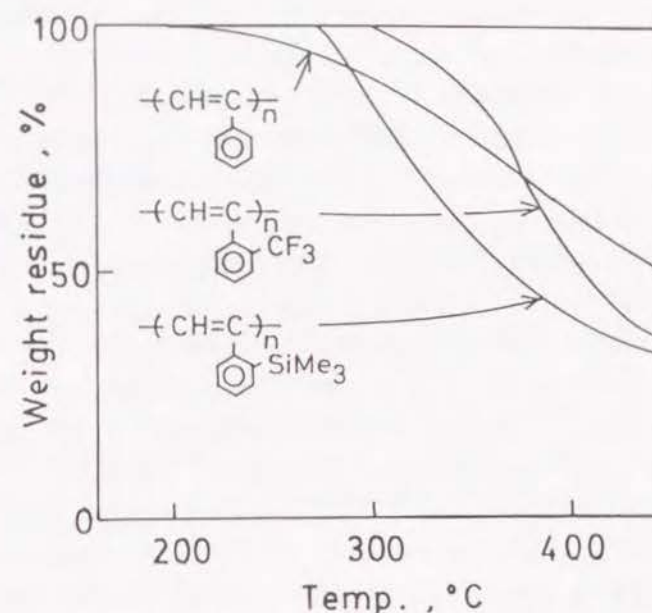


Figure 6. TGA curves of poly(*o*-Me₃SiPA) and related polymers [poly(*o*-Me₃SiPA) sample from Table II, no. 2; in air, heating rate 10 °C/min; other data from ref 2b].

temperature is higher than that for poly(PA) and is close to that for poly(*o*-CF₃PA). Further, the thermal stability of a polymer can be evaluated by the α value, which is the probability of main-chain scission on heat treatment in air at 120 °C for 20 h (defined as follows):⁷

$$\alpha = (1/\overline{DP}_n) - (1/\overline{DP}_{n,0})$$

Here \overline{DP}_n and $\overline{DP}_{n,0}$ are the number-average degrees of polymerization after and before the heat treatment. The α values are as follows: poly(*o*-Me₃SiPA), 2.0×10^{-4} ; poly(*o*-CF₃PA),^{2b} 2.5×10^{-3} ; poly(PA),⁷ 1.6×10^{-2} . These ortho-substituted poly(PA)s do not suffer any molecular weight decrease of oxidation even after they have been left in air at room temperature over a few months, while poly(PA) gradually undergoes a molecular weight decrease and is oxidized to some

extent. Thus, the ortho substituents are clearly effective in enhancing the stability of the poly(PA).

The tensile properties of poly(*o*-Me₃SiPA) at 25 °C are as follows:⁸ Young's modulus, 700 MPa; tensile strength, 23 MPa; elongation at break, 4.3%. Thus it is a hard and brittle polymer. The glass transition temperature observed by dynamic viscoelasticity is above 200 °C.⁸ The softening point was around 360 °C.

The electrical conductivity (σ) of poly(*o*-Me₃SiPA) at 25 °C was 4×10^{-15} S·cm⁻¹; i.e., it is a typical insulator like poly(PA) and poly(*o*-CF₃PA). This is in sharp contrast to the fact that polyacetylene is a semiconductor ($\sigma = 1 \times 10^{-5}$ S·cm⁻¹).⁹ The ESR spectrum in the solid state at 25 °C showed a singlet peak with a line width of 8.1 G and a *g* value of 2.0034; the unpaired-electron densities (25°C) of poly(PA) and poly(*o*-CF₃PA) (W catalyst) are 7.9×10^{16} and 6.1×10^{17} spin/g, respectively;^{2b,3b} that is, the value for poly(PA) is rather smaller. The high stability of these ortho-substituted poly(PA)s may be because it is difficult for oxygen to attack the main chain owing to the steric effect.

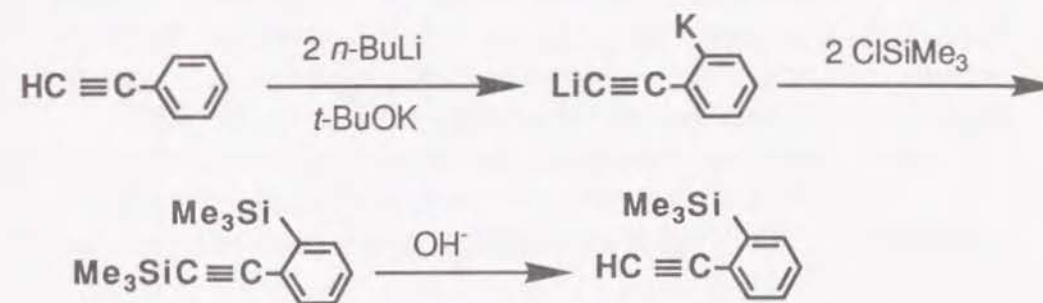
Concluding Remarks

Poly(*o*-Me₃SiPA), a new, high-molecular-weight polymer ($\bar{M}_w \sim 1 \times 10^6$), is produced with W and Mo catalysts. Since the monomer is readily prepared through one-pot reactions from PA, it can be said that the access to the present polymer is very easy. Basic properties of the polymer have been elucidated in this chapter. Among substituted polyacetylenes, this polymer has many salient features, such as deep color, good air-stability, and film-forming property. Photoconductivity,¹⁰ and electrochromism¹¹ of poly(*o*-Me₃SiPA) have recently been reported elsewhere. The author hopes that novel functions will be developed further with use of the present polymer.

Experimental

Materials

The monomer was prepared according to the following scheme with some modification of the method of Brandsma:¹²



A 1-L, three-necked, round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, a pressure-equalizing dropping funnel, and a magnetic stirring bar. The flask was flushed with dry nitrogen, and the subsequent procedures for the silylation reaction were carried out under a dry nitrogen. A hexane solution of *n*-butyllithium (265 mL, 1.6 M, 0.42 mol) was placed in the flask with a syringe, and the hexane (ca. 150 mL) was evaporated with an aspirator under magnetic stirring. After the flask was cooled at -20 °C, tetrahydrofuran (THF; 100 mL; dried over sodium) was gradually added. At the same temperature, a solution of PA (22 mL, 0.20 mol; distilled) in THF (50 mL) was added dropwise, and allowed to leave for 1 h. The dark red reaction mixture was cooled to -65 °C, and a solution of potassium *t*-butoxide (27 g, 0.24 mol) in THF (200 mL) was added dropwise, and the dark purple mixture was stirred at -10 °C for 1 h. Then chlorotrimethylsilane (53 mL, 0.42 mol; distilled) was gradually added at -50 °C and the pale yellow mixture was allowed to stand at room temperature overnight. Hexane and THF were evaporated with a rotary evaporator. A solution of potassium hydroxide (30 g) in 95%

ethanol (400 mL) was added to the white reaction mixture, and the flask was heated at 80 °C. The alkyne desilylation reaction was monitored by gas chromatography (GC) and shown to be complete within 1 h. Then, ice water (500 mL) was added. The product was extracted with diethyl ether, washed with water, and dried over anhydrous magnesium sulfate overnight. Diethyl ether was evaporated, and the product was distilled twice at reduced pressure from calcium hydride; bp 85 °C/10 mmHg (lit^{11a} 85 °C/10 mmHg), yield 75%, purity >99% (GC), d^{20} 0.883.

Transition-metal chlorides and organometallic cocatalysts were all commercially obtained, and used without further purification. Polymerization solvents were purified by the standard methods.

Procedure

Polymerization was carried out as described in Chapter 1. In the case of $W(CO)_6$ -hv and $Mo(CO)_6$ -hv catalysts, catalyst solutions were prepared by irradiation of CCl_4 solution of $W(CO)_6$ or $Mo(CO)_6$ with a 400-W high-pressure Hg lamp from a 5-cm distance at 30 °C for 30 min.

The molecular weights of polymers were determined by gel permeation chromatography (GPC) with use of a polystyrene calibration. The GPC peaks of the polymers had a common shape, sharp on the low-molecular-weight side and gentle on the high-molecular-weight side. Since the leadings on the high-molecular-weight side were partly out of the calibration limit, the \bar{M}_w and \bar{M}_n values are not very accurate. Especially at a very dilute concentration of polymer sample (e.g., 0.3 g/dL), the GPC peak shifted to the high-molecular-weight side, and the leading on the high-molecular-weight side was quite pronounced. This might be due to a polymer-electrolyte-like property resulting from the doping by some impurities. This was not a case at high concentrations (1.5 - 3.0 g/dL), at which almost all the measurements were carried out.

Intrinsic viscosities ($[\eta]$) of polymers were measured in toluene at 30 °C by using a Ubbelohde-type viscometer in the concentration range 0.1 - 0.4 g/dL. The plots of η_{sp}/c vs. c were all linear.

Mass spectra were observed with a Shimadzu QP-1000 mass spectrometer equipped with a thermospray unit (Vestec, Model 750B). Sample solutions were prepared by dissolving samples (~0.5 mM) and ammonium acetate (0.1 M) in methanol, and the solutions (20 μ L) were injected into the thermospray unit. Then samples were chemically ionized with the aid of an electron beam of 200 eV.

NMR spectra were measured on a JEOL FX90Q spectrometer. IR and UV-visible spectra were recorded with Shimadzu IR-435 and Shimadzu UV190 spectrophotometers, respectively. TGA was conducted with a Shimadzu 20B thermal analyzer (in air, heating rate 10 °C/min).

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Chapter 6

Polymerization and Polymer Properties of [*o*-(Dimethylphenylsilyl)phenyl]acetylene

Abstract

[*o*-(Dimethylphenylsilyl)phenyl]acetylene (*o*-Me₂PhSiPA) polymerized with W catalysts in good yields to form high-molecular-weight polymers ($\bar{M}_w > 10^6$). Mo, Nb, and Ta catalysts also provided polymers, though the polymer yields and molecular weights were lower than those with WCl₆. Effects of solvents and temperature on the polymerization were studied. Living polymerization occurred when MoOCl₄-*n*-Bu₄Sn-EtOH catalyst was used. The produced polymer was a dark purple solid soluble in various organic solvents. UV-visible spectrum and thermal stability of the polymer was similar to those of poly[*o*-(trimethylsilyl)phenylacetylene].

Introduction

Polymerization of various ortho-substituted phenylacetylenes has been recently studied; e.g., *o*-methylphenylacetylene,¹ *o*-(trifluoromethyl)phenylacetylene,^{2,3} *o*-(trimethylsilyl)phenylacetylene (*o*-Me₃SiPA),⁴ and derivatives of *o*-Me₃SiPA.⁵ These monomers showed the following characteristics: i) they polymerize in good yields by W and Mo catalysts to form linear, soluble polymers; ii) the molecular weight of the produced polymers increases with increasing steric crowding in the monomer irrespective of the electronic effect of the substituents; iii) monomers with bulky ortho substituents undergo living polymerization in the presence of Mo-based three-component catalysts; iv) the absorption of polymer in the UV-visible spectrum shows a red shift as the ortho-substituent becomes bulkier; v) the gas permeability of the polymers tends to increase with increasing bulkiness of the ortho substituent.

o-Me₃SiPA has the bulkiest substituent among the ortho-substituted phenylacetylenes whose polymerization has been examined. The above-stated characteristics are evidently seen with *o*-Me₃SiPA.⁴

It is of interest to examine whether such characteristics are strengthened or not if an even bulkier substituent is introduced into the ortho position of phenylacetylene. As one of such monomers the author chose [*o*-(dimethylphenylsilyl)phenyl]acetylene (*o*-Me₂PhSiPA). This chapter reports on the polymerization and polymer properties of *o*-Me₂PhSiPA. The results obtained are compared with those of *o*-Me₃SiPA.

Results and Discussion

Polymerization

Table I shows results of the polymerization by various catalysts. The WCl₆-Et₃SiH (1:1) catalyst, which is known to be very effective in the polymerization of *o*-Me₃SiPA, produced a methanol-insoluble polymer in the highest yield. The methanol-soluble products were mixture of linear oligomers and cyclotrimers. The product polymer, poly(*o*-Me₂PhSiPA), was soluble in toluene and CHCl₃, whose \bar{M}_w reached 73x10⁴. The W(CO)₆-hv catalyst also gave a polymer in high yield. The \bar{M}_w of the polymer exceeded 1x10⁶, being higher than that with WCl₆-Et₃SiH. When MoCl₅-Et₃SiH was used both yield and molecular weight of polymer decreased as compared with the WCl₆ counterpart. In general, both WCl₆- and MoCl₅-based catalysts are effective in the polymerization of phenylacetylene and its ortho-substituted derivatives, though the former is more active

Table I
Polymerization of *o*-Me₂PhSiPA by Various Catalysts^a

Catalyst	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
WCl ₆ -Et ₃ SiH	100	83	730	96
W(CO) ₆ -hv ^d	100	79	1300	550
MoCl ₅ -Et ₃ SiH	85	62	100	47
NbCl ₅ -Et ₃ SiH ^e	100	19	240	109
TaCl ₅ -Et ₃ SiH ^e	100	14	190	68

a Polymerized in toluene at 30 °C for 24 h; [M]₀ = 0.50 M, [cat] = [Et₃SiH] = 10 mM.

b Methanol-insoluble part.

c Determined by GPC.

d Polymerized in CCl₄.

e Polymerized at 80 °C.

than the latter.⁶ This tendency holds also with *o*-Me₂PhSiPA.

NbCl₅-Et₃SiH, a catalyst based on a group 5 transition metal, also provided poly(*o*-Me₂PhSiPA) with \bar{M}_w of ca. 20x10⁴, though the polymer yield remained low. The TaCl₅-Et₃SiH catalyst also showed some activity like NbCl₅-Et₃SiH. It is known that group 5 transition-metal chlorides selectively cyclotrimerize most monosubstituted acetylenes. Monomers with a very bulky substituent, however, produce polymers with such catalysts [e.g., HC≡CC₆H₂-*o,o*-Me₂-*p-t*Bu,⁷ HC≡CC₆H₄-*o*-Ph]. Thus, the above results manifest that the steric effect of the ortho-substituent of *o*-Me₂PhSiPA is considerably large.

Effects of solvents on the polymerization were studied by using WCl₆-Et₃SiH which achieved the highest polymer yield (Table II). Polymers were obtained in good yields not only in toluene but also in other solvents like hexane, (CH₂Cl)₂ and anisole. It has been noted that the polymerization by TaCl₅ does not occur in anisole, while that by WCl₆, MoCl₅, and NbCl₅ does take place in anisole. The present result corresponds to the precedents. Though the \bar{M}_w values varied depending on the

Table II
Solvent Effects on the Polymerization of *o*-Me₂PhSiPA by WCl₆-Et₃SiH^a

Solvent	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
toluene	100	83	730	96
cyclohexane	100	82	210	77
(CH ₂ Cl) ₂	85	68	900	290
PhOMe	100	79	540	220

a Polymerized at 30 °C for 24 h; [M]₀ = 0.50 M, [WCl₆] = [Et₃SiH] = 10 mM.

b Methanol-insoluble part.

c Determined by GPC.

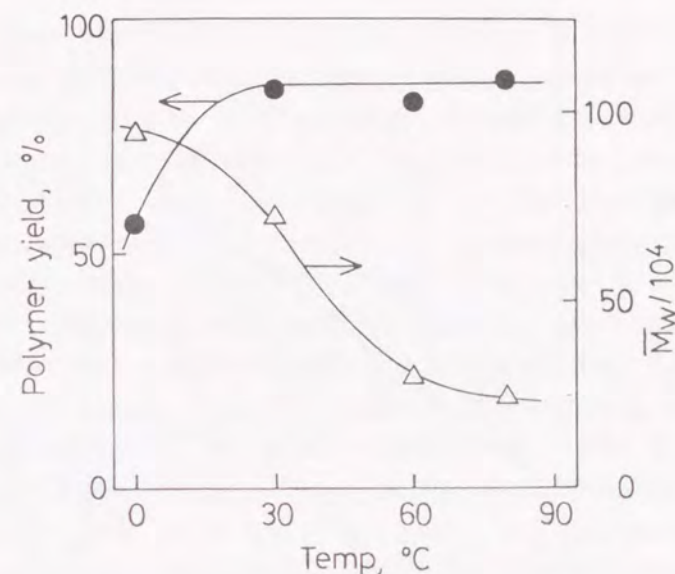


Figure. 1 Effect of temperature on the polymerization of *o*-Me₂PhSiPA by WCl₆-Et₃SiH (in toluene, 24 h, [M]₀ = 0.50 M, [WCl₆] = [Et₃SiH] = 10 mM).

solvents, they all reached several hundred thousand.

Figure 1 depicts the effect of temperature on the polymerization by WCl₆-Et₃SiH. The polymer yield is 56% at 0 °C (monomer conversion is 91%), and increases to about 80% at 30 °C and above. The \bar{M}_w value, which is ~1x10⁶ at 0°C, decreases with rising polymerization temperature. These results indicate that temperatures around 30 °C are optimal to obtain a high-molecular-weight polymer in good yield.

Living Polymerization

o-Me₃SiPA undergoes living polymerization in the presence of MoOCl₄-*n*-Bu₄Sn-EtOH (1:1:1) catalyst to form a polymer with narrow molecular weight distribution (MWD; $\bar{M}_w/\bar{M}_n \sim 1.1$).⁸ Thus, living polymerization of *o*-Me₂PhSiPA by this catalyst was attempted. As seen in Figure 2, the number-average molecular weight of polymer (\bar{M}_n) increased in direct proportion to

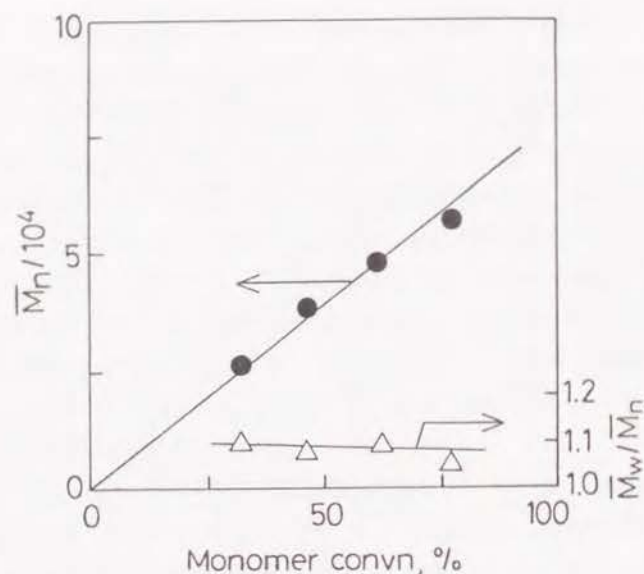


Figure. 2 \bar{M}_n and \bar{M}_w/\bar{M}_n as functions of conversion in the polymerization of *o*-Me₂PhSiPA by MoOCl₄-*n*-Bu₄Sn-EtOH (in toluene, 30 °C, [M]₀ = 0.50 M, [MoOCl₄] = [*n*-Bu₄Sn] = [EtOH] = 10 mM).

monomer conversion. The polymerization rate was rather slow; i.e., even when *o*-Me₂PhSiPA was polymerized for 6 h, the monomer conversion was 85% and not quantitative. The MWD remained narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the polymerization. These results manifest that *o*-Me₂PhSiPA polymerizes in a living manner with the MoOCl₄-based three-component catalyst like *o*-Me₃SiPA. Thus, it is obvious that the *o*-dimethylphenylsilyl group, a very bulky ortho substituent, of phenylacetylene does not necessarily lower the livingness of its polymerization.

Polymer Properties

Since it was found that properties of poly(*o*-Me₂PhSiPA) do not depend on the polymerization conditions, those of the poly(*o*-Me₂PhSiPA) obtained by WCl₆-Et₃SiH in toluene at 30 °C will be described.

Poly(*o*-Me₂PhSiPA) is a dark purple solid. It is completely soluble in aromatic hydrocarbons (toluene, benzene), chlorinated hydrocarbons (CCl₄, CHCl₃, CH₂Cl₂), and tetrahydrofuran. Its nonsolvents include aliphatic hydrocarbons (cyclohexane, hexane), ethers (anisole, diethyl ether, 1,4-dioxane), ketones (acetone, acetophenone), esters (ethyl acetate, methyl benzoate), and triethylamine. Poly(*o*-Me₃SiPA) dissolves in cyclohexane and triethylamine, which indicates that the present polymer is less soluble than poly(*o*-Me₃SiPA). A free-standing film could be prepared by casting poly(*o*-Me₂PhSiPA) from toluene solution.

The absorption maximum of poly(*o*-Me₂PhSiPA) lie at 532 nm (ϵ_{\max} 5700 M⁻¹·cm⁻¹) and the absorption extends up to ca. 700 nm (Figure 3). The absorption of *o*-substituted poly(phenylacetylene) shows red shifts with increasing bulkiness of substituent; e.g., λ_{\max} 466 nm (*o*-CH₃),¹ 542 nm (*o*-SiMe₃).⁴

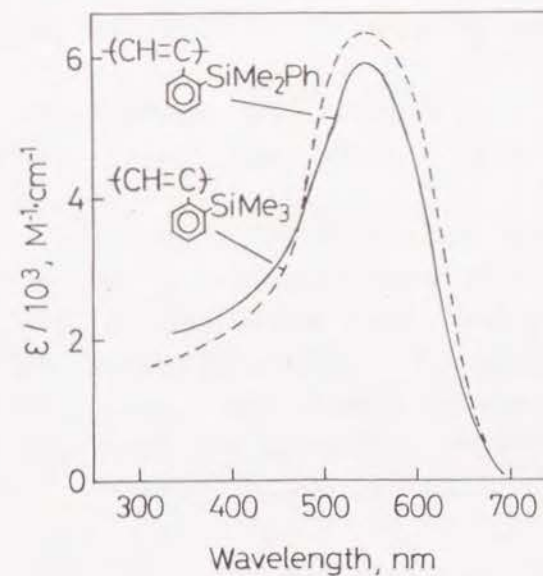


Figure. 3 UV-visible spectra of poly(*o*-silylphenylacetylenes) (measured in tetrahydrofuran).

Absorption of poly(*o*-Me₂PhSiPA) is, however, similar in wavelength to that of poly(*o*-Me₃SiPA).

Poly(*o*-Me₃SiPA) begins to lose weight in thermogravimetric analysis (TGA) in air at 280 °C, having relatively high thermal stability among substituted acetylene polymers. The weight loss of poly(*o*-Me₂PhSiPA) started at 275 °C, indicating that thermal stability of poly(*o*-Me₂PhSiPA) is similar to that of poly(*o*-Me₃SiPA).

Experimental

o-Me₂PhSiPA (new compound) was prepared with reference to the method for *o*-Me₃SiPA described in Chapter 5 using ClSiMe₂Ph instead of ClSiMe₃. The crude product was purified by flush column chromatography (Nakarai Tesque Co., silica gel 60; eluent, hexane). Overall yield 30%, purity >95% (by GC).

Transition metal chlorides and organometallic compounds were commercially obtained and used without further purification.

Polymerization was carried out as described in Chapter 5. Monomer conversions were determined by GC, and molecular weights of polymers were determined by gel permeation chromatography (GPC; eluent, CHCl₃, polystyrene calibration).

UV-visible spectra were recorded with a Shimadzu UV-2200 spectrophotometer. TGA was performed with a Shimadzu 20B thermal analyzer (heating rate 10 °C/min).

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Chapter 7

Polymerization and Polymer Properties of 3-Silyl-1-hexynes

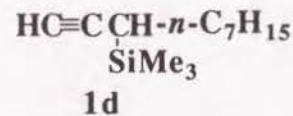
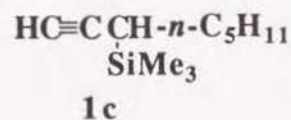
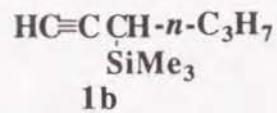
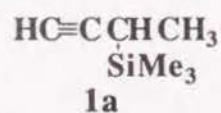
Abstract

3-(Dimethyl-*n*-hexylsilyl)-1-hexyne and 3-(dimethyl-phenylsilyl)-1-hexyne [$\text{HC}\equiv\text{CCH}(\text{SiMe}_2\text{R})\text{-}n\text{-C}_3\text{H}_7$; R = *n*-C₆H₁₃, Ph; new compounds] formed polymers in excellent yields in the presence of Mo and W catalysts. The highest weight- and number-average molecular weights (\bar{M}_w and \bar{M}_n) of poly[3-(dimethyl-*n*-hexylsilyl)-1-hexyne] were ca. 4×10^5 and 2×10^5 , respectively (MoCl₅-Ph₃Sb as catalyst), while the highest \bar{M}_w and \bar{M}_n of the corresponding phenyl-substituted polymer were ca. 2×10^5 and 8×10^4 (WCl₆-Ph₃Sb). Both of the present polymers were yellow solids, whose structure could be represented as $[-\text{CH}=\text{C}(\text{CHSiMe}_2\text{R-}n\text{-C}_3\text{H}_7)\text{-}]_n$. They dissolved in many common organic solvents and could be cast from solution into films. Mechanical, thermal, and some other properties of the polymers are discussed.

Introduction

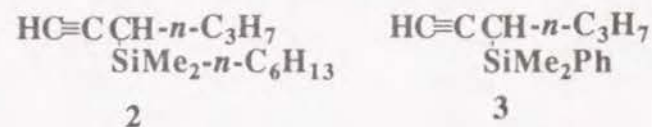
Recently, many polymers have been synthesized from substituted acetylenes by use of transition metal catalysts.¹ Among the polymers, Si-containing polyacetylenes often exhibit unique properties and functions (e.g., high gas permeability²); thus their synthesis is an intriguing subject. One of the simplest Si-containing acetylenes is (trimethylsilyl)acetylene. This monomer, however, usually produces a polymer partly insoluble in common organic solvents,³ and the molecular weight of its soluble fraction is no more than ca. 1×10^4 . Monomers in which one of the methyl groups in (trimethylsilyl)acetylene is replaced by other groups such as *n*-hexyl and phenyl also provide only polymers with similar molecular weights.⁴

In a previous study,⁵ 3-(trimethylsilyl)-1-alkynes [$\text{HC}\equiv\text{CCH}(\text{SiMe}_3)\text{-}n\text{-alkyl}$, **1**] were employed as another type of Si-containing monosubstituted acetylenes, and their polymerization was studied. 3-(Trimethylsilyl)-1-butyne (**1a**) and -1-hexyne (**1b**) polymerized with Mo and W catalysts, but the polymers did not completely dissolve in any solvents. In contrast, 3-(trimethylsilyl)-1-octyne (**1c**) and -1-decyne (**1d**), homologues with longer alkyl chains, gave polymers which were totally soluble in solvents such as toluene and chloroform and had high molecular weights up to 5×10^5 . Though the insolubility of polymers of **1a** and **1b** is assumed to be due to rather poor flexibility of the side chain, it is not necessarily evident.



From the previous investigations, it has been observed that in the polymerization of substituted acetylenes molecular weight of the produced polymer increased with increasing bulkiness of substituent.¹ Thus, it can be expected that molecular weight becomes higher than the case of **1c** if one of the methyl groups on the silicon atom in **1b** is replaced by bulkier groups. Further, it is of interest to study the effect of bulkier silyl group on polymer properties. Especially, soluble polymers might be obtained from these monomers.

This chapter reports on the polymerization of 3-(dimethyl-*n*-hexylsilyl)-1-hexyne (**2**) and 3-(dimethylphenylsilyl)-1-hexyne (**3**), both of which are novel compounds belonging to the monomer group of 3-silyl-1-hexynes.



Results and Discussion

*Polymerization of 3-(Dimethyl-*n*-hexylsilyl)-1-hexyne (2)*

The polymerization of this monomer was first examined with various catalysts (Table I). Under the polymerization conditions shown in Table I, the monomer was completely consumed in the presence of the Mo, W, and Nb catalysts, except for the case of Ph_3Bi as cocatalyst. The major products with the Mo, W, and Nb catalysts were methanol-insoluble poly[3-(dimethyl-*n*-hexylsilyl)-1-hexyne]s [poly(**2**)], whose yields were in the range ca. 40-100%.⁶ In contrast, the polymer yields with Ta catalysts were zero. It is very interesting that 3-silyl-1-alkynes [**1c**,⁵ **1d**,⁵ and the present monomers] polymerize in the presence of Nb catalysts when it is taken into account that most monosubstituted acetylenes are selectively cyclotrimerized with

Table I
Polymerization of 3-(Dimethyl-*n*-hexylsilyl)-1-hexyne by Various Catalysts^a

no.	Catalyst	Monomer convn, %	Polymer ^b		
			yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
1	MoCl ₅	100	89	260	140
2	MoCl ₅ -Ph ₃ Sb	100	93	410	200
3	MoCl ₅ -Ph ₃ Bi	60	42	130	47
4	MoCl ₅ -Ph ₃ SiH	100	89	260	120
5	MoCl ₅ -Et ₃ SiH	100	81	210	87
6	MoCl ₅ -Ph ₄ Sn	100	92	270	150
7	MoCl ₅ - <i>n</i> -Bu ₄ Sn	100	78	230	100
8	Mo(CO) ₆ -hv ^d	100	96	200	98
9	WCl ₆	100	56	59	18
10	WCl ₆ -Ph ₃ Sb	100	80	110	43
11	WCl ₆ -Ph ₃ Bi	88	61	47	28
12	WCl ₆ -Ph ₃ SiH	100	62	55	16
13	WCl ₆ -Et ₃ SiH	100	81	68	23
14	WCl ₆ -Ph ₄ Sn	100	88	140	32
15	WCl ₆ - <i>n</i> -Bu ₄ Sn	100	61	53	16
16	W(CO) ₆ -hv ^d	100	88	76	13
17	NbCl ₅	100	56	41	12
18	NbCl ₅ -Ph ₃ Sb	100	65	100	27
19	NbCl ₅ -Ph ₃ SiH	100	81	87	40
20	NbCl ₅ -Ph ₄ Sn	100	52	34	9
21	TaCl ₅	86	0		
22	TaCl ₅ -Ph ₃ Sb	32	0		

a Polymerized in toluene at 0 °C (Mo, W) or 30 °C (Nb, Ta) for 24 h; [M]₀ = 0.50 M, [cat] = [cocat] = 10 mM.

b Methanol-insoluble product.

c Determined by GPC.

d Polymerized in CCl₄ at 30 °C.

Nb and Ta catalysts.⁷ The methanol-soluble product in the polymerizations was a mixture of linear oligomers and cyclotrimers according to gel permeation chromatography (GPC) as well as IR and NMR spectra.

The weight- and number-average molecular weights (\bar{M}_w and \bar{M}_n) of poly(2) obtained with MoCl₅-Ph₃Sb (Table I, no. 2) were 41x10⁴ and 20x10⁴, respectively, being the highest among the values in the table.⁶ It is noted that not only polymer yield but also molecular weight is rather low with MoCl₅-Ph₃Bi, though Ph₃Bi is a Group 5 organometallic compound like Ph₃Sb. The molecular weight of polymer was usually lower when W and Nb catalysts were used instead of Mo catalysts.

As compared with MoCl₅ alone, catalysts composed of MoCl₅ and an organometallic cocatalyst more or less changed the polymerization rate, polymer yield, and molecular weight. For instance, the polymerization by MoCl₅ alone was finished after several hours, whereas the one by MoCl₅-Ph₃Sb was completed within 1 h. It is obvious in Table I that use of Ph₃Sb as cocatalyst increases the polymer molecular weight. As seen in Table I, the Mo(CO)₆-hv catalyst is as effective as MoCl₅-based catalysts. Similar tendencies are observed also with WCl₆-cocatalyst and W(CO)₆-hv systems.

Solvent effect on the polymerization was studied by using MoCl₅-Ph₃Sb which proved to be one of the most useful catalysts (Table II). Although the monomer was quantitatively consumed not only in toluene but also in anisole and halogen-containing solvents, the polymer yield in toluene was the highest (>90%). The \bar{M}_w of poly(2) became the highest in toluene among the solvents examined.

Figure 1 shows the effect of temperature on the polymerization by MoCl₅-Ph₃Sb in toluene. The monomer conversion at 0 °C and above was quantitative under the conditions in Figure 1. The polymer yield was about 90% in the range 0 - 60 °C, while it was lower at -20 °C. The \bar{M}_w of poly(2)

Table II
Solvent Effects on the Polymerization of 3-(Dimethyl-*n*-hexylsilyl)-1-hexyne by MoCl₅-Ph₃Sb^a

Solvent	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
toluene	100	91	410	200
PhOMe	100	57	270	110
PhCl	100	60	130	45
CCl ₄	100	52	230	89
(CH ₂ Cl) ₂	70	0		

a Polymerized at 0 °C for 24 h; [M]₀ = 0.50 M, [MoCl₅] = [Ph₃Sb] = 10 mM.

b Methanol-insoluble product.

c Determined by GPC.

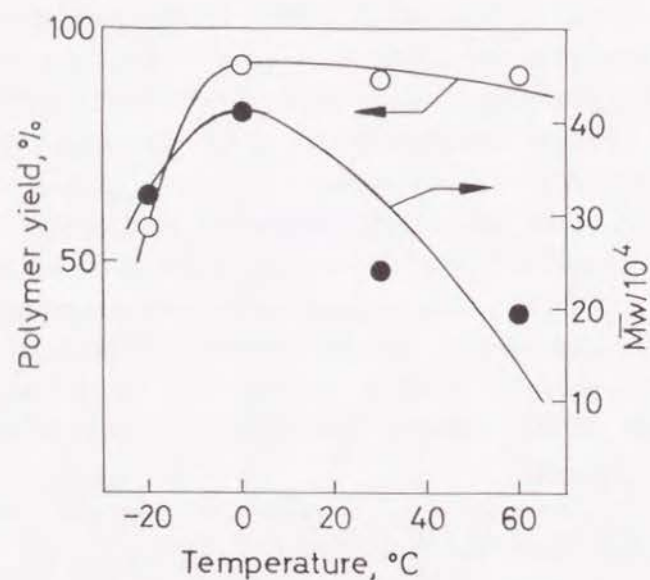


Figure 1. Effects of temperature on the polymerization of 3-(dimethyl-*n*-hexylsilyl)-1-hexyne by MoCl₅-Ph₃Sb (in toluene, 24 h, [M]₀ = 0.50 M, [MoCl₅] = [Ph₃Sb] = 10 mM).

exhibited a maximum around 0 °C. Therefore, 0 °C is suitable to obtain a high molecular weight polymer in high yield.

When this polymerization was carried out with MoCl₅-Ph₃Sb in toluene at 0 °C, all of monomer 2 was virtually consumed after 1 h, and at that point the yield of methanol-insoluble polymer reached about 90% (Figure 2). Then the \bar{M}_w of the poly(2) was as high as ca. 4×10^5 ; even though the polymerization was continued over 24 h, the molecular weight did not change, indicating that no polymer degradation occurred.

Polymerization of 3-(Dimethylphenylsilyl)-1-hexyne (3)

The polymerization of 3 was examined with various catalysts (Table III). In the case of this monomer, W catalysts usually achieved higher \bar{M}_w 's than did the corresponding Mo catalysts. Eventually, WCl₆-Ph₃Sb provided virtually

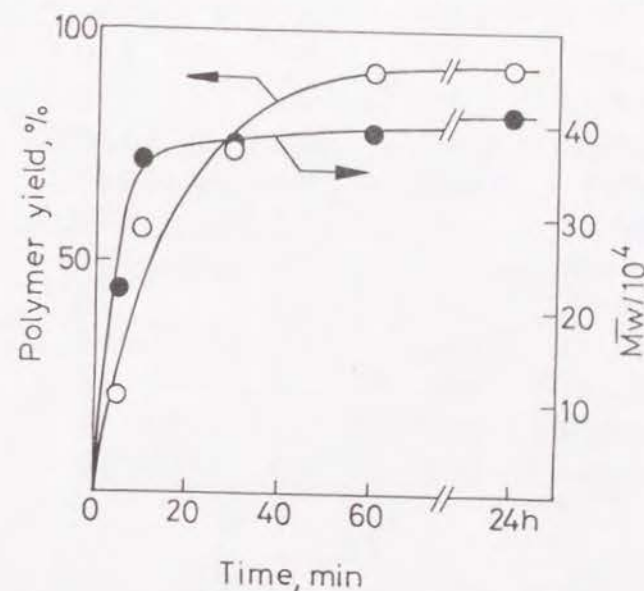


Figure 2. Time courses of the polymerization of 3-(dimethyl-*n*-hexylsilyl)-1-hexyne by MoCl₅-Ph₃Sb (in toluene, 0 °C, [M]₀ = 0.50 M, [MoCl₅] = [Ph₃Sb] = 10 mM).

Table III
Polymerization of 3-(Dimethylphenylsilyl)-1-hexyne by Various Catalysts^a

no.	Catalyst	Monomer convn, %	Polymer ^b		
			yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
1	MoCl ₅	28	20	46	22
2	MoCl ₅ -Ph ₃ Sb	49	43	76	33
3	MoCl ₅ -Ph ₃ Bi	0	0		
4	MoCl ₅ -Ph ₃ SiH	92	80	110	60
5	MoCl ₅ -Et ₃ SiH	94	91	180	72
6	MoCl ₅ -Ph ₄ Sn	77	73	120	45
7	MoCl ₅ - <i>n</i> -Bu ₄ Sn	36	17	56	29
8	Mo(CO) ₆ -hv ^d	100	87	62	25
9	WCl ₆	100	87	170	64
10	WCl ₆ -Ph ₃ Sb	100	98	210	82
11	WCl ₆ -Ph ₃ Bi	44	21	27	13
12	WCl ₆ -Ph ₃ SiH	94	86	140	39
13	WCl ₆ -Et ₃ SiH	100	91	160	54
14	WCl ₆ -Ph ₄ Sn	96	92	170	67
15	WCl ₆ - <i>n</i> -Bu ₄ Sn	97	88	170	56
16	W(CO) ₆ -hv ^d	97	84	50	24
17	NbCl ₅	100	55	27	13
18	NbCl ₅ -Ph ₃ Sb	100	21	18	7
19	NbCl ₅ -Ph ₃ SiH	100	53	24	14
20	NbCl ₅ -Ph ₄ Sn	100	62	19	9
21	TaCl ₅	73	4		
22	TaCl ₅ -Ph ₃ Sb	80	8		

- a Polymerized in toluene at 0 °C (Mo, W) or 30 °C (Nb, Ta) for 24 h; [M]₀ = 0.50 M, [cat] = [cocat] = 10 mM.
 b Methanol-insoluble product.
 c Determined by GPC.
 d Polymerized in CCl₄ at 30 °C.

quantitatively poly[3-(dimethylphenylsilyl)-1-hexyne] [poly(3)] having the highest \bar{M}_w (21x10⁴) and \bar{M}_n (8x10⁴). It proves that the effect of cocatalyst is different depending on the kinds of catalyst (WCl₆ and MoCl₅); e.g., Ph₃Sb is very effective when combined with WCl₆, while it is not as effective with MoCl₅. As in the case of monomer 2, Nb catalysts were useful to some extent in effecting polymerization, whereas Ta catalysts hardly produced poly(3).

Though the polymerization of monomer 3 by WCl₆-Ph₃Sb proceeded in solvents other than toluene, the polymer yield considerably decreased, and the \bar{M}_w reduced to about 1/10 the value with toluene (Table IV). As shown in Figure 3, the polymerization by WCl₆-Ph₃Sb in toluene exhibited the highest values for both yield and \bar{M}_w of polymer at 0 °C; the \bar{M}_w decreased sharply with increasing temperature. Thus, the selection of an appropriate temperature is very important in this

Table IV
Solvent Effects on the Polymerization of 3-(Dimethylphenylsilyl)-1-hexyne by WCl₆-Ph₃Sb^a

Solvent	Monomer convn, %	Polymer ^b		
		yield, %	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
toluene	100	98	210	82
PhOMe	100	56	19	9.9
PhCl	100	59	12	6.2
CCl ₄	100	60	25	11
(CH ₂ Cl) ₂	81	30	6.6	4.5

- a Polymerized at 0 °C for 24 h; [M]₀ = 0.50 M, [WCl₆] = [Ph₃Sb] = 10 mM.
 b Methanol-insoluble product.
 c Determined by GPC.

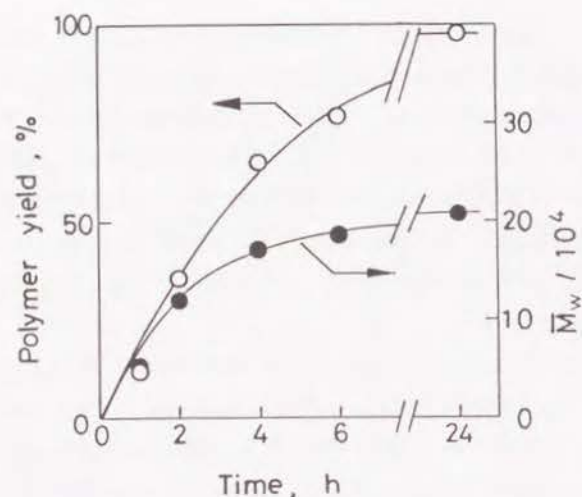


Figure 3. Effects of temperature on the polymerization of 3-(dimethylphenylsilyl)-1-hexyne by $\text{WCl}_6\text{-Ph}_3\text{Sb}$ (in toluene, 24 h, $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{WCl}_6] = [\text{Ph}_3\text{Sb}] = 10 \text{ mM}$).

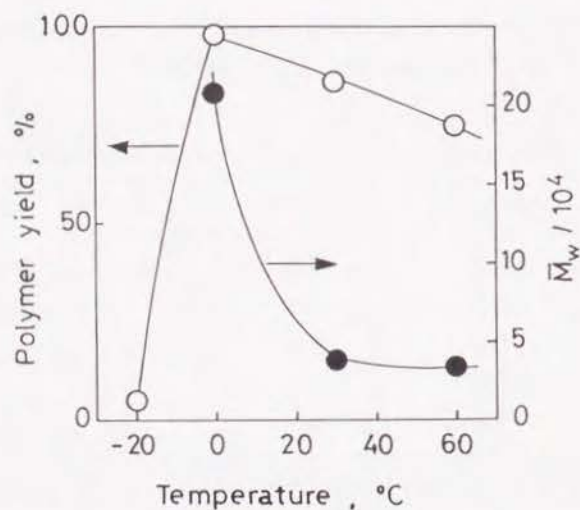


Figure 4. Time courses of the polymerization of 3-(dimethylphenylsilyl)-1-hexyne by $\text{WCl}_6\text{-Ph}_3\text{Sb}$ (in toluene, 0 °C, $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{WCl}_6] = [\text{Ph}_3\text{Sb}] = 10 \text{ mM}$).

polymerization. The polymerization of monomer 3 by $\text{WCl}_6\text{-Ph}_3\text{Sb}$ was not completed within a few hours (Figure 4), being slower than the polymerization of monomer 2 by $\text{MoCl}_5\text{-Ph}_3\text{Sb}$. The \bar{M}_w of polymer increased with polymerization time to reach ca. 2×10^5 after 24 h. The increase of \bar{M}_w with increasing polymer yield suggests the presence of long-lived propagating species.

Comparison of Polymerization of Various 3-Silyl-1-alkynes

When monomers 2 and 3 are compared with each other concerning their polymerization behavior, the following can be pointed out on the basis of the above-stated results: (i) 2 is more reactive than 3 according to the dependences on temperature and time; (ii) the highest \bar{M}_w 's differ (poly(2) 41×10^4 ; poly(3) 21×10^4); (iii) the kinds of catalysts which attain the highest \bar{M}_w 's differ ($\text{MoCl}_5\text{-Ph}_3\text{Sb}$ for 2; $\text{WCl}_6\text{-Ph}_3\text{Sb}$ for 3).

In a previous paper,⁵ polymers partly insoluble in toluene were obtained in the polymerization of monomer 1b by MoCl_5

Table V
Polymerization of 3-(Trimethylsilyl)-1-hexyne^a

no.	Catalyst	Polymer ^b yield, %
1	MoCl_5	92
2	$\text{MoCl}_5\text{-Ph}_3\text{Sb}$	96
3	WCl_6	83
4	$\text{WCl}_6\text{-Ph}_3\text{Sb}$	84

a Polymerized in toluene at 0 °C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{cat}] = [\text{cocat}] = 10 \text{ mM}$; the monomer conversions were all 100%.

b Methanol-insoluble product.

and WCl_6 in toluene at 30 °C. For the sake of comparison, a few polymerizations of this monomer were carried out under the same conditions as in Table I and III. As seen in Table V, methanol-insoluble poly[3-(trimethylsilyl)-1-hexyne] [poly(**1b**)] was obtained in high yields. The yields of poly(**1b**) were somewhat higher with Mo catalysts than with the W counterparts. The effect of Ph_3Sb as cocatalyst on the polymer yield was negligible. All of the poly(**1b**) in Table V was only partly soluble in common solvents such as toluene and CHCl_3 .

In the polymerization of monomer **1c**,⁵ Mo catalysts produce poly[3-(trimethylsilyl)-1-octyne] [poly(**1c**)] with higher molecular weight in better yields than W catalysts do; especially, $\text{MoCl}_5\text{-Et}_3\text{SiH}$ affords poly(**1c**) in ca. 90% yield with \bar{M}_w of 45×10^4 . These results resemble those for monomer **2**. The fact that monomer **3** behaves somewhat differently seems due to the steric effect of the phenyl group.

It was confirmed in the present study that 3-silyl-1-hexynes produce polymer with higher molecular weight than do silylacetylene. It is presumed that the silyl group directly bonded to the acetylenic carbon is more or less reactive to participate in the chain transfer in the polymerization of silylacetylenes.

Polymer Structure

Unless otherwise specified, the structure and properties of polymers were investigated with use of sample 2 of Table I for poly(**2**), sample 10 of Table III for poly(**3**), and sample 2 of Table V for poly(**1b**).

The elemental analysis values of the present polymers agreed fairly well with the theoretical values calculated for the polymerization products: Anal. Poly(**2**) Calcd for $(\text{C}_{14}\text{H}_{28}\text{Si})_n$: C, 74.91; H, 12.57. Found: C, 74.78; H, 12.79. Poly(**3**) Calcd for $(\text{C}_{14}\text{H}_{20}\text{Si})_n$: C, 77.71; H, 9.32. Found: C, 76.69; H, 9.28.

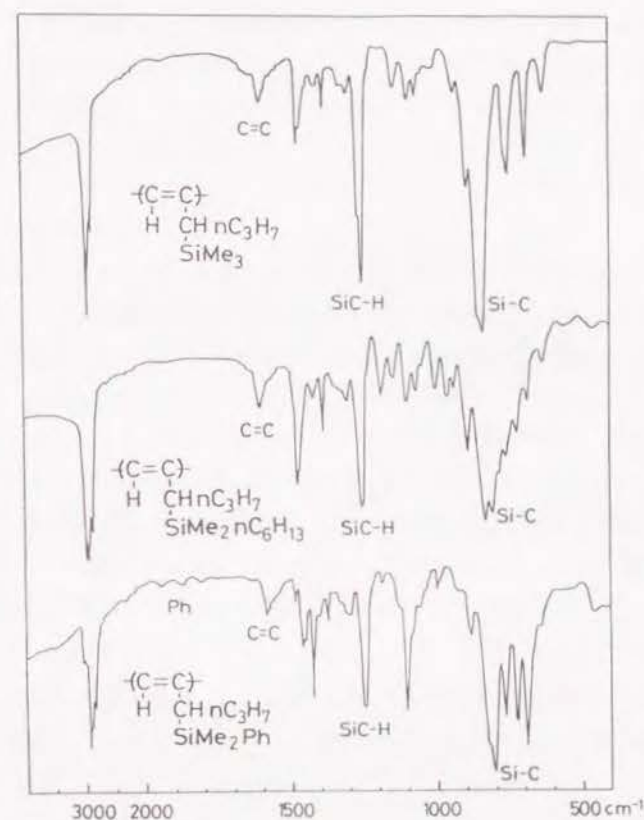


Figure 5. IR spectra of poly(3-silyl-1-hexynes) (KBr pellet; samples from Table I, no. 2, Table III, no. 10, and Table V, no. 2).

Figure 5 gives IR spectra of polymers. The absorption band at 1580 cm^{-1} in every polymer is assignable to C=C stretching. Though the absorption is not strong, it appears clearly unlike the case of the polymers from symmetrically disubstituted acetylenes. In these polymers are seen no signals characteristic of the $\text{C}\equiv\text{C}$ ($\sim 2150\text{ cm}^{-1}$) and $\equiv\text{C-H}$ ($\sim 3300\text{ cm}^{-1}$) bonds which appear in their monomers. Absorptions indicating the presence of Si atom are seen at 1250 cm^{-1} (SiC-H deformation) and in the range $800 - 700\text{ cm}^{-1}$ (Si-C stretching).

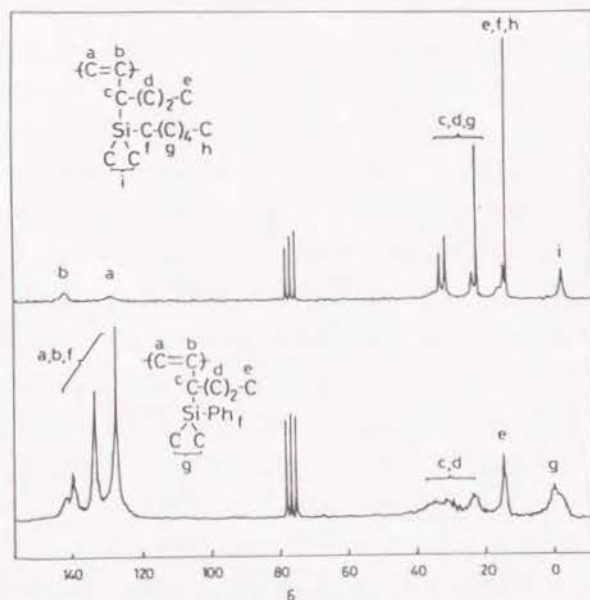


Figure 6. ^{13}C NMR spectra of poly(3-silyl-1-hexynes) (CDCl_3 solution; samples from Table I, no. 2 and Table III, no. 10).

The ^{13}C NMR spectrum of poly(2) shows two peaks δ 143 and 128 due to olefinic carbons (Figure 6). In the spectrum of poly(3), the peaks of olefinic carbons overlap with those of phenyl carbons. In both polymers, the signals of alkyl carbons appear in the range δ 40 - 0, among which the methyl carbons bonded to Si are just at δ 0. Acetylenic carbons which should appear between δ 90 and 65 are not seen in these polymers.

The data of UV-visible spectra of the polymers measured in cyclohexane are as follows: poly(2) UV_{max} 351 nm (ϵ 3900) (absorption ≤ 486 nm); poly(3) UV_{max} 350 nm (ϵ 2800) (absorption ≤ 480 nm). Corresponding to the UV-visible spectra, both polymers were yellow solids.

It will be reasonable to conclude from the above data that the present polymers possess the alternating double bond

structure, $[-\text{CH}=\text{C}(\text{CHSiMe}_2\text{R}-n-\text{C}_3\text{H}_7)-]_n$, which assumes appreciably twisted conformations. These data and conclusions are analogous with those for poly(1c) reported in a previous paper.

Polymer Properties

Whereas poly(1b) is partly insoluble in toluene and chloroform,⁵ the present polymers completely dissolve in these solvents. The flexible and/or bulky groups of *n*-hexyl and phenyl are able to interact with the solvent effectively, which should have made these polymers soluble, unlike poly(1b). At the same time, the idea that the insolubility of poly(1b) stems from crosslinking can be denied. As seen in Table VI, there is a considerable difference in the kind of solvents used for poly(2) and poly(3). For instance, poly(2) dissolves in hexane, an alkane,

Table VI
Solubility Properties of Poly(3-silyl-1-hexynes)^a

	<i>n</i> -C ₆ H ₁₃	Ph
hexane	sol ^b	insol ^b
cyclohexane	sol	sol
toluene	sol	sol
CCl ₄	insol	sol
(CH ₂ Cl) ₂	insol	sol
1,4-dioxane	sol	sol
diethyl ether	sol	sol
THF ^c	sol	sol
anisole	ptly sol ^b	sol
ethyl acetate	sol	sol
methyl benzoate	sol	sol

a Samples from Table I, no. 2, and Table III, no. 10.

b Sol, soluble; ptly sol, partly soluble; insol, insoluble.

c THF, tetrahydrofuran.

but does not dissolve in ethyl acetate, fairly polar solvent, whereas the opposite is the case with poly(3).

When the mechanical properties of poly(2) and poly(3) are compared (Table VII), the former polymer has a lower Young's modulus, a smaller tensile strength, and a larger elongation at break. This is explainable in terms of the difference in the nature of substituents *n*-hexyl and phenyl. It turns out that poly(1c) is close to poly(3) in mechanical properties, rather than to poly(2). Roughly talking, all these polymers are somewhat soft and ductile among various substituted polyacetylenes owing to the presence of relatively long alkyl groups.⁸

Most of the substituted polyacetylenes possess high glass transition temperatures (T_g) around 200 °C.⁸ Among substituted polyacetylenes, poly(2) has a relatively low T_g (Table VII), which is attributable to the presence of a flexible *n*-hexyl group. In contrast, poly(3), which does not have such a long alkyl group, exhibits a high T_g . By a similar reason, the softening points of these polymers are pretty different from each other. The T_g and softening point of poly(1c) are again closer to those of poly(3) than to those of poly(2).

The weight loss of the present two polymers in the thermogravimetric analysis (TGA) in air starts in the vicinity of 200 °C (Table VII). This means that the thermal stability of these polymers is medium and not very high among various substituted polyacetylenes.⁹ The presence of an allylic proton in these polymers seems responsible for this. When these polymers are heat-treated in air at 120 °C for 20 h, they suffer moderate decreases of molecular weight (Table VII) among substituted polyacetylenes.⁹ This also leads to a conclusion similar to that for TGA. The \bar{M}_w/\bar{M}_n ratio after the heat treatment is relatively close to two, which indicates that virtually only random degradation of the polymer takes place, and cross-linking is negligible.

The electrical conductivities of poly(2) and poly(3)

Table VII
Mechanical and Thermal Properties of Soluble, Film-Forming Poly(3-silyl-1-alkynes)^a

	$\begin{array}{c} \text{-(CH=C)}_n \\ \\ \text{CH(SiMe}_2\text{R)-}n\text{-C}_3\text{H}_7 \end{array}$		$\begin{array}{c} \text{-(CH=C)}_n \\ \\ \text{CH(SiMe}_3\text{)-}n\text{-C}_5\text{H}_{11} \end{array}$
	R = <i>n</i> -C ₆ H ₁₃ [poly(2)]	R = Ph [poly(3)]	[poly(1c)]
E , ^b MPa	210	660	630
σ_B , ^c MPa	6	22	27
γ_B , ^d %	65	40	11
T_g , ^e °C	~60	~200	~170
softening pt., ^f °C	185	310	290
wt loss, ^g °C			
start/10%/50%	200/240/300	180/280/330	190/240/320
heat treatment ^h			
$\bar{M}_w/10^3$	410→85	210→80	400→90
$\bar{M}_n/10^3$	200→36	82→33	170→44

a Samples from Table I, no. 2, and Table III, no. 10.

b Young's modulus.^{8b}

c Tensile strength.^{8b}

d Elongation at break.^{8b}

e Glass transition temperature measured by dynamic viscoelasticity.^{8b}

f Heating rate 10 °C/min.

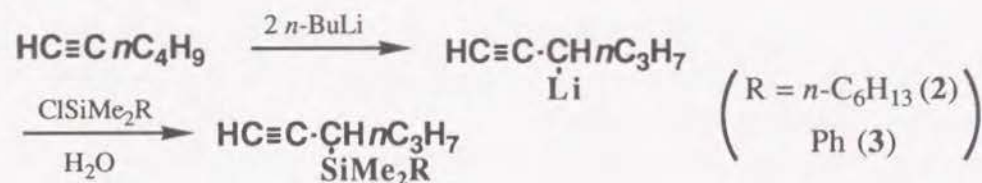
g Measured by thermogravimetric analysis (in air; heating rate 10 °C/min).

h Heat-treated in air at 120 °C for 20 h.

measured in the dark at 25 °C with dc current are 9×10^{-18} and 7×10^{-18} S·cm⁻¹, respectively. These values are indicative of typical insulators. The unpaired electrons in the present polymers were undetectable by the electron spin resonance measured at 25 °C in bulk. Therefore, their unpaired electron levels should be lower than 1×10^{15} spin·g⁻¹. These electrical and magnetic data suggest that the double bonds in the present polymers are conjugated only to a limit extent. The insulating and nonparamagnetic properties are common in many of the polyacetylenes with bulky substituents.^{1a}

Experimental

Monomers 2 and 3 were prepared with reference to the literature methods for synthesizing 3-(trimethylsilyl)-1-alkynes^{5,10} according to the following scheme:



Dimethyl-*n*-hexylsilyl chloride, a starting compound, was prepared according to ref 2b. Monomer 2 was prepared as follows: Under dry nitrogen, a flask was charged with a hexane solution (263 mL) of *n*-BuLi (0.42 mol). With ice cooling, a mixture of 1-hexyne (23.0 mL, 0.20 mol) and hexane (40 mL) was added dropwise; after the completion of addition, the mixture was stirred at room temperature for 2 h. A mixture of dimethyl-*n*-hexylsilyl chloride (42.3 mL, 0.20 mol) and hexane (80 mL) was added dropwise, while the flask was kept at -30 °C; then the reaction was completed by stirring the mixture at 60 °C for 2 h. Water was added dropwise at 0 °C to decompose residual

organo-Li compounds. The reaction mixture was washed with aqueous NH₄Cl solution and water. The hexane solution was dried over anhydrous sodium sulfate. Hexane was evaporated, and the crude product was distilled twice at reduced pressure from calcium hydride. Yield 55%; bp 75 °C/3 mmHg; purity 96% [gas chromatography (GC); the main impurity was the corresponding 1-silyl-1-hexyne (byproduct)]. IR (neat) 3300 (s, $\nu_{\text{C-H}}$), 2950 (s), 2850 (m), 2080 (m, $\nu_{\text{C}\equiv\text{C}}$), 1470 (m), 1250 (s, $\delta_{\text{Si-C-H}}$), 830 (s, $\nu_{\text{Si-C}}$), 625 (m), 590 (m) cm⁻¹. ¹³C NMR (CDCl₃) δ 86.6 (C₂), 68.4 (C₁), 33.3, 31.6, 23.7, 22.6, 18.5, 13.7, -4.9 (2Me-Si).

Since dimethylphenylsilyl chloride was less reactive than dimethyl-*n*-hexylsilyl chloride, the synthesis of monomer 3 was carried out in a mixture of hexane and diethyl ether instead of hexane alone: Under dry nitrogen, a hexane solution (263 mL) of *n*-butyllithium (0.42 mol) was placed in the flask, and a part of the hexane (ca. 100 mL) was removed by evaporation with an aspirator. The concentrated solution of *n*-BuLi was diluted slowly with diethyl ether (200 mL; dried over sodium) at -50 °C. 1-Hexyne (23.0 mL, 0.20 mol) was added dropwise while keeping the flask at -30 °C; after the addition, the mixture was gradually heated and refluxed at ca. 35 °C for 2 h. At -10 °C, dimethylphenylsilyl chloride (Shin-Etsu Silicon, Japan; 33.1 mL, 0.20 mol) was added dropwise; then the mixture was stirred at ambient temperature for 2 h. Water was added at 0 °C, and the reaction was worked up similarly to the case of monomer 2. Yield 45%; bp 95 °C/5 mmHg; purity 95% (GC). IR (neat) 3300 (s, $\nu_{\text{C-H}}$), 3050 (m), 2950 (s), 2860 (m), 2100 (m, $\nu_{\text{C}\equiv\text{C}}$), 1430 (m), 1250 (s, $\delta_{\text{Si-C-H}}$), 1105 (s), 820 (s, $\nu_{\text{Si-C}}$), 790 (m), 725 (m), 700 (m), 630 (m) cm⁻¹. ¹³C NMR (CDCl₃) δ 136.8 (C_{sp2-Si}) 133.9 (2C_O), 129.2 (2C_P), 127.7 (2C_M), 86.2 (C₂), 69.0 (C₁), 31.2 (C₄), 22.4 (C₅), 19.0 (C₃), 13.5 (C₆), -4.4 (Me-Si), -5.2 (Me'-Si).

Transition metal chlorides and organometallic compounds were commercially obtained and used without further purification.

Polymerization and analyses were carried out in the same manner as described in Chapter 5.

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Part III

**Polymerization and
Polymer Properties of
Fluorine-Containing Monosubstituted
Acetylenes**

Chapter 8

Polymerization and Polymer Properties of [2,5-Bis(trifluoromethyl)phenyl]acetylene

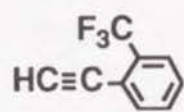
Abstract

[2,5-Bis(trifluoromethyl)phenyl]acetylene [BTFFPA; $\text{HC}\equiv\text{CC}_6\text{H}_3\text{-2,5-(CF}_3)_2$] polymerized with W, Mo, and Nb catalysts to produce methanol-insoluble polymers in high yields. The poly(BTFFPA) produced by the W(CO)_6 -based catalysts at 30 °C was soluble in $p\text{-(CF}_3)_2\text{C}_6\text{H}_4$, and had relatively high molecular weight ($[\eta] = 0.352 \text{ dL/g}$ in $p\text{-(CF}_3)_2\text{C}_6\text{H}_4$). The main chain of the polymer was composed of alternating double bonds, and the polymer was a dark brown solid. The temperature at which the weight loss of the polymer started in air was higher than 300 °C. The polymerization behavior and polymer properties for BTFFPA are compared with those for phenylacetylene and [*o*-(trifluoromethyl)phenyl]acetylene.

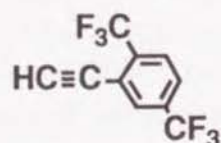
Introduction

Fluorine-containing polymers often show unique properties such as high thermal stability and resistance to chemicals.¹ Rather few fluorine-containing polyacetylenes, however, have been known, whose recent examples include; $\text{-(CH=C-}n\text{-C}_4\text{F}_9\text{)}_n$,² $\text{-(CMe=CC}_6\text{F}_5\text{)}_n$,³ poly[1-ethynyl-5-(trifluoromethyl)naphthalene].⁴

o-(Trifluoromethyl)phenylacetylene (*o*-CF₃PA) produced a soluble polymer whose weight-average molecular weight (\bar{M}_w) reaches 1×10^6 .^{5,6} This polymer is film-forming unlike poly(phenylacetylene), and possesses thermal stability higher than that of poly(phenylacetylene). In the polymerization of substituted acetylenes by group 5 and 6 transition-metal catalysts, a general tendency has been observed that when the substituent of monomer possesses suitable bulkiness, a high-molecular-weight polymer is formed.⁷ Further, it is expected that a polymer with high fluorine content shows unique properties. From these viewpoints, it is of interest to study the polymerization of phenylacetylenes having more than one CF₃ groups.



o-CF₃PA



BTfPA

In this chapter, the author investigated the polymerization and polymer properties of [2,5-bis(trifluoromethyl)phenyl]-acetylene (BTfPA). This monomer is featured by steric crowding and high fluorine content. The results obtained are compared with those for *o*-CF₃PA.

Results and Discussion

Polymerization

Table I summarizes results for the polymerization of BTfPA by group 5 and 6 transition-metal catalysts. When W catalysts such as WCl₆-Ph₄Sn and W(CO)₆-hv were used, methanol-insoluble polymers were obtained virtually quantitatively. Among Mo catalysts, MoCl₅-Ph₄Sn produced a polymer in high yield, while no polymer was obtained with Mo(CO)₆-based catalyst. Interestingly, NbCl₅-Ph₄Sn also produced polymer in good yield, and methanol-soluble part was cyclotrimers. It has been known that NbCl₅-based catalysts selectively give cyclotrimers from most monosubstituted acetylenes except those with bulky substituents.⁷ *o*-CF₃PA provides only cyclotrimers in

Table I
Polymerization of HC≡CC₆H₃-2,5-(CF₃)₂
by Various Catalysts^a

Catalyst	Monomer convn, %	Polymer ^b yield, %
WCl ₆ -Ph ₄ Sn	96	95
W(CO) ₆ -hv ^c	100	94 ^d
MoCl ₅ -Ph ₄ Sn	89	86
Mo(CO) ₆ -hv ^c	10	0
NbCl ₅ -Ph ₄ Sn ^e	100	73
TaCl ₅ -Ph ₄ Sn ^e	10	0

a Polymerized in toluene at 30 °C for 24 h; [M]₀ = 0.50 M, [cat] = [Ph₄Sn] = 20 mM.

b Methanol-insoluble part.

c Polymerized in CCl₄; [cat] = 10 mM.

d $[\eta] = 0.352$ dL/g (in *p*-(CF₃)₂C₆H₄, 30 °C).

e Polymerized at 80 °C.

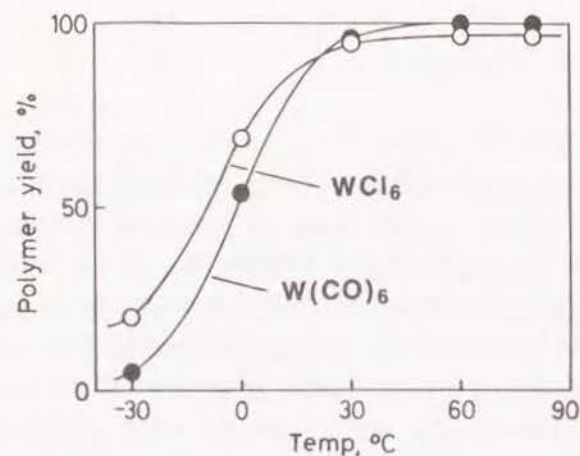


Figure 1. Effect of temperature on the polymerization of $\text{HC}\equiv\text{CC}_6\text{H}_3\text{-2,5-(CF}_3)_2$ ($\text{WCl}_6\text{-Ph}_4\text{Sn}$, in toluene, 24 h, $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{WCl}_6] = [\text{Ph}_4\text{Sn}] = 20 \text{ mM}$; in CCl_4 , $[\text{W(CO)}_6] = 10 \text{ mM}$ in the case of the W(CO)_6 -based catalyst).

the presence of NbCl_5 . Hence, it can be concluded that the meta CF_3 group of the present monomer sterically plays an important role in polymerization. The intrinsic viscosity of the polymer obtained with $\text{W(CO)}_6\text{-hv}$ at 30°C was 0.352 dL/g in $p\text{-(CF}_3)_2\text{C}_6\text{H}_4$ suggesting that the polymer has a relatively high molecular weight.

Figure 1 shows temperature dependences of the polymerizations by $\text{WCl}_6\text{-Ph}_4\text{Sn}$ and $\text{W(CO)}_6\text{-hv}$ both of which produced polymer in good yields. The polymer yield with these catalysts remained low at a low temperature of -30°C . In contrast, polymers were obtained virtually quantitatively at 30°C and above. Though the W(CO)_6 -based catalyst is generally less active than the WCl_6 -based catalyst, these catalysts show similar activities for the present monomer.

Table II shows solvent effects on the polymerization of BTFPA by $\text{WCl}_6\text{-Ph}_4\text{Sn}$. Polymers were obtained in good yields not only in toluene but also in chlorine- and fluorine-containing solvents. No substantial difference in the polymerization

Table II
Solvent Effects on the Polymerization of $\text{HC}\equiv\text{CC}_6\text{H}_3\text{-2,5-(CF}_3)_2$ by $\text{WCl}_6\text{-Ph}_4\text{Sn}^a$

Solvent	Monomer convn, %	Polymer ^b yield, %
toluene	96	95
$(\text{CH}_2\text{Cl})_2$	100	94
$\text{CCl}_2\text{FCClF}_2$	100	80
$m\text{-(CF}_3)_2\text{C}_6\text{H}_4$	100	78
PhOMe	25	0
PhCOMe	0	0

a Polymerized at 30°C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{WCl}_6] = [\text{Ph}_4\text{Sn}] = 20 \text{ mM}$.

b Methanol-insoluble part.

behavior was observed between the polymerization in $(\text{CH}_2\text{Cl})_2$ (nonsolvent of the polymer) and that in fluorine-containing solvents (relatively good solvents of the polymer). On the other hand, no polymer was obtained in oxygen-containing solvents such as anisole and acetophenone.

To compare the reactivity of the present monomer with that of $o\text{-CF}_3\text{PA}$, copolymerization of BTFPA with $o\text{-CF}_3\text{PA}$ was examined (Figure 2). $o\text{-CF}_3\text{PA}$ reacted faster than BTFPA. In general, a monomer with less bulky substituent is more reactive in the copolymerization of substituted acetylenes.⁷ Further, the ^{13}C NMR chemical shifts of acetylenic carbons of these monomers were similar to each other. Therefore, it can be said that the meta CF_3 group of BTFPA affected the copolymerization sterically to reduce its reactivity.

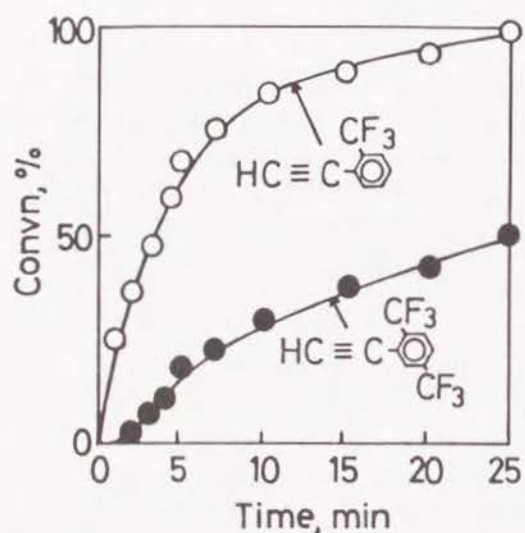


Figure 2. Copolymerization of $\text{HC}\equiv\text{CC}_6\text{H}_3\text{-}2,5\text{-(CF}_3)_2$ with $\text{HC}\equiv\text{CC}_6\text{H}_4\text{-}o\text{-CF}_3$ by $\text{WCl}_6\text{-Ph}_4\text{Sn}$ (in toluene, 30°C , $[\text{M}_1]_0 = [\text{M}_2]_0 = 0.50\text{ M}$, $[\text{WCl}_6] = [\text{Ph}_4\text{Sn}] = 20\text{ mM}$).

Structure and Properties of Polymer

The elemental composition of the polymer agreed well with the one for the addition polymerization products (Anal Calcd for $(\text{C}_{10}\text{H}_4\text{F}_6)_n$: C, 50.45; H, 1.67; F, 47.88. Found: C, 51.03; H, 1.43; F, 47.54).

Figure 3 exhibits the IR spectra of BTFFPA monomer and its polymer. The spectrum of the polymer shows no absorptions characteristic of the $\equiv\text{C-H}$ (3300 cm^{-1}) and $\text{C}\equiv\text{C}$ (2200 cm^{-1}) bonds which are seen in the spectrum of the monomer. Instead, an absorption due to the $\text{C}=\text{C}$ bond is observed at 1620 cm^{-1} in the polymer. The strong complicated band at $1350 - 1000\text{ cm}^{-1}$ are assignable to C-F stretching. Absorptions due to a 1,2,5-trisubstituted benzene are also seen at 780 and 700 cm^{-1} . The analytical and IR spectral data support that the main chain of the polymer is composed of alternating double bonds as shown in Figure 3.

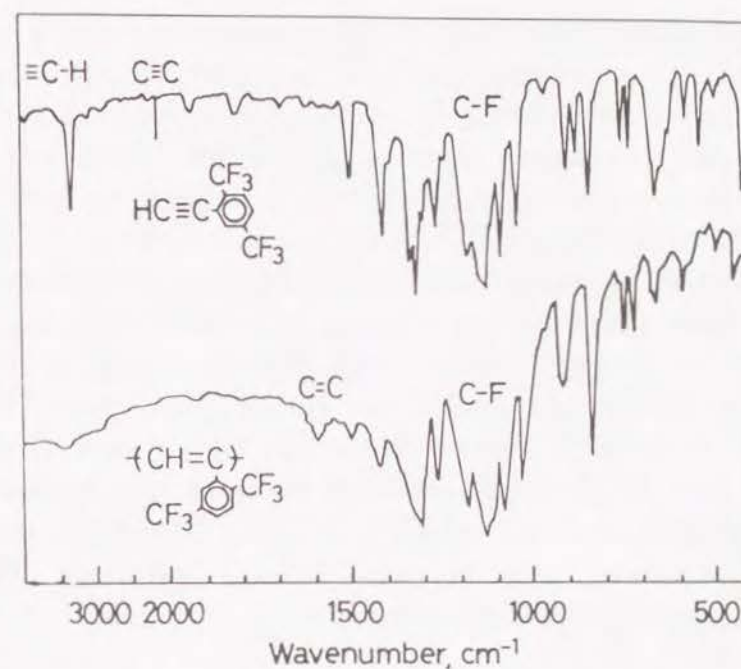


Figure 3. IR spectra of $\text{HC}\equiv\text{CC}_6\text{H}_3\text{-}2,5\text{-(CF}_3)_2$ and its polymer (KBr pellet).

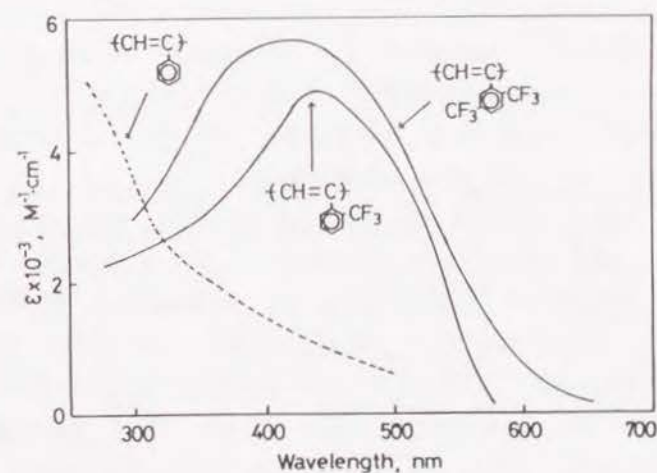


Figure 4. UV-visible spectra of poly(phenylacetylenes) (measured in tetrahydrofuran, but poly(BTFFPA) in $p\text{-(CF}_3)_2\text{C}_6\text{H}_4$).

The poly(BTFPA) obtained in the present study was a dark brown solid. The polymer produced with the $W(CO)_6$ -based catalyst was completely soluble in p -(CF_3) $_2C_6H_4$, though polymers obtained in other conditions were partly insoluble in this solvent. Regarding other solvents, poly(BTFPA) was partly soluble in tetrahydrofuran, C_6F_6 , and CCl_2FCClF_2 (soluble part 30 - 70%), virtually insoluble in hexane, $CHCl_3$, and $(CH_2Cl)_2$. The proportion of soluble part varied to some extent with the polymerization conditions. The polymer obtained with $W(CO)_6$ in CCl_4 at 30 °C was the most soluble (the soluble part in C_6F_6 was about 70%). Poly(*o*- CF_3 PA) is totally soluble in common organic solvents such as toluene and $CHCl_3$, but insoluble in some polyfluorinated hydrocarbons such as C_6F_6 and p -(CF_3) $_2C_6H_4$. The difference in solubility in these two polymers should originate from differences in the fluorine-content and the stiffness of the polymer chain.

Figure 4 shows the UV-visible spectrum of poly(BTFPA). An absorption maximum of the polymer lies at about 420 nm, and no absorption is seen above 680 nm. This absorption band is almost similar to that of poly(*o*- CF_3 PA), and is in a region of fairly long wavelength as compared with that of poly(phenylacetylene). Generally, the absorption maximum of an ortho-substituted phenylacetylene polymer shifts to longer wavelength with increasing bulkiness of the substituent.⁷ Poly(BTFPA) also exhibits this tendency.

Figure 5 shows results of thermogravimetric analysis (TGA) of the present and analogous polymers. Poly(phenylacetylene) begins to lose weight at a relatively low temperature of 200 °C. In contrast, the temperatures at which weight loss starts are 300 °C and 320 °C with poly(*o*- CF_3 PA) and poly(BTFPA), respectively. These polymers are thermally more stable than poly(phenylacetylene), because bulky CF_3 groups twist the main chain making the radical formation difficult and further preclude the reaction of the radical with oxygen.

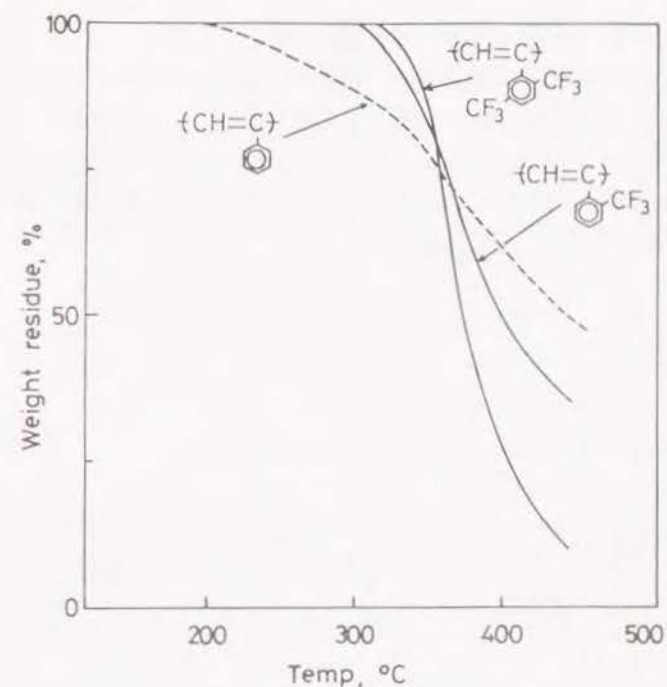
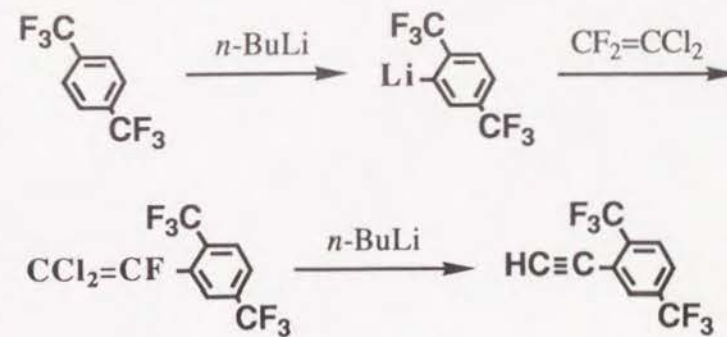


Figure 5. TGA curves of poly(phenylacetylenes) (in air, heating rate 10 °C/min).

Experimental

The monomer, BTFPA, was prepared according to the following procedure reported by Okuhara et al.:⁸



Overall yield 55%, bp 65 °C/30 mmHg, d^{20} 1.310

Transition metal chlorides and organometallic compounds were commercially obtained and used without further purification.

Polymerization and analyses were carried out in the same manner as described in Chapter 5.

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Chapter 9


Polymerization and Polymer Properties of (Perfluoro-*n*-alkyl)acetylenes

Abstract

(Perfluoro-*n*-alkyl)acetylenes ($\text{HC}\equiv\text{CR}_f$; $\text{R}_f = n\text{-C}_6\text{H}_{13}$, $n\text{-C}_4\text{H}_9$) polymerized with the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ catalyst to produce methanol-insoluble polymers in good yields. The intrinsic viscosities of the polymers (in C_6F_6) were ca. 0.05 dL/g, being relatively small. No large difference was observed between the polymerization in toluene (heterogeneous) and that in C_6F_6 (homogeneous). The main chain of the polymers was composed of alternating double bonds. These polymers were white solids soluble in C_6F_6 . The temperatures at which the weight loss of the polymers started were higher than 200 °C, which indicates improved thermal stability as compared with the corresponding poly(1-alkynes).

Introduction

Fluorine-containing polymers such as poly(tetrafluoroethylene) are known to show unique properties such as water and oil repellency, thermal stability, and resistance to chemicals. Thus far several polymers have been obtained from fluorine-containing aromatic acetylenes by using groups 5 and 6 transition-metal catalysts; e.g., poly(1-pentafluorophenyl-1-alkynes) (insol.),¹ poly[*o*-(trifluoromethyl)phenylacetylene] (high MW),^{2,3} poly[1-ethynyl-5-(trifluoromethyl)naphthalene] (medium MW).⁴

On the other hand, the polymerization of fluorine-containing aliphatic acetylenes is virtually restricted to a few examples as follows: polymerization of HC≡CCF₃ with PdCl₂/DMF or *n*-BuLi⁵ and of CF₃C≡CCF₃ with /KF,⁶ both of which only produce insoluble polymers.

1-Alkynes polymerized with WCl₆ catalysts in good yield.⁷ The polymer which is soluble in organic solvents such as toluene is not thermally stable. It is expected that thermal stability is improved if perfluoroalkyl group is introduced instead of alkyl group.

This chapter deals with the polymerization of (perfluoro-*n*-alkyl)acetylenes having relatively long perfluoroalkyl groups (HC≡CR_f; R_f = *n*-C₆F₁₃, *n*-C₄F₉). These monomers polymerized with WCl₆-Ph₄Sn catalyst to produce new polymers which are white, totally soluble in C₆F₆, and more stable than the corresponding poly(1-alkynes).

Results and Discussion

Polymerization of (Perfluoro-*n*-alkyl)acetylenes

Table I lists results for the polymerization of (perfluoro-*n*-hexyl)acetylene. When polymerization was carried out with

Table I
Polymerization of HC≡C-*n*-C₆F₁₃^a

Catalyst	Solvent	Monomer convn, %	Polymer ^b	
			yield, %	[η], dL/g ^c
WCl ₆ -Ph ₄ Sn	toluene	72	52	0.047
WCl ₆ -Ph ₄ Sn	CCl ₄	100	30	
WCl ₆ -Ph ₄ Sn	C ₆ F ₆	80	30	
WCl ₆ -Ph ₄ Sn	<i>m</i> -(CF ₃) ₂ C ₆ H ₄	25	15	
WCl ₆ -Ph ₄ Sn	CCl ₂ FCClF ₂	100	30	0.080
WCl ₆	toluene	24	0	
W(CO) ₆ -hv ^d	CCl ₄	0	0	
MoCl ₅ -Ph ₄ Sn	toluene	0	0	

a Polymerized at 30 °C for 24 h; [M]₀ = 0.50 M, [cat] = [Ph₄Sn] = 20 mM.

b Methanol-insoluble part.

c Measured in C₆F₆ at 30 °C.

d Polymerized in CCl₄; [cat] = 10 mM.

WCl₆-Ph₄Sn as catalyst in toluene solution, a methanol-insoluble polymer was obtained in ca. 50% yield. The methanol-soluble product was a mixture of linear oligomers and cyclotrimers. Apart from toluene as solvent, polymers could be obtained in CCl₄ and various fluorine-containing solvents. The polymer yields in these solvents, however, were 15 - 30%, being lower than that in toluene. The intrinsic viscosities of the polymers produced in toluene and CCl₂FCClF₂ were in the range of ca. 0.05 - 0.08 dL/g, indicating that the molecular weight of the polymers are rather low like poly(1-alkynes). The intrinsic viscosities of the polymers did not greatly change with the kind of polymerization solvents. It is noted that no substantial difference in the yield and molecular weight of polymer is

observable between toluene or CCl_4 (non-solvents of the polymer) and fluorine-containing solvents (relatively good solvents of the polymer). When WCl_6 alone was used as catalyst, or when $n\text{-Bu}_4\text{Sn}$, Ph_3SiH , Et_3SiH , Ph_3Bi , and Ph_3Sb were added as cocatalysts to WCl_6 , no methanol-insoluble polymer was obtained. No reaction occurred with $\text{W}(\text{CO})_6\text{-hv}$ or $\text{MoCl}_5\text{-Ph}_4\text{Sn}$. Ziegler-catalysts such as $\text{Fe}(\text{acac})_3\text{-3Et}_3\text{Al}$ and $\text{Ti}(\text{O-}n\text{-Bu})_4\text{-4Et}_3\text{Al}$ produced only methanol-soluble oligomers. Thus it has turned out that the effective catalyst for this monomer is restricted to $\text{WCl}_6\text{-Ph}_4\text{Sn}$.

Table II gives data for the polymerization of (perfluoro-*n*-butyl)acetylene, a homologue with a shorter perfluoroalkyl group. When the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ catalyst was used in conjunction with the solvents shown in the table, monomer was completely consumed and methanol-insoluble polymers were obtained in

Table II
Polymerization of $\text{HC}\equiv\text{C-}n\text{-C}_4\text{F}_9^a$

Catalyst	Solvent	Monomer convn, %	Polymer ^b	
			yield, %	$[\eta]$, dL/g ^c
$\text{WCl}_6\text{-Ph}_4\text{Sn}$	toluene	100	86	0.050
$\text{WCl}_6\text{-Ph}_4\text{Sn}$	C_6F_6	100	82	0.059
$\text{WCl}_6\text{-Ph}_4\text{Sn}$	$\text{CCl}_2\text{FCClF}_2$	100	76	0.062
$\text{W}(\text{CO})_6\text{-hv}^d$	CCl_4	0	0	
$\text{MoCl}_5\text{-Ph}_4\text{Sn}$	toluene	8	0	

a Polymerized at 30 °C for 24 h; $[\text{M}]_0 = 0.50$ M, $[\text{cat}] = [\text{Ph}_4\text{Sn}] = 30$ mM.

b Methanol-insoluble part.

c Measured in C_6F_6 at 30 °C.

d Polymerized in CCl_4 ; $[\text{cat}] = 10$ mM.

high yields around 80%. The intrinsic viscosities of the produced polymers were 0.05 - 0.06 dL/g, no large difference being observed irrespective of the kind of solvents.

Copolymerization of (perfluoro-*n*-hexyl)acetylene with 1-octyne by $\text{WCl}_6\text{-Ph}_4\text{Sn}$ catalyst was attempted (polymerization conditions: in toluene, 30 °C, 24 h, $[\text{M}_1]_0 = [\text{M}_2]_0 = 0.25$ M, $[\text{WCl}_6] = [\text{Ph}_4\text{Sn}] = 20$ mM). Consequently, 1-octyne was completely converted within 1 h, while (perfluoro-*n*-hexyl)acetylene was not consumed at all even after 24 h. Further, 1-(perfluoro-*n*-hexyl)-1-pentyne ($n\text{-C}_6\text{F}_{13}\text{C}\equiv\text{C-}n\text{-C}_3\text{H}_7$) was not consumed at all in the polymerization by $\text{MoCl}_5\text{-}n\text{-Bu}_4\text{Sn}$ catalyst⁸ (polymerization conditions: in toluene, 30 °C, 24 h, $[\text{M}]_0 = 0.25$ M, $[\text{WCl}_6] = [\text{Ph}_4\text{Sn}] = 20$ mM); it gives striking contrast to the fact that internal alkynes polymerize well in the presence of $\text{MoCl}_5\text{-}$ and/or $\text{WCl}_6\text{-}$ based catalysts.⁹ These results suggest that the coordinating ability of fluorine-containing acetylenes are inferior to that of the corresponding aliphatic acetylenes.

Structure and Properties of Polymers

The structure and properties of the present polymers did not essentially differ with polymerization conditions. Hence, the data for the polymer samples prepared with $\text{WCl}_6\text{-Ph}_4\text{Sn}$ in toluene will be described below.

The elemental analysis values for the polymers agreed fairly well with the values calculated for the addition polymerization products (e.g., Anal Calcd for $(\text{C}_8\text{H}_1\text{F}_{13})_n$: C, 27.91; H, 0.30; F, 71.80. Found: C, 28.30; H, 0.45; F, 70.21).

Figure 1 exhibits the IR spectra of (perfluoro-*n*-hexyl)acetylene and its polymer. The spectrum of the polymer shows no absorptions characteristic of the $\equiv\text{C-H}$ and $\text{C}\equiv\text{C}$ bonds which are clearly seen in the spectrum of the monomer. Instead, an absorption due to the $\text{C}=\text{C}$ bond is observed at 1620 cm^{-1} in the polymer. The strong complicated band at $1350 - 1000\text{ cm}^{-1}$ is due to C-F stretching. These analytical and IR spectral data

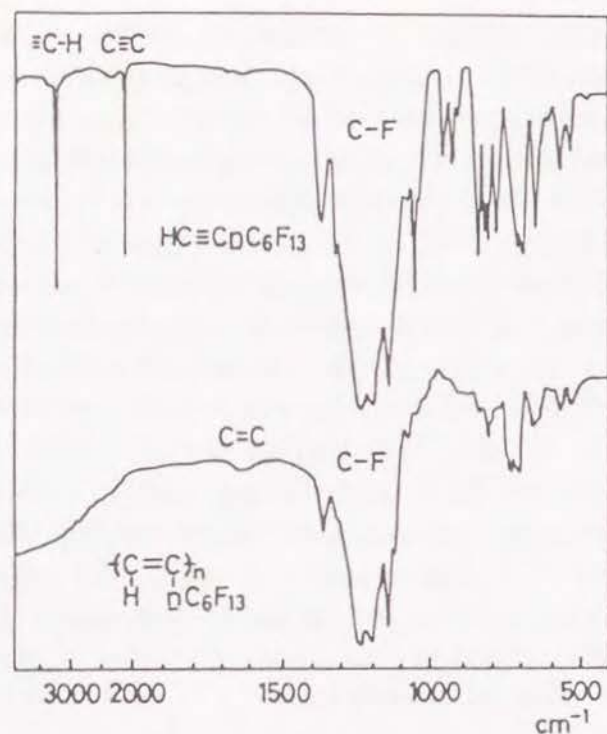


Figure 1. IR spectra of $\text{HC}\equiv\text{C}-n\text{-C}_6\text{F}_{13}$ and its polymer (KBr pellet).

indicate that the polymer has alternating double bonds along the main chain as shown in Figure 1.

The poly[(perfluoro-*n*-alkyl)acetylenes] obtained in the present study are white solids. These polymers completely dissolved in C_6F_6 , and were partly soluble in other fluorine-containing solvents such as $\text{CCl}_2\text{FCClF}_2$, but did not dissolve in hydrocarbons and ethers at all. Poly(1-alkynes), corresponding hydrocarbon polyacetylenes, are soluble in hydrocarbon solvents such as toluene. Thus it is evident that polymer solubility greatly differs owing to the presence or absence of the fluorine atoms.

TGA curves of poly[(perfluoro-*n*-alkyl)acetylenes] in air are shown in Figure 2. Poly(1-alkynes) have poor thermal stability;

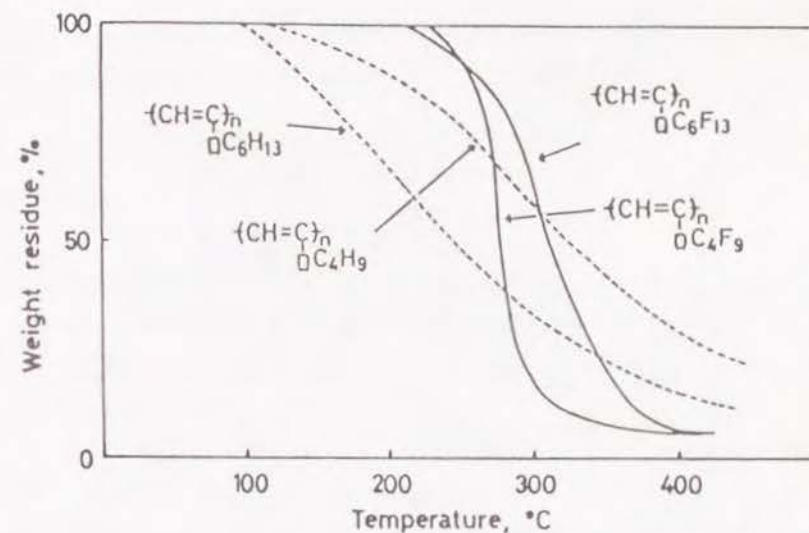


Figure 2. TGA curves of poly[(perfluoro-*n*-alkyl)acetylenes] (in air, heating rate $10\text{ }^\circ\text{C}/\text{min}$).

their weight loss starts below $150\text{ }^\circ\text{C}$ in TGA.⁹ In contrast, the temperatures at which these fluorine-containing polymers started to lose weight were fairly high ($220 - 230\text{ }^\circ\text{C}$), indicating enhanced thermal stability. It can be said that the present polymers have fairly good thermal stability among monosubstituted acetylene polymers because of bulkiness of the side chain and/or lack of H atom in the perfluoroalkyl groups.⁹

As shown in Figure 3, the UV-visible spectra of poly[(perfluoro-*n*-alkyl)acetylenes] exhibited an absorption maximum at around $250 - 300\text{ nm}$, and no absorption above 340 nm . These absorption bands are in a shorter wavelength region than are those of the corresponding poly(1-alkynes). This can be explained in terms that the bulky perfluoroalkyl groups twist the polymer backbone to reduce the extent of conjugation. These spectra correspond well with the fact that the present polymers

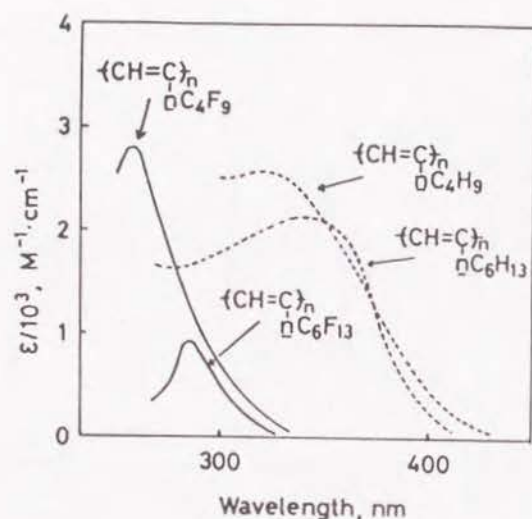


Figure 3. UV-visible spectra of poly[(perfluoro-*n*-alkyl)acetylenes] (measured in C_6F_6 or CCl_4).

are white, whereas the poly(1-alkynes) are yellow to orange. The absorption of the present polymers weakened with increasing length of perfluoroalkyl group.

The electrical conductivities of poly[(perfluoro-*n*-alkyl)acetylenes] were in the order of 10^{-17} S·cm $^{-1}$, indicative of typical electrical insulators.

Experimental

Monomers were offered by Japan Halon Co., Ltd.: $HC\equiv C-n-C_6F_{13}$ bp 96 °C/760 mmHg, purity [gas chromatography (GC)] 99%; $HC\equiv C-n-C_4F_9$ bp 47 °C/760 mmHg, purity (GC) 98%.

Transition metal chlorides and organometallic compounds were commercially obtained and used without further purification.

Polymerization and analyses were carried out in the same manner as described in Chapter 5.

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- Chapter 1 J. Am. Chem. Soc., **113**, 8548 (1991).
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- Chapter 2 J. Polym. Sci., Part A, Polym. Chem., submitted.
- Chapter 3 Polym. J., **23**, 1273 (1991).
- Chapter 4 Part of Chapters 1 and 2.
- Chapter 5 Macromolecules, **23**, 1374 (1990).
- Chapter 6 Polym. J., in press.
- Chapter 7 Macromolecules, **22**, 1036 (1989).
- Chapter 8 Polym. Bull., **23**, 505 (1990).
- Chapter 9 Polym. Bull., **20**, 343 (1988).

Other publications

1. Effects of Ultraviolet Irradiation on Substituted Polyacetylenes
J. Polym. Sci., Part A, Polym. Chem., **29**, 471 (1991).
2. Glow-Discharge-Induced Graft Polymerization of Acrylic Acid onto Poly[1-(trimethylsilyl)-1-propyne] Film
J. Appl. Polym. Sci., **43**, 423 (1991).

Acknowledgments

This thesis presents the studies which the author has carried out at the Department of Polymer Chemistry, Kyoto University, during the years from 1986 to 1991.

The author would like to express his sincere gratitude to Professor Toshinobu Higashimura for his continuous guidance, helpful suggestions, and encouragement throughout the course of this work.

Grateful acknowledgment is due to Associate Professor Toshio Masuda for his constant guidance, valuable suggestions, and encouragement.

The author wishes to express his gratitude to Dr. Mitsuo Sawamoto for his suggestions and discussions.

The author is indebted to Dr. Takeji Hashimoto and Mr. Kenji Saijo (Department of Polymer Chemistry, Kyoto University) for the measurement of X-ray diffraction, and to Dr. Takashi Kawamura (Gifu University) for the measurement of ESR.

Greatful thanks are due to Mr. Toshiyuki Hamano for his kind guidance in experimental techniques and discussions, and also to Messrs. Tatsuya Oshita and Shin-ichiro Katahira for their collaborations. Appreciations are also due to all of his colleagues in the Higashimura Laboratory for their invaluable suggestions.

Finally, the author heartily wishes to thank his parents, Toyoji Tsuchihara and Hiroko Tsuchihara, for their care and encouragement.

March, 1992

Kenji Tsuchihara