Synthesis and Properties of Fullerene-Containing Polymers with Well-Defined Structures

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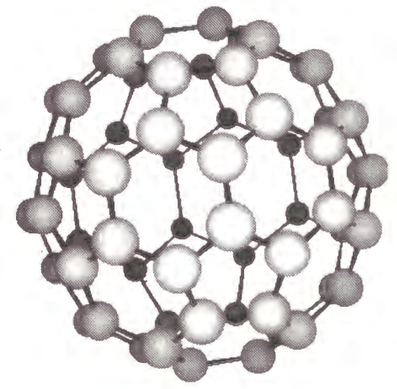
CONTENTS

GENERAL INTRODUCTION

1. Properties of Fullerene C_{60}

Fullerenes,[1] a new family of carbon allotropes, were discovered experimentally in 1985 by Kroto, Smalley, and Curl.[2] In contrast to the classical carbon allotropic forms such as graphite (planer sp^2) and diamond (tetrahedral sp^3), fullerenes have spherical structures composed of distorted sp^2-carbons and are soluble in some organic solvents. The second breakthrough in the fullerene research was achieved in 1990 by Krätschmer and Huffman, who discovered the macroscopic generation of fullerenes by resistive heating of graphite.[3] Since then, the physical properties and functionalization of fullerenes have vigorously been studied, particularly for the most abundant carbon sphere, buckminsterfullerene C_{60}. It should be noted that the 1996 Novel Prize in Chemistry was awarded to Kroto, Smalley, and Curl for their seminal discovery. The most spectacular findings for C_{60} and its derivatives include that upon suitable treatment they provide superconductors, organic ferromagnets, with non-linear optics materials, and bioactive materials with anti-HIV activity and DNA cleavage ability.



Fullerene C_{60}

However, C_{60} is only sparingly soluble in most organic solvents and insoluble in water; e.g., the solubility in common aromatic solvents like benzene and toluene is a few milligrams or less per milliliter. Thus, the poor processability of the fullerene is a major problem in the research and development for its practical applications. This obstacle could be, at least in part, surmounted by the functionalization chemistry of the fullerenes.

2. Polymeric Modification of C_{60}

In recent years, much attention has been paid to the chemical modification of fullerene C_{60} because of its potential applicabilities to advanced materials.[1,4]

The chemical reactivity of C_{60} is typical of a fairly localized, electron-deficient polyolefin. In fact it readily forms adducts with radicals and nucleophiles and participates thermal cycloaddition reactions as the electron-deficient dienophile. Therefore, incorporation of C_{60} into polymers is of considerable interest for the following reasons: (i) the fullerene properties can be combined with those of specific polymers, (ii) fullerenes covalently embedded in polymers become more easily processable, and (iii) the material properties are precisely tunable by designing the polymer architecture.

As shown in Figure 1, the fullerene-containing polymers reported so far can be classified into four types. The first type is the polymers containing the fullerene as a part of the main chain [(a), in-chain type].[5] The simplest way to incorporate fullerenes into the main chain may be radical or anionic copolymerization of an olefinic fullerene and a vinyl monomer. However, most of the products will be crosslinked and have ill-defined structures, because multiple additions to the fullerene double bonds randomly occur. Gügel et al. have demonstrated the synthesis of soluble C_{60}-in-chain polymer by the repetitive Diels-Alder reaction with employing functionalized bis-*o*-quinodimethanes.[6] In addition, the polycondensation reaction of C_{60}-based bifunctional monomers afforded pseudo C_{60}-in-chain polymers.

The second type is the polymers bearing pendant fullerenes [(b), on-chain type].[7] They are obtained by two main ways: (1) The reaction of C_{60} or a C_{60} derivative with a preformed polymer; and (2) polymerization or copolymerization of a monomer containing C_{60} residues. In the former, the addition reactions of C_{60} with amine, azide, or diene functions are usually employed. The third type is the fullerene-incorporated polymer networks [(c), cross-link type], where fullerene acts as a cross-linking site. They are

obtained either by a radical copolymerization of C_{60} and a vinyl monomer, as pointed out above, or by the reactions of polyfunctionalized C_{60} such as fullerenols, $C_{60}(OH)_n$, with telechelic polymers.[8] The fourth type is the polymers having one or two fullerene end units [(d), end-chain type].[9] Frey et al.[9a] prepared a C_{60} end-capped polystyrene by the reaction of C_{60} with an amino-terminated polystyrene. This polymer had a well-defined structure, e.g., the low polydispersity and the controlled molecular weight, because its precursor was prepared by living polymerization.[10] Star-shaped polymers with a C_{60} core and polystyrene or polyacrylonitrile arms were also prepared based on the living polymerization technique.[9b] Another well-controlled structure can be found in the dendrimer-modified C_{60} derivatives.[9c]

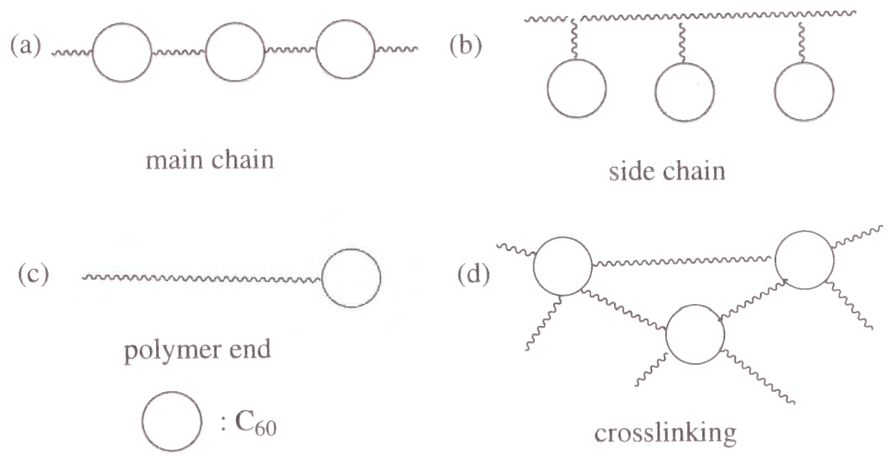


Figure 1. Schematic representations of C_{60}-containing polymers.

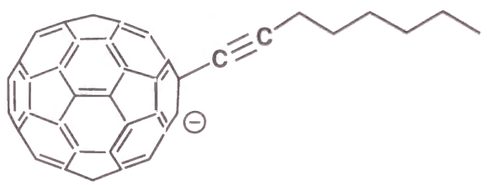
3. C_{60}-Containing Polymers with Well-Defined Structures

The incorporation of fullerenes into polymers potentially endows the products with most of the fullerene properties. In the use of such fullerene-containing polymers as functional materials in a wide variety of scientific fields, one should precisely control their

structures to make them function most effectively. In other words, well-controlled structures are indispensable for precise tuning of the materials properties of C_{60}-containing polymers.

Living polymerizations[10] are among the most effective, versatile and straightforward methods for the controlled synthesis of polymers. Therefore, these techniques are expected to be applicable to the controlled synthesis of fullerene-containing polymers.

To realize this, in this thesis two principal approaches were adopted: One is the reaction of 1-octynyl-C_{60} anion (**1**) with living vinyl ether oligomers obtained by living cationic polymerization,[11] and the other is the reaction of C_{60} with living polymer radicals prepared by the nitroxide-mediated 'living' radical polymerization.[12]



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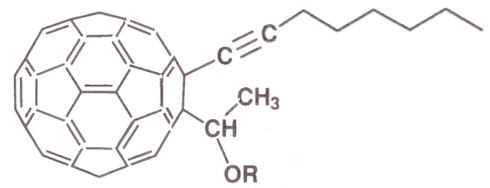
Another effective method for the synthesis of C_{60}-containing polymers with well-defined structure is the use of regioselective reactions. A preliminary study in this line will be reported herein on the synthesis of C_{60}-bearing polysaccharides.

4. Outline of This Thesis

This thesis consists of three parts: **Part I** (Chapter 1-3) deals with the synthesis of C_{60} end-capped vinyl ether (VE) oligomers by living cationic polymerization and their solubility behavior. **Part II** (Chapter 4-6) concerns the synthesis of C_{60} derivatives with a pair of styrene-based polymer arms by the nitroxide-mediated 'living' radical polymerization and their solubility characteristics. **Part III** (Chapter 7) describes the

synthesis of non-ionic water-soluble C_{60}-bearing polysaccharides by regioselective reactions and their water solubility.

In **Chapter 1**, disubstituted 1,2-dihydro[60]fullerenes (**2**) having functional groups such as ester are synthesized by the electrophilic addition of vinyl ether (VE)-hydrochloric acid adducts to the mono-octynylfulleride anion. The products are fully characterized by UV-vis, ^{1}H and ^{13}C NMR spectroscopy and subjected to cyclic voltammetry to examine their redox properties.



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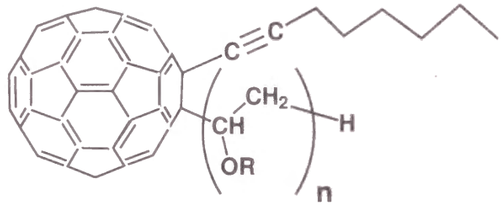
Chapter 2 focuses on the synthesis of C_{60} end-capped VE oligomers (**3**) with well-controlled structures in a similar manner as shown in Chapter 1. In this chapter, however, are employed the oligomeric electrophiles of aliphatic and functionalized VEs obtained by the living cationic polymerization. The UV-vis, ^{1}H, and ^{13}C NMR spectroscopy are performed on the structural verification of the products. It is expected that such C_{60}-containing oligomers are effective in homogeneously dispersing C_{60} in a polymer matrix. In order to experimentally demonstrate this for C_{60} end-capped VE oligomers, blend films are cast from their solutions and subjected to microscopic observation.



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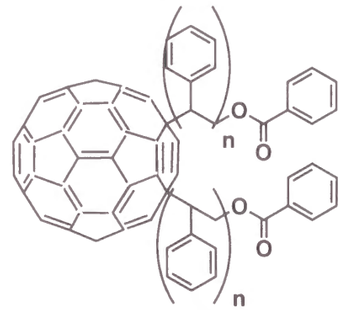
In **Chapter 3**, an attempt was made to synthesize highly water-soluble C_{60} end-capped VE oligomers with well-defined structures. To this end, ester-carrying VEs are employed for precursor synthesis. Namely, the precursor oligomers are synthesized by living cationic polymerization as described in the preceding chapters. Hydrolysis of the precursors' ester pendant groups affords the water-soluble oligomers with hydroxyl and carboxyl groups, respectively. The structural analyses of the precursor and the hydrolysis products are performed by UV-vis, ^{1}H and ^{13}C NMR spectroscopy. The saturation solubility of the C_{60} end-capped oligomers is estimated and compared to those of the water-soluble C_{60} derivatives hitherto reported.

Part II describes an alternative methodology for the controlled synthesis of C_{60}-containing polymers, where C_{60} is chemically modified with reactive polymers prepared through the nitroxide-mediated 'living' radical polymerization. This strategy is simple, versatile and suited for large-scale synthesis compared to the method based on the living cationic polymerization, and enables us to prepare a series of C_{60}-containing polystyrene derivatives with different molecular weights and/or pendant functions. With these samples, the relationships between the physical properties and chemical structure can be examined.

In **Chapter 4** is described the first report of the controlled synthesis of 1,4-disubstituted C_{60} polymer derivatives by the nitroxide-mediated radical mechanism.

TEMPO (2,2,6,6-tetramethyl-piperidinyl-1-oxy) end-capped polystyrenes with low polydispersity indices, which can be separately prepared by the nitroxide-mediated 'living' radical polymerization, are allowed to react with an excess molar amount of C_{60} in *o*-dichlorobenzene at 145 °C. The resultant 1,4-dipolystyryldihydro[60]fullerenes (**4**) are fully characterized by various spectroscopic methods. A possible mechanism by which disubstituted derivatives are preferentially produced is discussed on the basis of the model reaction employing 2-benzoyloxy-1-phenylethyl adduct with TEMPO, a low-mass model compound as a radical source.



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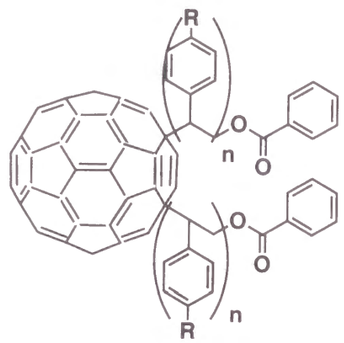
The solubility of the C_{60}-substituted polymers plays a significant role in their application in materials science and technology. Thus, **Chapter 5** focuses on the solubility and aggregation characteristics of 1,4-disubstituted C_{60} polymer derivatives (**5**) with well-controlled structures. To this end, the author synthesized a series of styrene-based C_{60} derivatives having two polymer arms where chain lengths, pendant functions and block copolymer sequence vary. The solutions of **5** in organic solvents are subjected to size exclusion chromatography (SEC), light scattering (LS), and UV-vis analyses. The structure-solubility relationship will be discussed in terms of the micellization behaviors in organic solvents. The saturation solubility (S_{C60}) of the C_{60} moiety in the polymers is

evaluated as a measure of the extent of solubilization by derivatization.



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In **Chapter 6** is examined the chain length dependence of C_{60}-substituted polymers on the miscibility with their parent homopolymers. As in solution, the miscibility of C_{60} compounds with polymers is presumed to be closely related to their micellization behavior. In this study, the micellization behavior of the 1,4-disubstituted C_{60} polystyrene derivatives in polystyrene matrix is followed by measuring the absorption changes in UV-vis spectra which are characteristic of the aggregation of C_{60} moieties.

Part III (Chapter 7) describes the synthesis of non-ionic water-soluble pullulans bearing pendant C_{60} using the cycloaddition reaction of azide-substituted pullulans and their water solubility. The azide-substituted pullulans can be prepared from regioselectively chlorinated pullulans. The products are characterized by IR, UV, and NMR spectroscopy, and their water solubility is examined in terms of the degree of substitution.

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Part I

Synthesis and Properties of C_{60} End-Capped Vinyl Ether Oligomers by Living Cationic Polymerization

Chapter 1

Synthesis and Characterization of Disubstituted C_{60} Derivatives with Functionalized Vinyl Ether Moieties

ABSTRACT

The author reports the preparation of disubstituted 1,2-dihydro[60]fullerenes having functional groups, namely 1-(1-octynyl)-2-(1-isobutoxyethyl)-1,2-dihydro[60]fullerene and 1-(1-octynyl)-2-[1-(2-acetoxyethoxy)ethyl]-1,2-dihydro[60]fullerene, by coupling 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion with carbon electrophiles derived from vinyl ethers. The structure and redox properties of the products were examined by ^{1}H and ^{13}C NMR spectra and cyclic voltammetry.

INTRODUCTION

Low solubility and poor processability are two major disadvantages of [60]fullerene in the application to advanced materials. In order to overcome these disadvantages, various chemical modifications of fullerene have extensively been studied.[1] However, only a few studies have been reported on the disubstituted derivatives of 1,2-dihydro[60]fullerene with well-defined structure.[2-5] Such derivatives are advantageous in that not only the solubility is improved but also two different functional groups could be incorporated.

Recently, Murata et al. have succeeded in preparing a stable carbanion of a C_{60} derivative with the well-defined structure, i.e., 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion.[3] The precursor of this anion can be synthesized in high yield, and the anion can be generated quantitatively. It was expected to obtain C_{60} derivatives having two organic addends, especially those with functional groups, by addition of electrophilic species having a functional group to this carbanion.

This chapter focuses on the establishment of new synthetic routes to introduce electrophilic species into a C_{60} moiety. This reaction will be easily extended to end-type C_{60} polymer derivatives with well-defined structure using electrophilic species obtained by living cationic polymerization of vinyl ethers.[6]

In this chapter, the author reports the preparation of such disubstituted 1,2-dihydro[60]fullerenes having functional groups by coupling 2-(1-octynyl)-1,2-dihydro[60] fulleren-1-ide ion with carbon electrophiles derived from vinyl ethers. The structure and redox properties of the products were examined by ^1H and ^{13}C NMR spectra and cyclic voltammetry.

EXPERIMENTAL

Measurements

NMR spectra were observed at 400 MHz for ^1H and 75 MHz and 67.5 MHz for ^{13}C NMR. Cyclic voltammetry was conducted using a three-electrode cell with a glassy carbon working electrode, a platinum counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The potential was read with respect to ferrocene added as an internal standard.

Materials

C_{60} was separated from a commercial C_{60} /C_{70} mixture (ca. 80:20 by weight; Term Co.) by the use of a Norit carbon-silica gel column eluted with toluene. THF was freshly distilled from sodium benzophenone ketyl before use. AcOVE was prepared as reported previously.[7] Hexane, IBVE, and AcOVE were distilled over CaH_2. Benzonitrile was distilled from P_2O_5. Reactions were conducted under nitrogen atmosphere in predried glassware. 1-(1-Octynyl)-1,2-dihydro[60]fullerene (**1**) was prepared according to the literature method.[3] The IBVE-HCl adduct (**3a**) and AcOVE-HCl adduct (**3b**) were prepared by bubbling HCl gas to the corresponding IBVE hexane solutions of vinyl ethers in hexane.[7,8]

1-(1-Octynyl)-2-(1-isobutoxyethyl)-1,2-dihydro[60]fullerene (4a)

A solution of 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion (**2**) was prepared by adding 0.16 mL (0.0144 mmol) of 0.0881 N *t*-BuOK in THF to a stirred solution of **1** (12.33 mg, 0.0144 mmol) in 20 mL of THF at room temperature and stirring the mixture for 15 min at 0 °C.[3] To a vigorously stirred solution of **2** was added a 1.4 N solution of **3a** in hexane (0.06 mL, 0.084 mmol) dropwise over 2 min. After the reaction of 2 h, the resulting brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluting with hexane. From the first fraction was obtained unreacted **1** (3.44 mg, 31 %). From the second fraction was isolated the product **4a** (4.33 mg, 39 %) as a dark brown solid: ^1H NMR (400 MHz, $CDCl_3$)

δ 5.72 (q, 1H), 3.80 (m, 1H), 3.69 (m, 1H), 2.60 (t, 2H), 2.27 (d, 3H), 2.07 (m, 1H), 1.83 (quint, 2H), 1.61 (quint, 2H), 1.41 (m, 6H), 1.04 (d, 6H), 0.94 (t, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 155.16, 154.44, 154.18, 152.74, 148.04, 147.85, 147.82, 147.68, 147.59, 146.47, 146.41, 146.27, 146.24, 146.20, 146.19, 149.14, 146.01, 145.92, 145.45, 145.43, 145.39, 145.31, 145.28, 145.26, 145.14, 145.04, 144.79, 144.68, 144.66, 144.57, 143.10, 143.09, 143.06, 142.60, 142.57, 142.34, 142.20, 142.14, 142.13, 142.06, 141.89, 141.63, 141.61, 141.46, 141.33, 141.18, 140.32, 140.20, 139.27, 138.78, 135.71, 135.22, 134.08, 134.01 (54 signals, sp^2-carbons in the C_{60} core), 85.71 (C≡C), 80.52 (CHO), 80.44 (C≡C), 76.76 (CH_2O), 71.32, 59.02 (quaternary sp^3-C in the C_{60} core), 31.43, 29.70 (CH_2), 29.18 (CH), 28.96, 22.67 (CH_2), 20.54, 19.77 (CH_3 in IBVE), 19.65 (CH_2), 14.12 (CH_3); UV-vis (cyclohexane) λ_{max} 213 nm (log ε 5.13), 256 (5.08), 328 (4.58), 432 (3.61), 702 (2.68); MS (DCI^-) *m/z* 930, (M^-), 720, (C_{60}^-).

1-(1-Octynyl)-2-[1-(2-acetoxyethoxy)ethyl]-1,2-dihydro[60]-fullerene (4b)

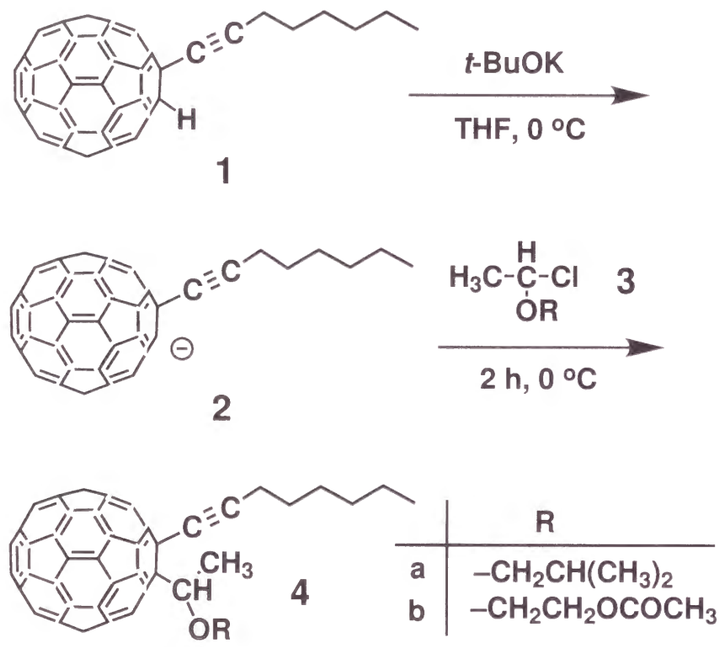
Similarly, a solution of 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion (**2**) was prepared by adding 0.63 mL (0.046 mmol) of 0.0725 N *t*-BuOK in THF to a stirred solution of **1** (38.11 mg, 0.046 mmol) in 40 mL of THF at room temperature and stirring for 15 min at 0 °C. To a vigorously stirred solution of **2** was added a 0.70 N solution of **3b** in hexane (0.4 mL, 0.28 mmol) dropwise over 2 min. After 2 h, the brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluting with hexane. From the first fraction was obtained unreacted **1** (7.90 mg, 18 %). From the second fraction was isolated the product **6** (23.70 mg, 54 %) as a dark brown solid: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.80 (q, 1H), 4.39 (m, 2H), 4.20 (m, 2H), 2.62 (t, 2H), 2.29 (d, 3H), 2.04 (s, 3H), 1.82 (quint, 2H), 1.61 (quint, 2H), 1.41 (m, 6H), 0.94 (t, 3H); ^{13}C NMR(75 MHz, CD_2Cl_2) δ 170.41 (CO), 154.87, 154.12, 153.36, 152.15, 147.72, 147.71, 147.52, 147.40, 147.28, 146.18, 146.17, 145.96, 145.92, 145.90, 145.85, 145.71, 145.62, 145.10, 145.09, 145.05, 144.95, 144.93, 144.72, 144.64, 144.45, 144.37, 144.28, 144.19, 142.80, 142.74, 142.31, 142.29, 142.03, 141.84, 141.79, 141.52, 141.43, 141.31, 141.28, 141.19, 141.04, 140.91, 140.01, 139.91, 139.86, 138.91, 138.55, 135.52, 135.18, 133.73, 133.67 (51 signals, sp^2-carbons in the C_{60} core), 85.93 (C≡C), 80.92 (CHO), 79.83 (C≡C), 70.87 (quaternary sp^3-C in the C_{60} core), 68.04, 63.31 (CH_2O), 58.70 (quaternary sp^3-C in the C_{60} core), 31.38, 28.61 (CH_2), 28.46 (CH_3CO), 28.37, 22.33 (CH_2), 20.30 (CH_3 in AcOVE), 19.17 (CH_2), 13.54 (CH_3); UV-vis (cyclohexane) λ_{max} 213 nm (log ε 5.13), 255 (5.08), 328 (4.58), 432 (3.61), 701 (2.68); MS (DCI^-) *m/z* 829, (M^- – AcOVE), 720, (C_{60}^-).

RESULTS AND DISCUSSION

Synthesis of Disubstituted Derivatives of 1,2-Dihydro[60]fullerene

Disubstituted derivatives of 1,2-dihydro[60]fullerene, **4a** and **4b**, were prepared by addition of carbon electrophiles **3**, derived from vinyl ethers, to 2-(1-octynyl)-1,2-dihydro-[60]fulleren-1-ide ion as shown in Scheme 1. 2-(1-Octynyl)-1,2-dihydro[60]-fulleren-1-ide ion (**2**) was generated by deprotonation of 1-(1-octynyl)-1,2-dihydro[60]-fullerene prepared according to the method of Murata et al.[3] The electrophiles **3** were prepared by bubbling HCl gas into the hexane solution of corresponding vinyl ether (VE), i.e., isobutyl vinyl ether (IBVE) and 2-acetoxyethyl vinyl ether (AcOVE) at 0 °C.[6,7] To a dark green solution of 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion **2** in THF was slowly added 6 equiv of a hexane solution of VE-HCl adduct **3** with vigorous stirring. After the reaction of 2 h, the resulting brownish solution was quenched with methanol and subjected to the chromatographic separation using hexane as eluent. The products **4a** and **4b** were obtained as dark brown powders in 39% and 54% yield, respectively. The addition of the electrophile having a more polar substituent seems to give the product in a higher yield. The starting material **1** was recovered in 31% and 18%, respectively. The C_{60} derivatives with two organic addends, **4a** and **4b**, are soluble not only in nonpolar organic solvents

such as toluene, $CHCl_3$ and CS_2, but also in polar organic solvents such as THF in a considerably high concentration of at least 34 mg of **4b**/mL as an example. Thus, the structural modification in the present study was found to be an effective means for improvement on solubility of the [60]fullerene derivatives.



Scheme 1

Structural Identification

In previous studies, the positional selectivity in the addition of the electrophile to C_{60} carbanion having an organic addend was shown to be highly dependent on the organic group already present on the C_{60} core. In the case of 2-*tert*-butyl-1,2-dihydro[60]fulleren-1-ide ion, a stable carbocation such as the tropylium ion was found to add at the 4-position.[5] In contrast, in the case of 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion, simple alkyl group such as methyl and ethyl groups add at the 2-position, while tropylium ion adds at both the 2- and 4-positions and benzoyl group adds selectively at the 4-position.[3] Thus, it is of considerable interest to examine which mode of addition would occur for the present electrophiles.

As shown in Figure 1, the UV-vis spectra of both **4a** and **4b** exhibited an absorption pattern with a sharp absorption at around 430 nm, which is diagnostic of the C_{60} derivative with two organic groups attached at the 1,2-positions of the 6,6-juncture bond.

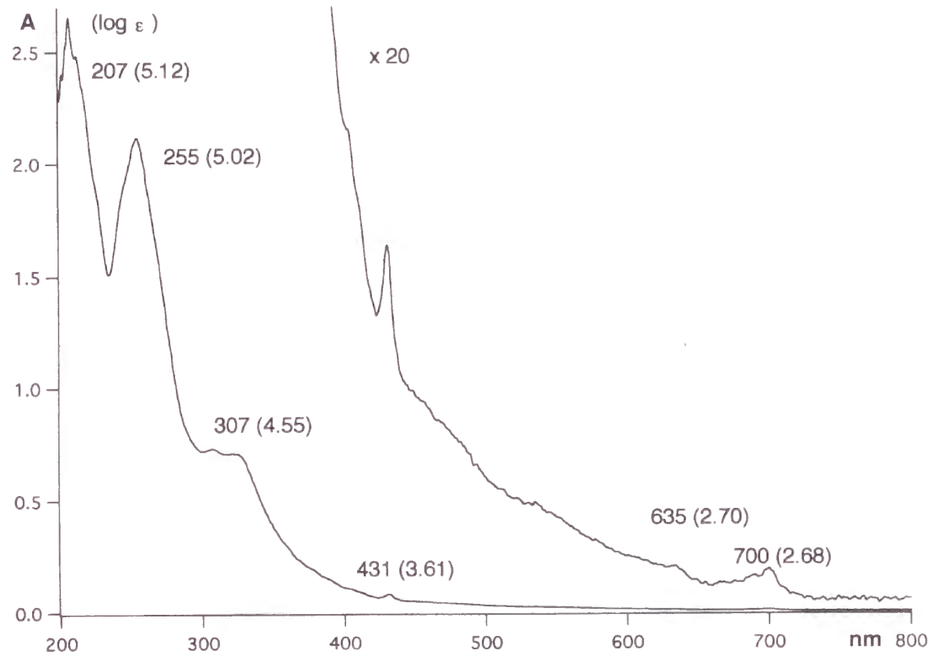


Figure 1. UV-vis spectrum of the product **4a** (2.04×10^{-5} M in cyclohexane). Compound **4b** showed a similar spectrum.

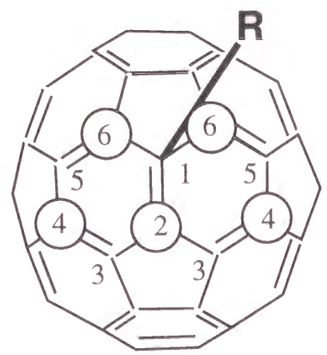


Figure 2. Schematic presentation of reaction sites.

The ^{1}H NMR spectrum of **4a** was shown in Figure 3. The signal intensity of α proton for alkyne group (**f**) is twice larger than that of methine (**b'**) protons of the 1-isobutoxyethyl group of **4a**, which confirmed the formation of 1 to 1 adduct and the product **4a** was a single isomer. The methyl (**a'**) and methine (**b'**) protons of **4a** exhibited a marked downfield shift for the alkoxyethyl group, (δ 5.72 and 2.27, respectively) as compared with those of 1-isobutoxyethyl chloride, i.e., IBVE-HCl adduct **3a** (δ 5.69 and 1.70, respectively). This is attributed to the deshielding effect of the C_{60} core[8] and also to the triple bond attached in close proximity.

The ^{13}C NMR spectrum exhibited signals for one pair of acetylenic carbons (δ 85.71, 80.52), sp^3 carbons in the C_{60} core (δ 71.32, 59.02), and sp^3 carbons in the octynyl and alkoxy groups, and, most importantly, partly overlapped 58 signals for the sp^2 carbons of the C_{60} core (Figure 4). The similar general features were also observed in the ^{1}H and ^{13}C NMR spectra of **4b**.

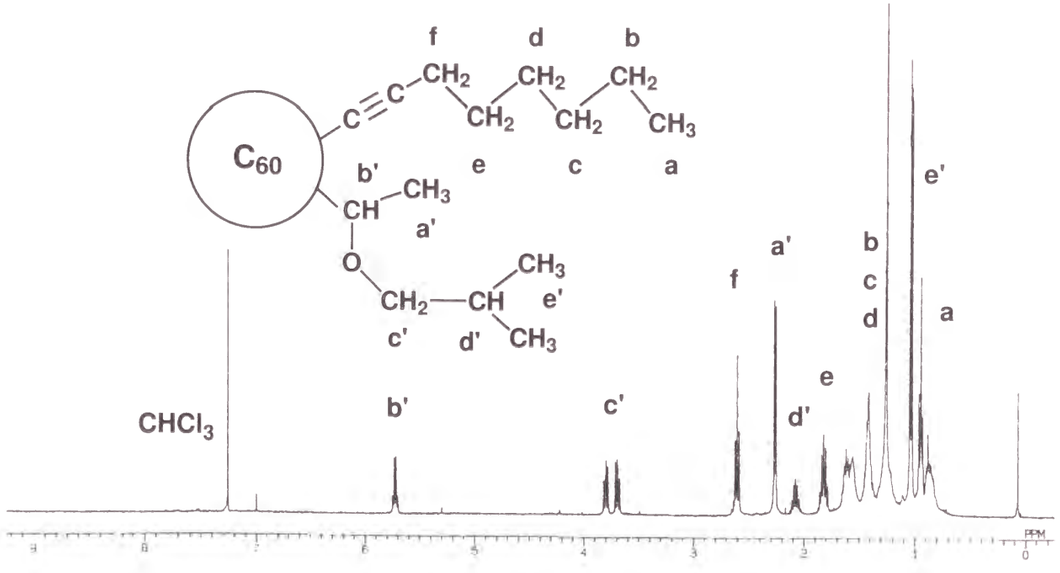
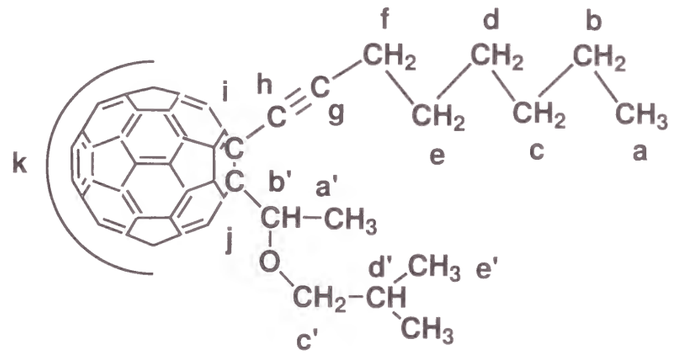


Figure 3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the product **4a**.



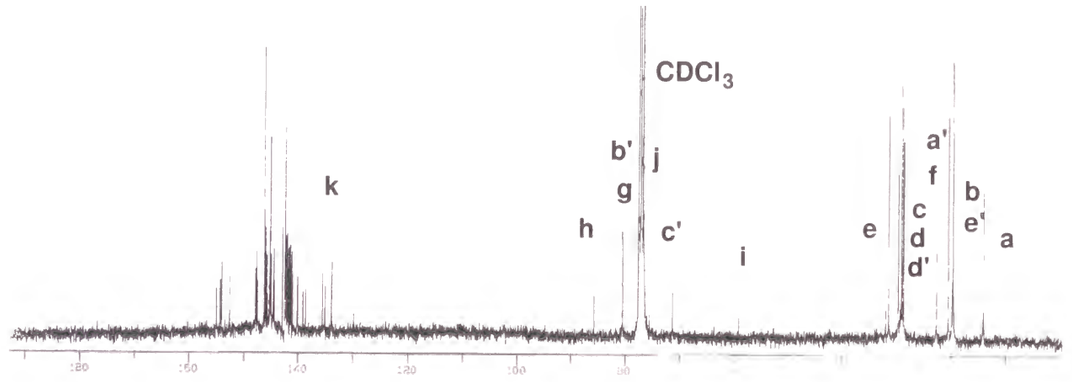
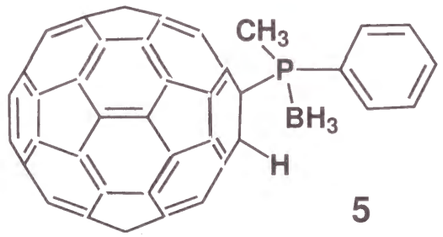


Figure 4. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of the product **4a**.

The most C_{60} derivatives so far reported to have two different organic groups at the 1,2-positions of the 6,6-juncture bond, have a C_s symmetry with the plane of symmetry bisecting the C_{60} core along the 6,6-bond. In contrast, the 1,2-bisadducts, **4a** and **4b**, of the present study do not have the C_s symmetry due to the asymmetric carbon of the 1-alkoxyethyl group directly attached to the C_{60} core, and therefore exhibit nearly 60 signals for the sp^2 carbons of the C_{60} core. The similar phenomenon is observed in the case of the C_{60} derivative having a chiral phosphine-borane moiety such as in **5**.[10] Thus, from all the spectral data, the products in the present study are concluded to have the two organic groups at the 1,2-positions of the 6,6-juncture bond.

Figure 5 shows a negative chemical ionization mass spectrum of the product **4a**, A molecular ionization peak (M^-) was clearly observed at *m/z* = 930, which indicates the formation of **4a**. In the case of the product **4b**, on the other hand, the molecular ionization peak could not be observed while the small peak of *m/z* = 829, which corresponds to M^- – AcOVE, was observed because of its unstability.



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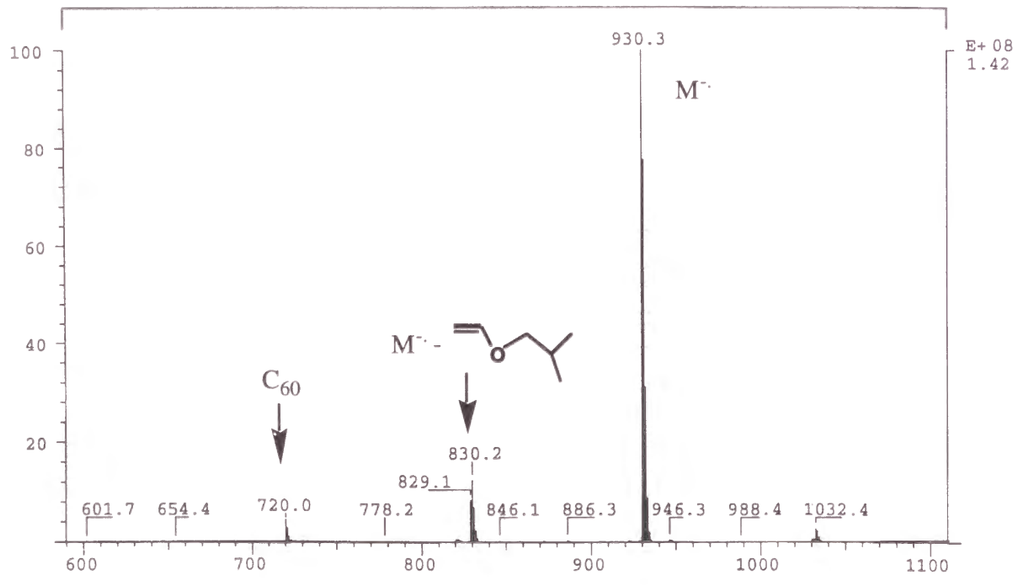

Figure 5. DCI⁻ mass spectrum of the product **4a**.

Redox Properties

The redox properties of the newly obtained **4a** and **4b** were examined by cyclic voltammetry in benzonitrile (Figure 6). The voltammograms exhibited a single irreversible oxidation peak and three reversible reduction waves as in the case of C_{60}. The results are shown in Table 1. The reduction potentials of **4a** and **4b** were more negative by slightly more than 0.1 V as have been commonly observed for the disubstituted 1,2-dihydro[60] fullerenes.[11]

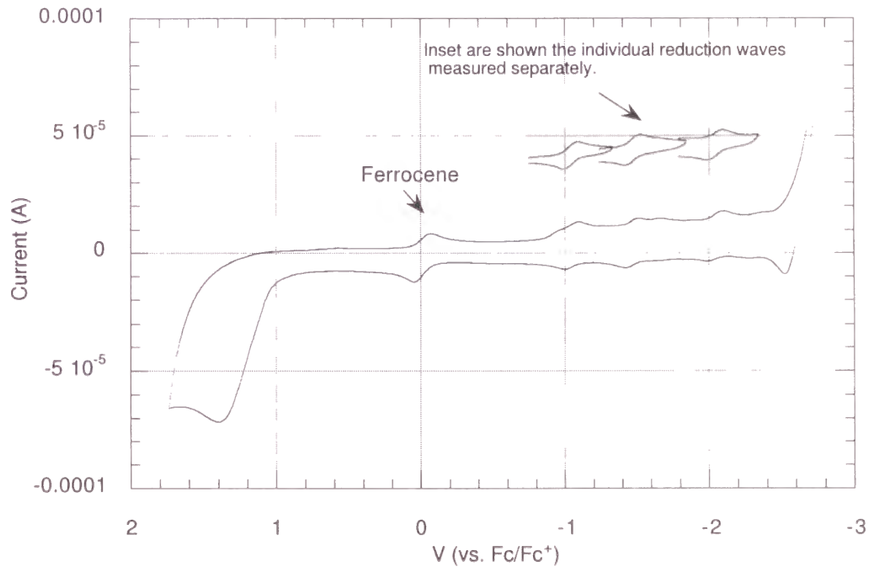

Figure 6. Cyclic voltammogram of the product **4a**.

Table 1. Results of Cyclic Voltammetry[a]

compound	E_{ox} irreversilble peak potential	reversible, $E_{1/2}$		
		E_{red}^1	E_{red}^2	E_{red}^3
C_{60}	+1.41	-0.93	-1.36	-1.85
4a	+1.43	-1.05	-1.48	-2.05
4b	+1.44	-1.04	-1.46	-2.01

[a] Potential in volts vs ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0.05 M) as a supporting electrolyte; scan rate, 0.1V s^{-1}.

It is of interest to note that the alkyl chlorides, the reactivity of which is generally lower than bromides or iodides, smoothly reacted with anion **2**. The presence of the alkoxy group, which has the strong ability to polarize the C-Cl bond, must be responsible to this high reactivity. These results clearly demonstrated that the VE-HCl adducts can react with the carbanion of a C_{60} derivative to give a 1,2-bisadduct with a well-defined structure. As an extension of this reaction, the synthesis of C_{60} end-capped vinyl ether polymers with well-defined structure will be reported in the next chapter.

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Chapter 2

Synthesis and Properties of C_{60} End-Capped Alkyl Vinyl Ether Oligomers with Well-Defined Structures

ABSTRACT

This chapter concerns the synthesis of C_{60} end-capped vinyl ether (VE) oligomers with well-defined structure by living cationic polymerization technique. The VE oligomers bearing C_{60} at the chain end were prepared by addition reaction between mono-octynylfulleride anion and living cationic VE oligomers. Living oligo (isobutyl vinyl ether) (IBVE) and oligo (methyl vinyl ether) (MVE) were synthesized using $CH_3CH(O\textit{i}Bu)Cl/ZnI_2$ as initiating system. The C_{60} end-capped VE oligomers were obtained as dark brown gummy solid in 28% for IBVE and 34% for MVE. The UV-vis and ^{13}C NMR spectra indicated the formation of C_{60} end-capped oligomers via 1,2-addition reaction. It was also found that the films of blends of C_{60} end-capped oligomers with poly (IBVE) and polystyrene (5 wt% C_{60}) are homogeneous on a micron scale and transparent, resulting from a good dispersion of C_{60} in the polymer matrix.

INTRODUCTION

In recent years, much attention has been paid to the chemical transformation of fullerene C_{60} because of its potential applications to advanced materials.[1,2] Incorporation of the C_{60} molecules into polymer chains is gaining interest as one of the effective methods for improving the processability of fullerene.[3-7]

As described in the General Introduction, fullerene-containing polymers reported so far can be classified into four types, i.e., in-chain type,[3] on-chain type,[4] cross-link type,[5] and end-chain type.[6,7] The fullerene is prone to undergo nucleophilic reactions.[8] However the addition of nucleophiles to C_{60} molecules sometimes results in the formation of a mixture of polyadducts, which are different in both the number of addends and the positions of addition. Thus, it is of great importance and interest to prepare the fullerene-containing polymers with well-defined structures.[6]

Recently Murata et al. reported the synthesis and full characterization of a stable carbanion, 1-octynyl-C_{60}^- (**1**), derived from 1-octynyl-1,2-dihydro[60]fullerene.[9] This carbanion can be generated quantitatively from its precursor and has been shown to react with various carbon electrophiles as described in Chapter 1. The author has been motivated by these results to perform this study. The aim of this chapter is to prepare the end-chain type oligomers with well-defined structure using living cationic polymerization technique.[10]

Thus, in this chapter, 1-octynyl-C_{60} anion **1** was allowed to react with living vinyl ether oligomers obtained by living cationic polymerization of vinyl ethers (VEs)[11,12] using appropriate initiating systems.

EXPERIMENTAL

Materials

Commercial methyl vinyl ether (MVE) (Tokyo Kasei; purity > 99%) was dried by

passing the gaseous monomer through columns packed with calcium chloride and calcium hydride. Toluene, dichloromethane, and carbon tetrachloride were purified by the usual methods and distilled over calcium hydride prior to use. Diethyl ether (Dojin, anhydrous) was distilled in the presence of calcium hydride before use. ZnI_2 (Aldrich; purity > 99.99%) was used as received.

Measurements

Size exclusion chromatography (SEC) was carried out in tetrahydrofuran on a TOSOH HLC-802UR chromatograph equipped with polystyrene gel columns (TOSOH G2500H6 + G3000H6 + G4000H6; exclusion limit = 1.0 x 10^6; 8.0 mm i.d. x 60 cm each) and refractive index/ultraviolet dual-mode detectors. The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of the precursor oligo(IBVE) were estimated on the basis of a polystyrene calibration.

Cyclic voltammetry was conducted on a BAS electro-analyzer CV-50W using a three-electrode cell with a glassy carbon working electrode, a platinum counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The potential was read with respect to ferrocene added as an internal standard.

The samples for the microscopic observation were prepared by the following procedures; for the poly(IBVE) matrix films, C_{60} (1.00 mg), octynyl-C_{60} (1.15 mg) and C_{60}-oligo(IBVE) (**6**) (3.20 mg) were dissolved in toluene (1 mL) and 19 mg, 18.85 mg and 16.80 mg of poly(IBVE) (M_w = 2.34 x 10^5, M_w/M_n = 2.7) were added respectively. The films were prepared to contain the same concentration of C_{60} component, i.e., 5 wt% in the polymer matrix. For polystyrene matrix films, C_{60} (1.00 mg), octynyl-C_{60} (1.15 mg) and C_{60}-oligo(MVE) (**7**) (1.80 mg) were dissolved in toluene (1 mL), and 19 mg, 18.85 mg and 18.20 mg of polystyrene (M_w = 1.01 x 10^5, M_w/M_n = 1.47) were added, respectively (ca. 5 wt% for polystyrene matrix). Each solution was applied on a slide glass and allowed to air-dry at room temperature. Optical microscopic images were obtained on a Nicon AFX-II optical

microscope.

Oligomerization Procedures

Oligomerization was carried out at -40 °C under dry nitrogen in a vessel equipped with a three-way stopcock. The reaction was initiated by sequential addition of chilled solutions of IBVE-HCl (**2**) as an initiator and of ZnI_2 under dry nitrogen. For the reference sample, the reaction mixture was terminated with prechilled ammoniacal methanol, washed with 10% aqueous sodium thiosulfate solution, and then with water to remove the initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to yield the product.

Addition Reactions

1-Octynyl-2-(oligoIBVE)-1,2-dihydrofullerene (6)

The reaction conditions for the preparation of living IBVE oligomer **3** were as follows; $[M]_0 = 0.5$ mol L^{-1}, $[\mathbf{2}]_0 = 25$ mmol L^{-1}, $[ZnI_2]_0 = 0.50$ mmol L^{-1} in toluene at -40 °C. The living oligo(IBVE) with a molecular weight of 1600, which was prepared in the reaction time of 40 min (monomer conversion of ca. 80%), was used for the subsequent reaction. To a solution of **1** (9.02×10^{-5} mol) was added oligo(IBVE) **3** (2.5 mL, 6.25×10^{-5} mol) dropwise over 2 min under vigorous stirring at 0 °C in THF. After the reaction of 3 h, the resulting brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluted with hexane-benzene to remove decomposed C_{60} products. The product eluted with benzene was subjected to fractional precipitation using the benzene/methanol system to give pure product **6** (42.0 mg, 28% based on **3**) as a dark brown powder.

1-Octynyl-2-(oligoMVE)-1,2-dihydro[60]fullerene (7)

The reaction conditions for the preparation of living MVE oligomer **4** were as follows; $[M]_0 = 1.0$ mol L^{-1}, $[\mathbf{2}]_0 = 50$ mmol L^{-1}, $[ZnI_2]_0 = 5.0$ mmol L^{-1} in dichloromethane at -40 °C. The living oligo(MVE) with a molecular weight of 1050, which was prepared with a

reaction time of 2 h (monomer conversion of ca. 90%), was used for the subsequent addition reaction. To a solution of **1** (1.40×10^{-4} mol) was added oligo(MVE) **4** (2.0 mL, 1.00×10^{-4} mol) dropwise over 2 min under vigorous stirring at 0 °C in THF. After reaction of 4 h, the resulting brown solution was evaporated under vacuum. The crude product was washed with water to remove unreacted oligo(MVE) and was then separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluted with hexane-benzene to remove monomeric derivatives of C_{60}. The pure product **7** (59.6 mg, 34% based on **4**) was obtained from the benzene fraction as a dark brown gummy solid after evaporation.

RESULTS AND DISCUSSION

Synthesis of C_{60} End-Capped Oligomers

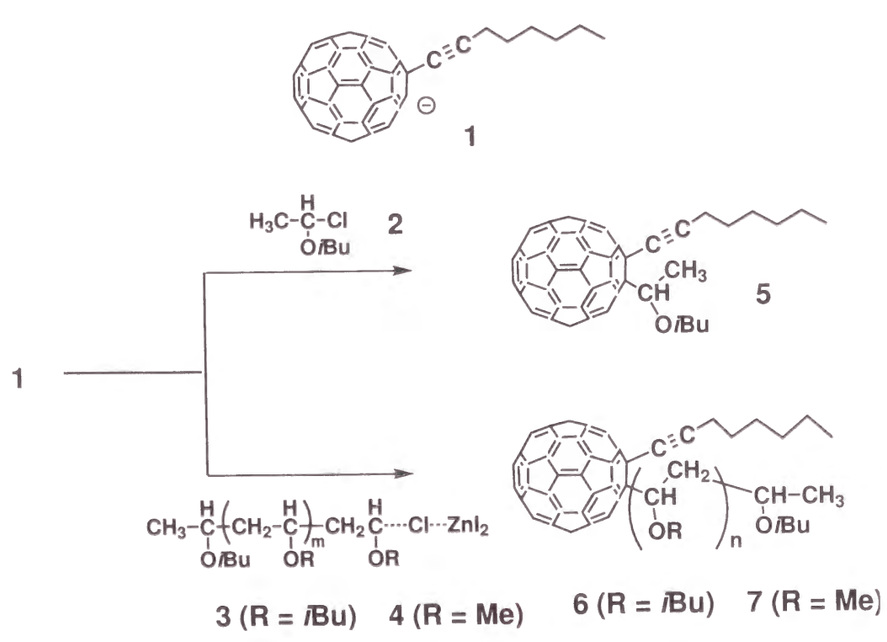
1-Octynyl-C_{60} anion **1** was prepared by deprotonation of 1-octynyl-1,2-dihydro[60]fullerene, which was obtained by reacting C_{60} with 1-octynyllithium in THF.[9]

Two types of vinyl ether oligomers were prepared by the use of living cationic polymerization technique. The combination of HCl and ZnI_2 is one of the best studied initiating systems suitable for the living cationic polymerization of vinyl ether (VE) monomers.[10] Living oligo(isobutyl vinyl ether) (IBVE) (**3**)[11] and oligo(methyl vinyl ether) (MVE) (**4**)[12] were prepared by the above-mentioned initiating system. For the purpose of comparison, an adduct of monomeric isobutyl vinyl ether (IBVE) and HCl, i.e., $CH_3CH(O\mathit{i}Bu)Cl$ (**2**) was also prepared in hexane as reported.[11]

The addition reactions of 1-octynyl-C_{60} carbanion **1** to these living cationic species were carried out in THF at 0 °C. In the case of adduct **2**, 6 equiv of a hexane solution of adduct **2** was added to a vigorously stirred solution of carbanion **1** in THF, which exhibited a characteristic dark green color, at 0 °C over 3 min. After the reaction of 3 h, the resulting brownish solution was quenched with methanol and subjected to the

chromatographic separation. The pure product **5**, i.e., C_{60}-IBVE, was isolated as dark brown powder in 33% yield as described in Chapter 1. The addition reaction of carbanion **1** to the living oligo(IBVE) (**3**) was conducted in a similar way for 3 h in THF at 0 °C. The reaction solution gradually turned from deep green to brown, indicating that the addition reaction proceeded. Unreacted C_{60} and other monomeric C_{60} derivatives were separated by column chromatography. The separation of the product **6**, herein referred to as C_{60}-oligo(IBVE), from unreacted oligo(IBVE) was made by fractional precipitation using benzene/methanol system. The pure product **6** was isolated in 28% yield as a dark brown gummy solid. The product **7**, i.e., C_{60}-oligo(MVE), was similarly prepared by addition reaction of carbanion **1** to the living oligo(MVE) in 34% yield as a dark brown gummy solid, after purification in the same way as described above.

Scheme 1



Structural Identification

The structure of products was determined by UV and NMR analyses. Figure 1 shows the ^{1}H NMR spectrum of C_{60}-oligo(IBVE) (**6**), together with that of C_{60}-IBVE **5** for comparison. Assignment of each signal is given in the figure.

At first glance, the two spectra appear quite different, but by close examination it is found that the ^{1}H NMR spectrum of **6** is composed of weak signals for an 1-octynyl group and an oligo(IBVE) moiety.

The ^{13}C NMR spectra of **5** and **6** shown in Figure 2 more clearly indicate that compound **6** contains the C_{60} core, 1-octynyl groups, and an oligo(IBVE) moiety.

The signals for the sp^2-carbons of the C_{60} core are somewhat broadened reflecting the non-homogeneity of the molecular weight of the oligomer.

The comparison of the NMR data of **6** with those of **5** and also the UV-vis spectral data[13] indicates that compound **6** is a C_{60} derivative with the two organic groups added at the 1,2-positions of the 6,6-junction bond as described in Chapter 1.

Although the accuracy is low due to the considerably large error in peak area integration, the number-average degree of polymerization (DP_n) of oligo(IBVE) segments in the product was estimated from comparison of the peak intensity of the peaks of the octynyl group with that of the peaks **b'** and **c'** in the IBVE moiety. The DP_n value of oligo(IBVE) segments in product **6** was found to be 19.7 in reasonable agreement with that of the precursor. The precursor was obtained as a reference compound by quenching living oligo(IBVE) with methanol, and its DP_n value was determined, similarly by ^{1}H NMR spectroscopy, to be 16, which accidentally agreed with the polystyrene-calibrated SEC value. The author also notes that the weight- to number-average molecular weight M_w/M_n ratio of the precursor estimated by the SEC analysis was 1.08.

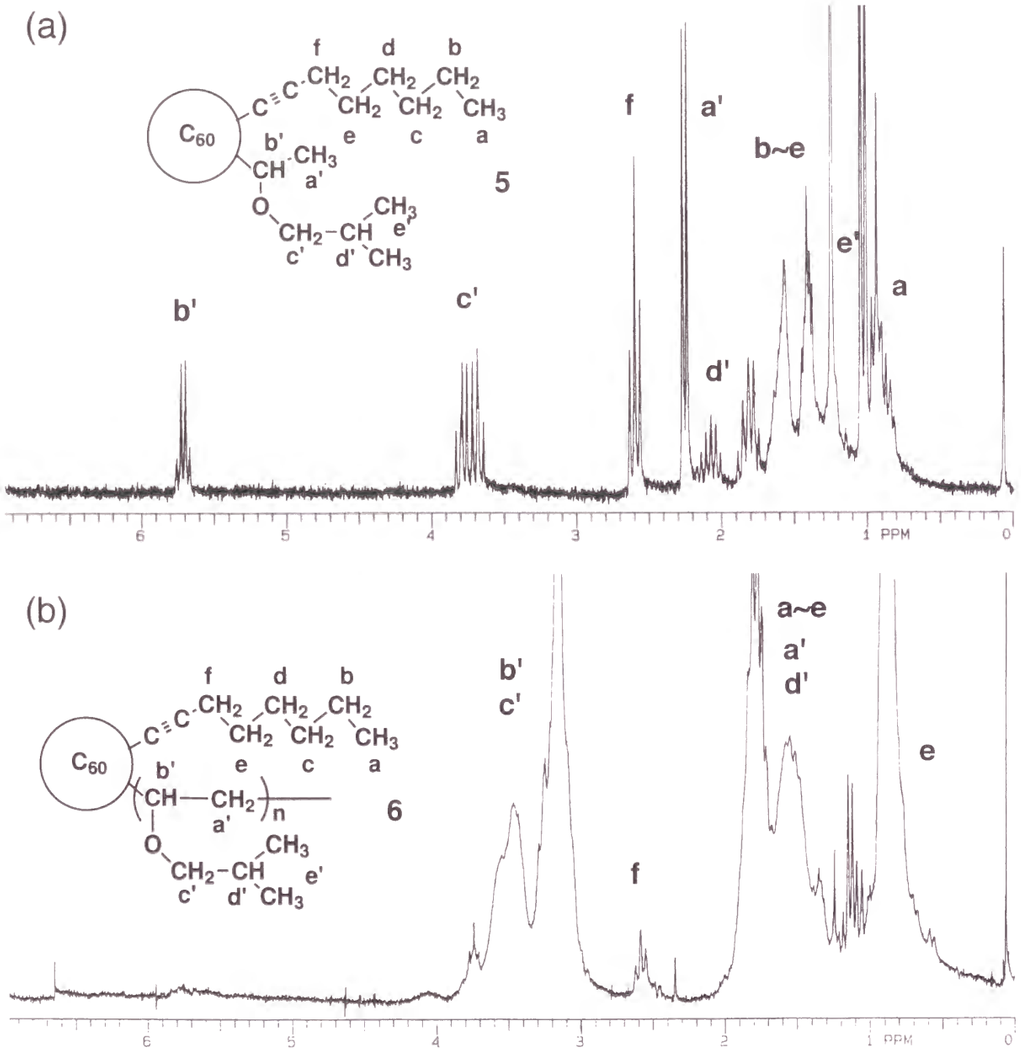


Figure 1. ^{1}H NMR spectra of (a) C_{60}-IBVE **5** and (b) C_{60}-oligo(IBVE) **6** in $CDCl_3$.

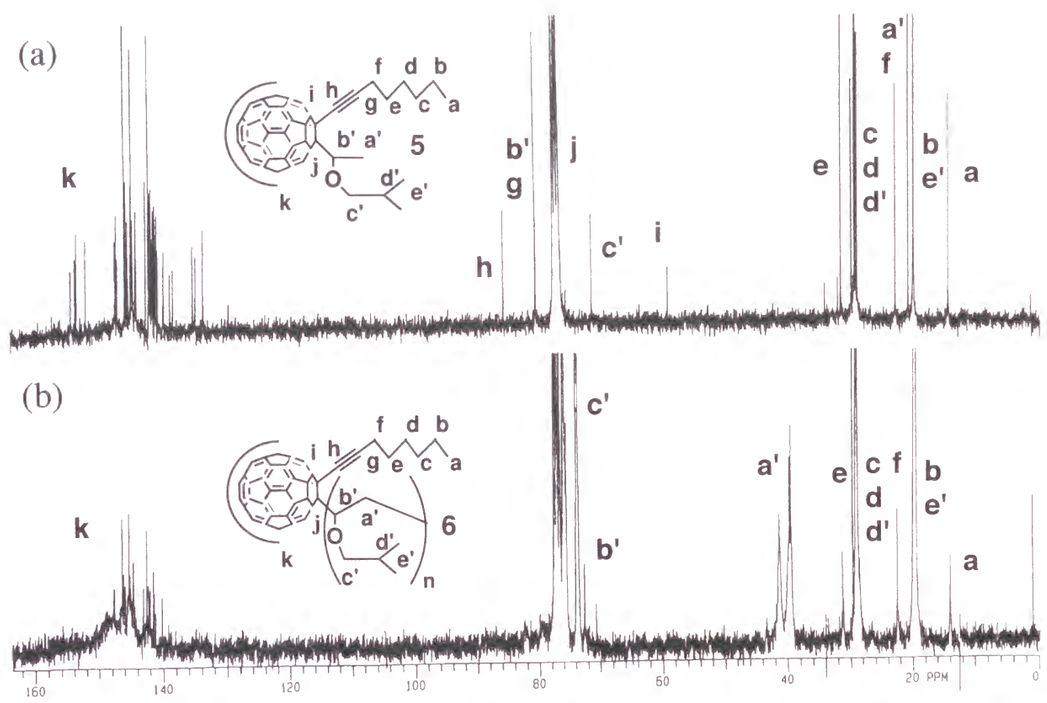


Figure 2. ^{13}C NMR spectra of (a) C_{60}-IBVE **5** and (b) C_{60}-oligo(IBVE) **6** in $CDCl_3$.

In Figure 3, the UV-vis spectrum of C_{60} end-capped oligomer **6** is compared with that of monomer adduct **5**. Both spectra exhibit a sharp absorption at around 430 nm which is diagnostic of the C_{60} derivatives with two addends at the 6,6-junction bond. The DP_n of IBVE segments can be also estimated from the spectrum of **6** using the absorbance at 256 nm with an assumption that the extinction coefficient is the same for these two compounds. The DP_n value was found to be 15.8 in good agreement with that of the precursor oligomer described above.

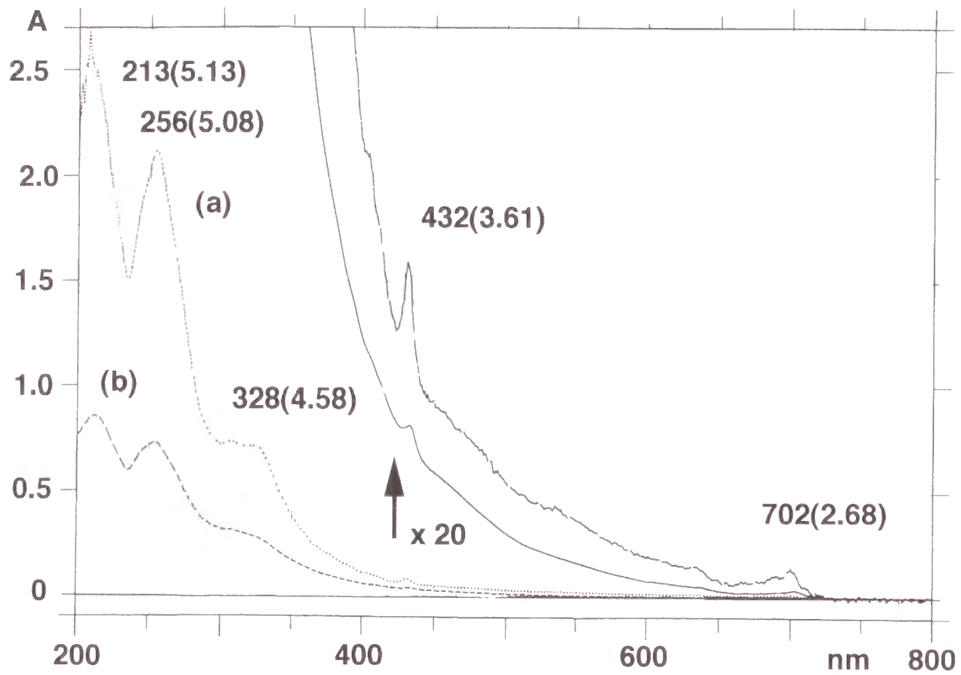


Figure 3. UV-vis spectra of (a) C_{60}-IBVE **5** (2.04 x 10^{-5} M) and (b) C_{60}-oligo(IBVE) **6** (6.89 x 10^{-6} M). The λ_{max} and log ε values are those of **5**.

The essentially same results were obtained on the addition of the living oligo(MVE) (**4**) to the 1-octynyl-C_{60} anion (**1**) affording C_{60}-oligo(MVE) (**7**). Namely, the structure of the product was proved to be 1,2-adduct on the 6,6-junction bond of C_{60}. On the other hand, the DP_n values of MVE segments in **7** estimated from ^{1}H NMR and UV-vis spectra were 10.9 and 10.3, respectively. These values are much lower than that of the precursor (DP_n = 18). This discrepancy is attributed to the water solubility of the C_{60}-oligo(MVE) **7**. It was found that the higher-molecular-weight fractions of **7** are partially soluble in water, just as poly(MVE) dissolves in water. Therefore, it is possible that the higher-molecular-weight fractions were lost during the purification of the sample by washing with water.

Redox Properties

The redox properties of the newly obtained derivatives were examined by the use of cyclic voltammetry in benzonitrile. Figure 4 demonstrates an example of the voltammograms obtained. Although some weak bumps are observed in the voltammograms with a wide sweeping range, the only reproducible waves were a single irreversible oxidation peak and three reversible waves as in the case of C_{60}. The numerical values obtained are summarized in Table 1. The reduction potentials of C_{60} end-capped oligo(VE) were more negative by slightly larger than 0.1 V, probably reflecting the electropositivity of the substituted groups. Similar results were observed on 1-alkynyl-2-hydro-dihydrofullerene.[9]

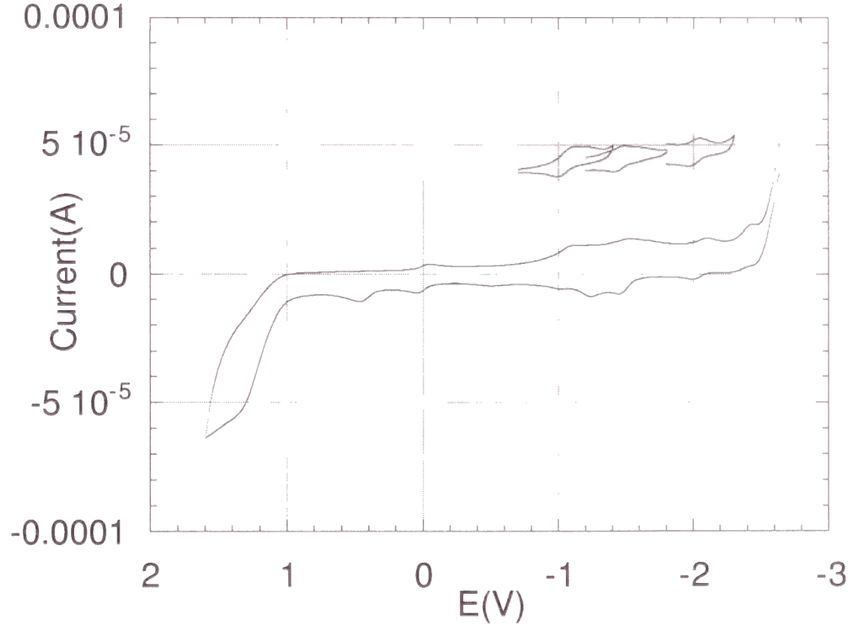


Figure 4. Cyclic voltammogram of C_{60}-oligo(IBVE) **6**. Insets are shown the individual reduction waves measured separately.

Table 1. Results of Cyclic Voltammetry[a]

compound	reversible, $E_{1/2}$		
	E_{red}^1	E_{red}^2	E_{red}^3
C_{60}	-0.93	-1.36	-1.85
6	-1.06	-1.46	-2.03
7	-1.04	-1.47	-2.03

[a] Potential in volts vs ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0.05 mol L^{-1}) as a supporting electrolyte; scan rate, 0.1 V s^{-1}.

Dispersion of C_{60} in Polymer Matrix

As already mentioned, one of the major disadvantages of fullerene C_{60} for the applications as advanced materials is its poor processing properties. Figures. 5a and b show typical examples of the dispersion of C_{60} molecules and 1-octynyl-2-hydro-1,2-dihydro[60]fullerene (octynyl-C_{60})[9] in poly(IBVE) matrix, examined using an optical microscope. It can be seen that C_{60} molecules tend to form comparatively large aggregates or clusters, due to the immiscibility with the polymer matrix. As shown in Figure 5c, on the other hand, in the case of C_{60}-oligo(IBVE), the film is homogeneous on a micron scale at the same content of C_{60} molecules with above two (5% by weight of C_{60}) and transparent, apparently this resulted from a better dispersion ability of C_{60} end-capped oligomer in the poly(IBVE) matrix.

Poly(MVE) is known to be compatible with polystyrene. Next the author examined the dispersion of C_{60}-oligo(MVE) in the polystyrene matrix. Figure 6 shows the optical micrographs of polystyrene composite films blended with C_{60} molecules, octynyl-C_{60} and C_{60}-oligo(MVE). It is obvious that the C_{60} molecules modified with oligo(MVE) result in a better dispersion of C_{60} in the polystyrene matrix.

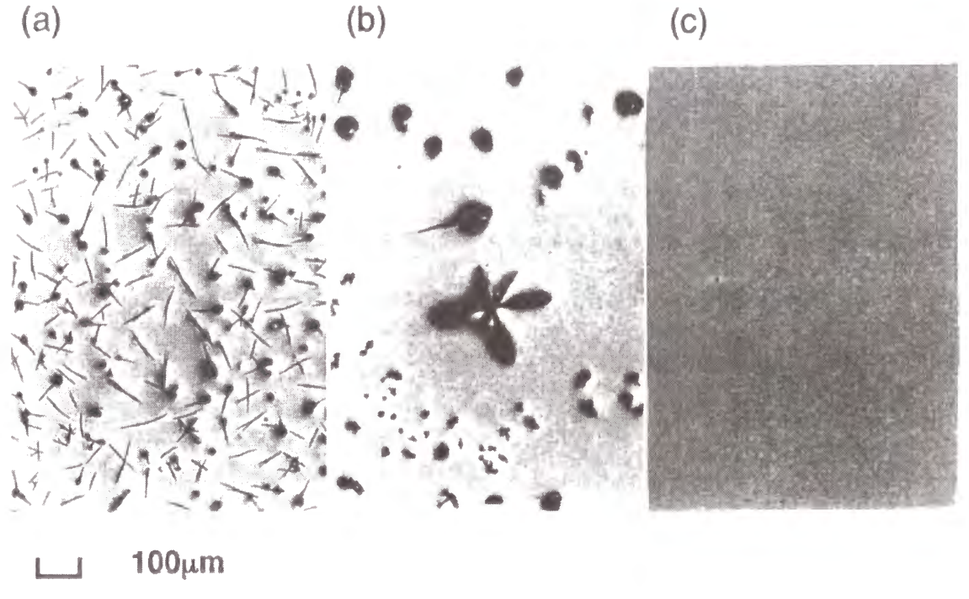


Figure 5. Optical microscopic images of blend films of (a) C_{60} (b) 1-octynyl-2-hydro-1,2-dihydro[60]fullerene and (c) C_{60}-oligo(IBVE) **6**.

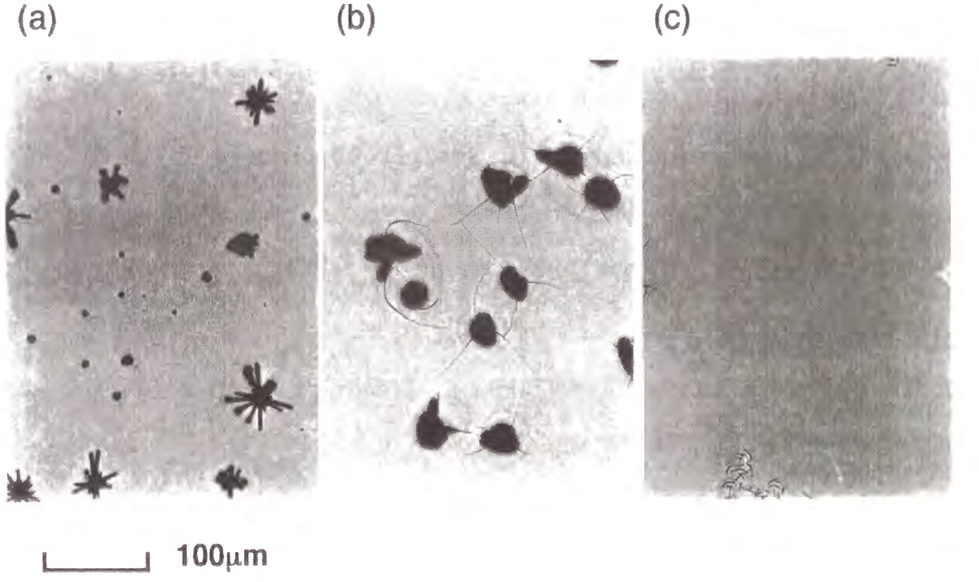


Figure 6. Optical microscopic images of blend films of (a) C_{60} (b) 1-octynyl-2-hydro-1,2-dihydro[60]fullerene and (c) C_{60}-oligo(MVE) **7**.

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(13) The C_{60} derivatives with two different addends at the 6,6-junction bond are normally supposed to have a C_s symmetry and exhibit 30 ^{13}C NMR signals for the sp^2 carbons of the C_{60} core. However, compound **5** having two addends at the 6,6-junction bond exhibits partially overlapped 54 signals due to the presence of chiral addend, i.e., the 1-alkoxy-1-ethyl group, at one of the 1,2-positions: Chapter 1 of this thesis; *J. Org. Chem.* **1996**, *61*, 8500.

Chapter 3

Synthesis of Water-Soluble C_{60} End-Capped Vinyl Ether Oligomers with Well-Defined Structures

ABSTRACT

Highly water-soluble [60]fullerene (C_{60}) end-capped vinyl ether (VE) oligomers with well-defined structure were synthesized by living cationic polymerization technique. The addition reaction between 1-octynylfulleride anion and oligomeric cationic species of VEs with pendant acetoxyl or malonic ester functions afforded the precursor C_{60} end-capped oligomers. The living cationic VE oligomers were prepared by living cationic polymerization of diethyl 2-(vinyloxy)ethylmalonate (VOEM) and 2-acetoxyethyl vinyl ether (AcOVE) by the $CH_3CH(OR)Cl/ZnI_2$ [R=$CH_2CH_2OCOCH_3$ and $CH_2CH_2CH(COOEt)_2$] initiating system, respectively. The precursors were obtained as dark brown gummy solid in 33% and 72% yield for AcOVE and VOEM, respectively. UV-vis and ^{13}C NMR spectroscopy indicated the formation of 1,2-disubstituted dihydrofullerene derivatives. Hydrolysis of the precursors was quantitatively proceeded to give the water-soluble C_{60} end-capped oligomers having oligo(sodium 2-vinyloxyethylmalonate) [oligo(VOEMNa)] and oligo(2-hydroxyethyl vinyl ether) [oligo(HOVE)] moieties. Solubility measurements revealed the water-soluble C_{60} end-capped oligomer with oligo(VOEMNa) chain to have the excellent aqueous solubility compared to the water-soluble C_{60} derivatives thus far known; the maximum solubility in water is 96.6 mg mL^{-1} which corresponds to 25.9 mg mL^{-1} of the C_{60} moiety.

INTRODUCTION

Since the first discovery of biological activity of fullerene (C_{60}) by Friedman,[1] a relatively large number of studies have been reported on the synthesis of water-soluble C_{60} derivatives and their biological activities *in vitro* and *in vivo*.[2] In most of these studies, C_{60} has been solubilized in water by attachment of a carboxylic acid residue(s) connected to C_{60} with an organic linker moiety.[1,3] These modified fullerenes possess amphiphilic character similar to detergents (detergent-type).[4] Other known water-soluble derivatives of C_{60} are those having a number of polar groups distributed (randomly) on the fullerene sphere (sphere-type). Such polar groups include hydroxyl (fullerol)[5] and amino groups.[6]

Introduction of C_{60} into water-soluble polymer is one of the simple and useful methods for solubilizing C_{60} in water. Concerning the water-soluble C_{60}-containing polymers, for example, Sun et al. reported that poly(propionylethylenimine-*co*-ethyleneimine) bearing C_{60} pendant groups has an excellent solubility in an aqueous solution (> 10 mg a C_{60} moiety mL^{-1}).[7] However, few of the water-soluble C_{60} polymer derivatives known so far possess well-controlled architecture. To examine the structure-properties relationships of water-soluble C_{60}-containing polymers, it is desirable to precisely control their structures. In Chapter 2, the author reported that C_{60}-capped vinyl ether (VE) oligomers with well-defined structure can be successfully synthesized by the addition reactions of carbocationic species obtained by living cationic polymerization of VEs[8] to 1-octynyldihydro[60]fulleride ion. In this chapter, the synthesis of highly water-soluble C_{60}-capped VE oligomers on the basis of the same synthetic strategy was described. To this end, 2-acetoxyethyl vinyl ether (AcOVE) and diethyl 2-(vinyloxy)ethylmalonate (VOEM) were employed as VE monomers. The VE oligomer moieties of the resultant C_{60} derivatives can be easily converted into highly hydrophilic oligomers by their hydrolysis.

EXPERIMENTAL

Measurements

NMR spectra were taken at 400 MHz for ^{1}H and 100 MHz for ^{13}C on JEOL GSX-400 spectrometer and 300 MHz for ^{1}H on Varian MERCURY-300 spectrometer. The polydispersity index (M_w/M_n) of the precursor oligo(AcOVE) and oligo(VOEM) were estimated on the basis of a polystyrene calibration. The number-average molecular weight (M_n) of those was estimated by ^{1}H NMR. Preparative SEC was performed in toluene on a JAI LC908 chromatograph equipped with polystyrene gel columns (JAI JAIGEL1H + JAIGEL2H; exclusion limit = 5.0 x 10^3, 25 mm i.d. x 60 cm) and an ultraviolet detector.

Materials

Chlorobenzene and 1,2,3,4-tetrahydronaphtalene were purified by the usual methods and distilled over calcium hydride prior to use. AcOVE[9] and VOEM[10] were prepared and purified as reported previously. The AcOVE-HCl adduct[11] and VOEM-HCl adduct **2** were prepared by bubbling HCl gas to the corresponding solutions of vinyl ethers in hexane.[12] Reactions were conducted under nitrogen atmosphere in pre-dried glassware.

1-(1-Octynyl)-2-{1-[3,3-di(ethoxycarbonyl)propoxy]ethyl}-1,2-dihydro[60]fullerene (C_{60}-VOEM) (5)

A solution of 1-octynyl-C_{60} anion (**1**) was prepared by adding 0.17 mL (0.17 mmol) of 1.0 mol L^{-1} solution of *t*-BuOK in THF to a stirred solution of 1-(1-octynyl)-1,2-dihydro[60]fullerene[8] (141.6 mg, 0.171 mmol) in 50 mL of THF at room temperature and stirring the mixture for 10 min at 0 °C. To a solution of **1** was added a 0.841 mol L^{-1} hexane solution of VOEM-HCl (**2**) (0.8 mL, 0.67 mmol) dropwise over 2 min under vigorously stirring. After the reaction of 6 h, the resulting brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluted with hexane:ethyl acetate = 10:1. From the second fraction was isolated product **5** (54.3 mg, 30%) as dark brown solid; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 5.71 (q, 1H), 4.22 (q, 2H), 4.05 (t, 2H), 3.72 (t, 1H), 2.60 (t, 2H), 2.37 (q, 2H), 2.24 (d, 3H), 1.81 (m, 2H), 1.57 (m, 2H), 1.43 (m, 2H), 1.41 (m, 2H), 1.25 (t, 3H), 0.94 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.27, 169.17 (C=O), 154.82, 154.17, 153.46, 152.22, 151.30, 147.68, 147.56, 147.34, 146.33, 146.14, 146.08, 146.06, 146.02, 145.85, 145.76, 145.32, 145.26, 145.20, 145.12, 144.92, 144.62, 144.54, 144.53, 144.45, 142.98, 142.97, 142.49, 142.45, 142.20, 142.03, 142.02, 141.93, 141.72, 141.50, 141.43, 141.35, 141.21, 141.09, 140.22, 140.10, 139.12, 138.82, 135.62, 135.30, 133.91, 133.84, 128.11, 125.37 (48 signals, sp^2-carbons in the C_{60} core), 85.98 (C≡C), 80.71 (CH–O), 80.31 (C≡C), 71.13 (quaternary sp^3-C in the C_{60} core), 67.11, 61.43 (CH_2–O), 59.06 (quaternary sp^3-C in the C_{60} core), 48.87 (CH), 31.51 (CH_2), 30.44 (CH_2 in VOEM), 29.47, 29.06, 22.78, 19.72 (CH_2), 14.29 (CH_3 in VOEM), 14.23 (CH_3); UV-vis (THF) λ_{max} 257 nm (log ε 5.02), 328 (4.55), 433 (3.66), 701 (2.45).

Oligomerization Procedures

Oligomerization of VEs was performed in the same manner as described in Chapter 2.

1-(1-Octynyl)-2-(oligoAcOVE)-1,2-dihydro[60]fullerene (6)

The reaction conditions for the preparation of living AcOVE oligomer (**3**) were as follows; $[M]_0$ = 0.50 mol L^{-1}, [AcOVE-HCl adduct]$_0$ = 20 mmol L^{-1}, $[ZnI_2]_0$ = 2.0 mmol L^{-1} in toluene at -15 °C. The living oligo(AcOVE) with a molecular weight of 3050 (monomer conversion of ca. 90%) was employed for the subsequent coupling reaction without isolation. To a solution of **1** (1.33 x 10^{-4} mol) was added oligo(AcOVE) **3** (7.5 mL, 1.50 x 10^{-4} mol) dropwise over 2 min under vigorous stirring at 0 °C in THF (100 mL). After the reaction of 12 h, the resulting brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluted with hexane-benzene to remove decomposed C_{60} products. The product eluted with benzene was subjected to fractional precipitation using the benzene/methanol system to give pure product **6** (166.3 mg, 33% based on **1**) as a dark brown powder.

1-(1-Octynyl)-2-(oligoVOEM)-1,2-dihydro[60]fullerene (7)

The reaction conditions for the preparation of living VOEM oligomer (**4**) were as follows; $[M]_0$ = 0.5 mol L^{-1}, $[\mathbf{2}]_0$ = 50 mmol L^{-1}, $[ZnI_2]_0$ = 1 mmol L^{-1} in toluene at -15 °C. The living oligo(VOEM) with a molecular weight of 1960 (monomer conversion of ca. 80%) was employed for the subsequent addition reaction. To a solution of **1** (1.35 x 10^{-4} mol) was added oligo(VOEM) **4** (6.0 mL, 3.38 x 10^{-4} mol) dropwise over 2 min under vigorous stirring at 0 °C in THF. After the reaction of 24 h, the resulting brown solution was evaporated under vacuum. The crude product was separated by a preparative SEC eluted with toluene to remove decomposed C_{60} products. The resulting solution was evaporated and subjected to fractional precipitation using the methanol/water system to give pure product **7** (278.3 mg, 72% based on **1**) as a dark brown powder.

1-(1-Octynyl)-2-(oligoHOVE)-1,2-dihydro[60]fullerene (8)

Oligo(AcOVE) moiety in **6** was converted into oligo(HOVE) moiety. A solution of **6** in 1,4-dioxane was mixed with 20% aqueous sodium hydroxide (3 equiv to the ester units in the oligomer) and the mixture was stirred at room temperature for 3 h, during which period partially hydrolyzed polymers precipitated. After 1,4-dioxane was removed by evaporation, the precipitate was dissolved in a large amount of water. The solution was stirred for a day at room temperature to complete the hydrolysis and concentrated by evaporation to a few milliliters. The concentrated solution was dialyzed against deionized water for 3 days. Finally the solution was concentrated by evaporation and freeze-dried to yield C_{60}-capped oligo(HOVE) **8** in a quantitative yield.

1-(1-Octynyl)-2-(oligoVOEMNa)-1,2-dihydro[60]fullerene (9)

Oligo(VOEM) moiety in **7** was converted into oligo(sodium vinyloxyethylmalonate) [Oligo(VOEMNa)] by base-catalyzed hydrolysis. A solution of **7** in 1,4-dioxane was mixed with 20% aqueous sodium hydroxide (5 equiv to the ester units in the oligomer) and the mixture was stirred at room temperature for 3 h, during which period partially

hydrolyzed polymers precipitated. After the water and 1,4-dioxane were removed by evaporation, the precipitate was dissolved in a large amount of water. The solution was stirred for 2 days at room temperature to complete the hydrolysis and concentrated by evaporation to a few milliliters. The concentrated solution was dialyzed against deionized water for 3 days. Finally the solution was concentrated by evaporation and freeze-dried to yield C_{60}-capped oligo(VOEMNa) **9** in a quantitative yield.

Saturation Solubilities in Water of C_{60} End-Capped Oligo(HOVE) 8 and Oligo-(VOEMNa) 9

All operations were conducted in an air-conditioned room kept at 25 °C. 40 mg of each polymer sample was mixed with 0.1 mL of water in a centrifuge tube. After 1 min. of sonication, the mixture was centrifuged. The supernatant (10 μL, measured by microsyringe) was diluted to 100 or 500 times by water and the concentration of the C_{60} moiety was determined by measuring the UV-vis absorption intensity at 430 nm calibrated against a molar absorption coefficient of C_{60}-AcOVE[11] or C_{60}-VOEM **5** at 430 nm.

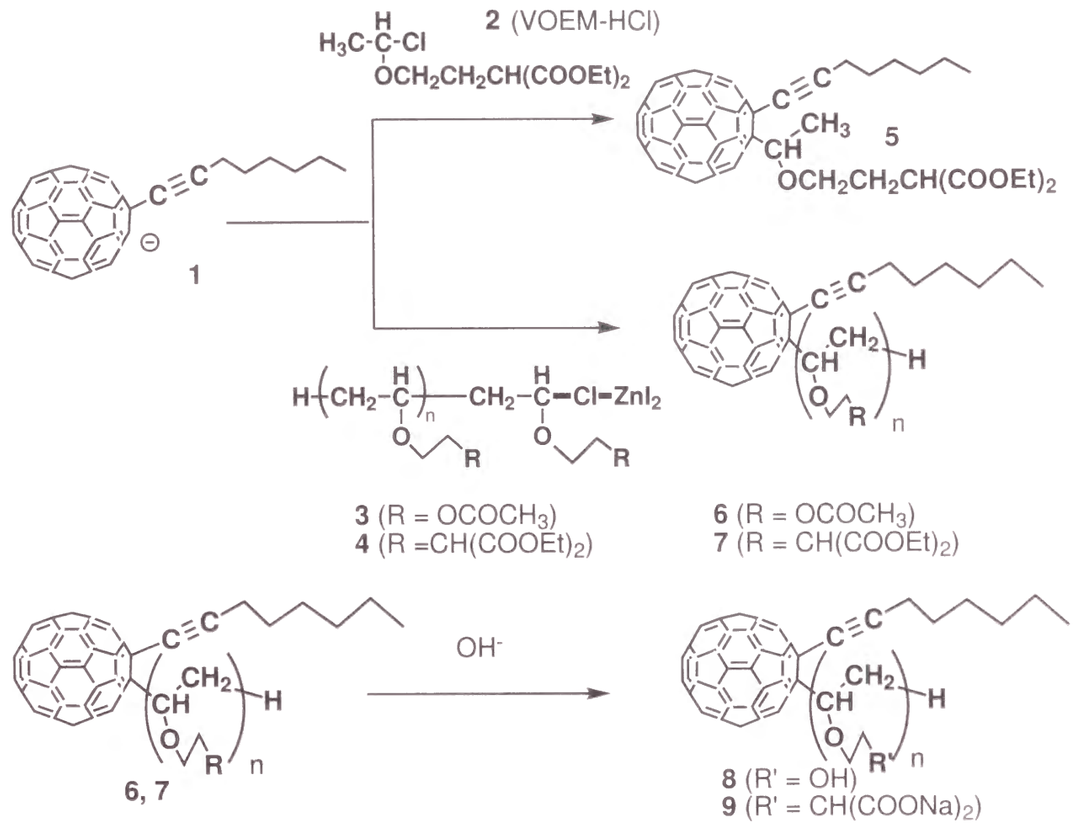
RESULTS AND DISCUSSION

Synthesis and Characterization of C_{60}-VOEM 5, C_{60}-Oligo(AcOVE) 6, and C_{60}-Oligo(VOEM) 7

It has been demonstrated that the HCl/ZnI_2 initiating system is useful for living cationic polymerization of ester-carrying VEs such as AcOVE and VOEM. In this study the adducts of AcOVE and VOEM with HCl (AcOVE-HCl and VOEM-HCl) were employed as initiators for the polymerization of the two VEs, respectively. VOEM-HCl was also employed for the synthesis of C_{60} derivatives with a monomeric VOEM residue (C_{60}-VOEM). The synthesis of C_{60} end-capped oligo(AcOVE) **6** and oligo(VOEM) **7** was according to the method described in Chapter 2.

As shown in Scheme 1, the addition reactions of VE-based carbocationic species as

Scheme 1



carbon electrophiles with 1-octynyl-C_{60} carbanion **1** were carried out in THF at 0 °C. To synthesize C_{60}-VOEM **5**, 2.5 equiv of adduct **2** in a hexane solution was added to a characteristic dark green solution of carbanion **1** in THF under vigorous stirring at 0 °C over 3 min. After the additional period of 3 h, the resulting brownish solution was quenched with methanol and subjected to the chromatographic separation. The pure product **5** was isolated as a dark brown powder in 30% yield. The addition reaction of carbanion **1** to living oligo(AcOVE) **3** was conducted in THF for 3 h at 0 °C. The reaction mixture gradually turned into brown from deep green, indicating that the addition reaction proceeded. Unreacted and decomposed C_{60} compounds were removed by column

chromatography. The separation of the target product **6**, herein referred to as C_{60}-oligo(AcOVE), from unreacted oligo(AcOVE) was made by fractional precipitation using benzene/methanol system. The pure product **6** was isolated in 33% yield as a dark brown gummy solid. The product **7**, i.e., C_{60}-capped oligo(VOEM), was similarly prepared in 72% yield as a dark brown gummy solid after purification.

Structural Identification

The structure of the products was determined by UV and NMR analyses. Figure 1 shows the ^{1}H NMR spectrum of C_{60}-oligo(VOEM) **7**, together with that of C_{60}-VOEM **5** for comparison. Assignment of each signal is given in the figure. At first glance, the two spectra appear quite different, but by close examination it is found that the ^{1}H NMR spectrum of **7** is composed of weak signals for an 1-octynyl group and an oligo(VOEM) moiety.

The ^{13}C NMR spectra of **5** and **7** shown in Figure 2 more clearly indicate that compound **7** contains the C_{60} core, 1-octynyl groups, and an oligo(VOEM) moiety. The signals for the sp^2-carbons of the C_{60} core are somewhat broadened reflecting the nonhomogeneity of the molecular weight of the oligomer. The comparison of the NMR and UV-vis spectral data of **7** with those of **5** indicate that compound **7** is a C_{60} derivative with two organic substituents at the 1,2-positions of the 6,6-junction bond.[13]

The UV-vis spectrum of C_{60}-oligo(VOEM) **7** is compared with that of monomeric counterpart **5** in Figure 3. As in the case of the previous work described in Chapter 2, both spectra exhibit a sharp absorption at around 430 nm which is diagnostic of the C_{60} derivatives with two addends at the 6,6-junction bond. The number-average degree of polymerization (DP_n) of VOEM segments can also be estimated from the spectrum of **7** using the absorbance at 430 nm with an assumption that the extinction coefficient is the same for **5** and **7**. The DP_n value was found to be 6.9, which is in agreement with that of

the precursor oligo(VOEM) (DP_n = 8.5, M_w/M_n = 1.08). The precursor oligo(VOEM) was obtained as a reference compound by quenching living oligo(VOEM) with methanol. Its DP_n value was independently determined by ^{1}H NMR spectroscopy.

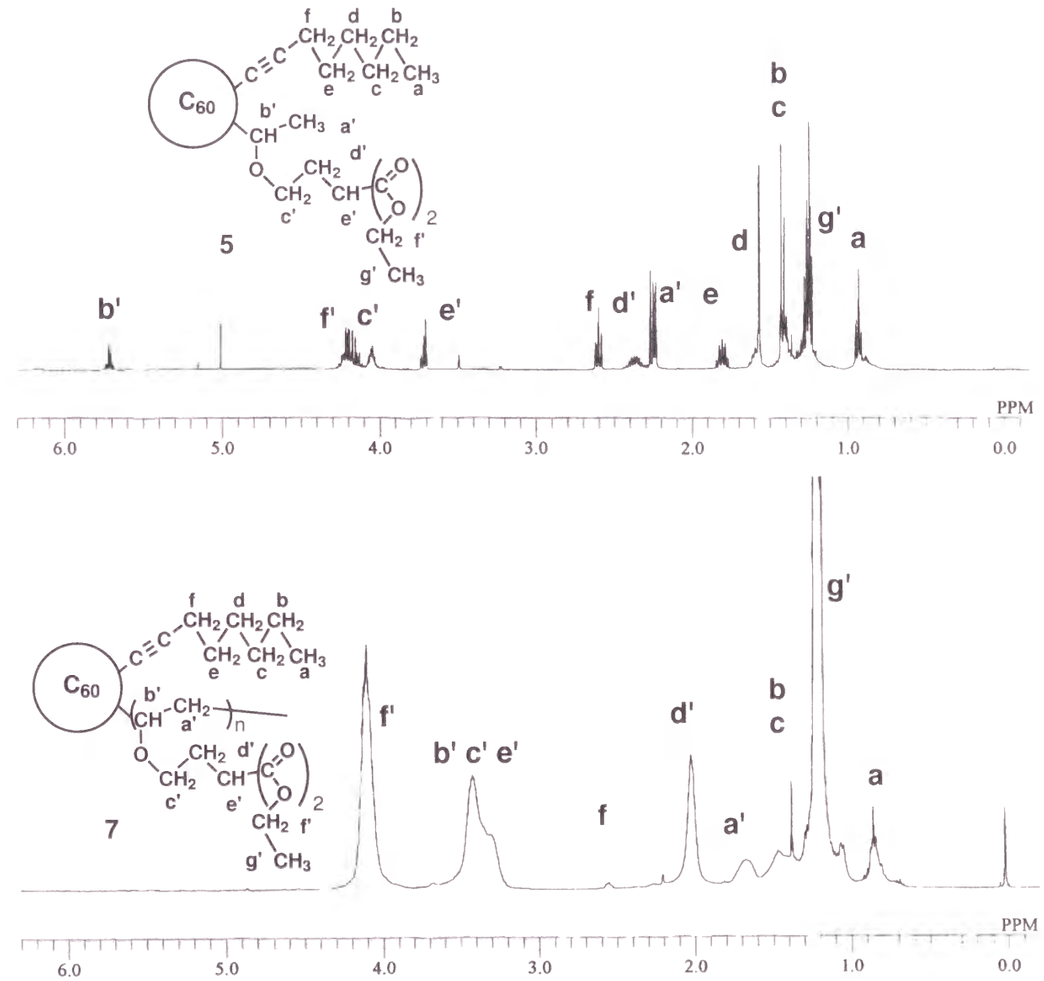
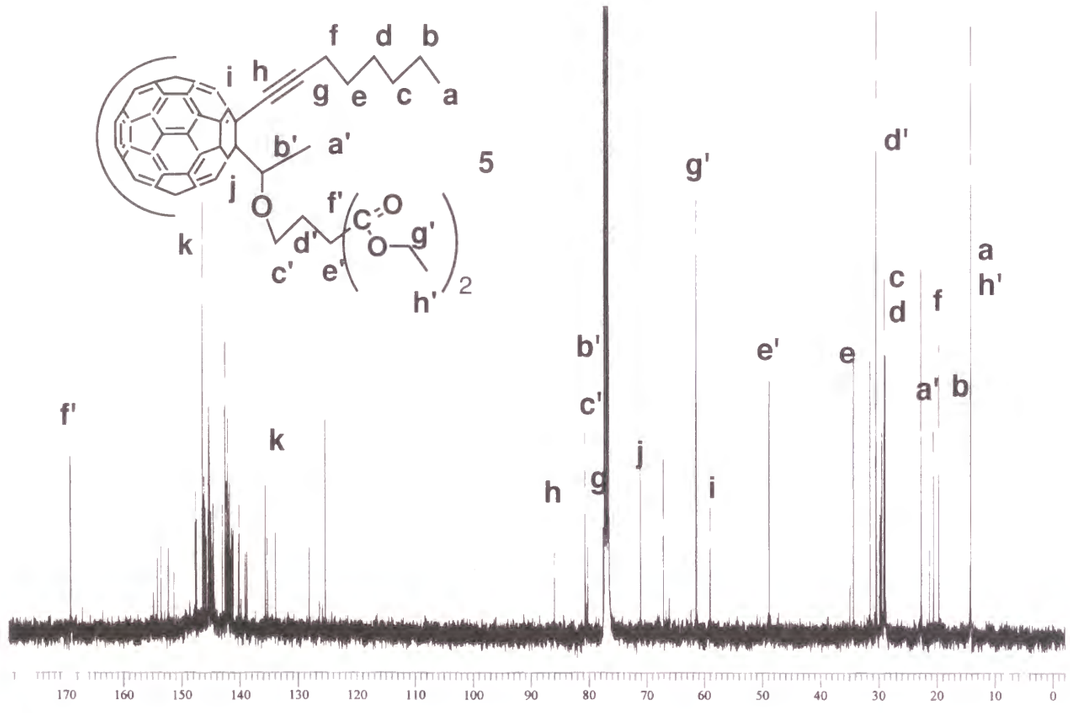


Figure 1. ^{1}H NMR spectra of C_{60}-VOEM **5** and C_{60}-oligo(VOEM) **7** in $CDCl_3$.



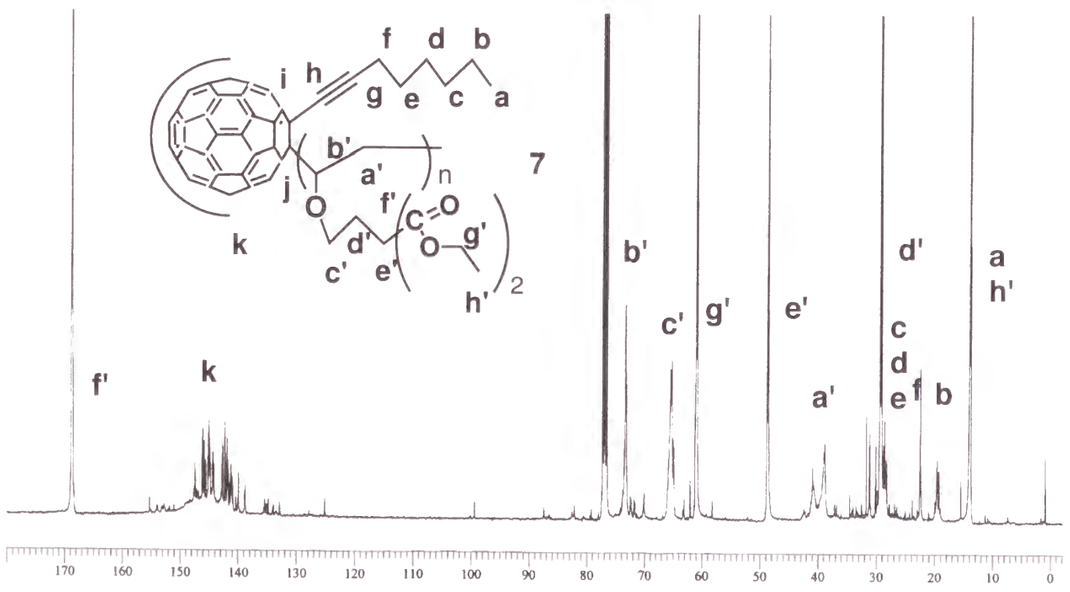


Figure 2. ^{13}C NMR spectra of C_{60}-VOEM **5** and C_{60}-oligo(VOEM) **7** in $CDCl_3$.

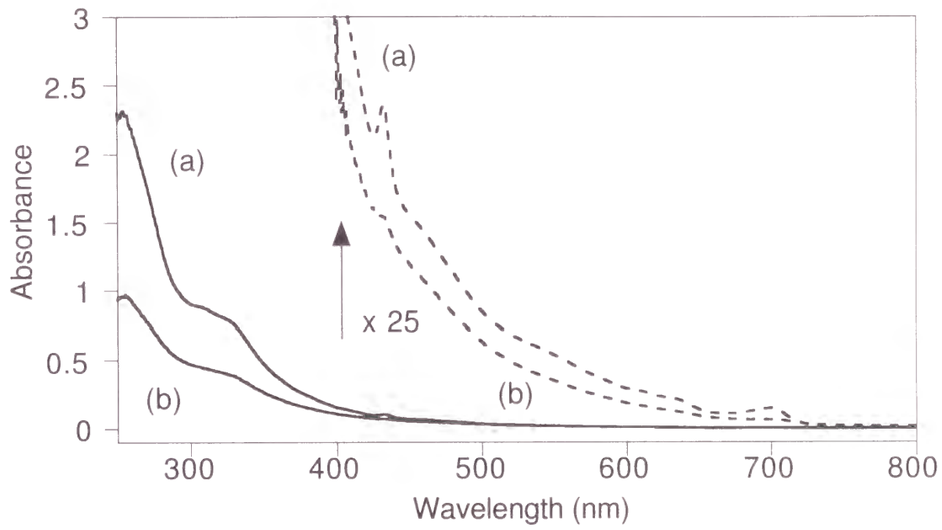


Figure 3. UV-vis spectra of (a) C_{60}-VOEM **5** (2.62×10^{-2} mg mL^{-1}) and (b) C_{60}-oligo(VOEM) **7** (5.53×10^{-2} mg mL^{-1}) in THF.

Although the accuracy may be low due to the considerably large error in peak area integration, the number-average degree of polymerization (DP_n) of oligo(VOEM) moiety in the product was also estimated from a comparison of the peak intensity of the octynyl group (peak **a**) with those of the VOEM moiety (peaks **b'** and **c'**) (see Figure 1). The DP_n value of the oligo(VOEM) segment in product **7** was found to be 7.2, which is in reasonable agreement with that of the precursor oligomer.

The essentially same results were obtained for the synthesis of C_{60}-oligo(AcOVE) **6** through the addition reaction of living oligo(AcOVE) **3** with 1-octynyl-C_{60} anion **1**. Namely, the structure of the product was proved to be 1,2-adduct on the 6,6-junction bond of C_{60} because of the similarity in UV-vis spectra of **6** and **7**. The DP_n values of AcOVE moiety in **6** estimated from UV-vis and ^1H NMR spectra were 24.2 and 23.7, respectively,

which are in good agreement with that of the precursor oligo(AcOVE) (DP_n = 22.5, M_w/M_n = 1.11).

Hydrolysis of C_{60}-oligo(AcOVE) 6 and C_{60}-oligo(VOEM) 7

Water-soluble C_{60}-oligo(HOVE) **8** and C_{60}-oligo(VOEMNa) **9** were obtained by hydrolysis of the acetoxyl and malonic ester functions in the precursor C_{60} derivatives, respectively (see the Experimental section). The ^{1}H NMR of C_{60}-oligo(VOEMNa) **9** in D_2O was shown in Figure 4 together with that of C_{60}-oligo(VOEM) **7** for comparison. The peak at 1.2 ppm ascribed to ethyl group in oligo(VOEM) disappeared, suggesting a complete hydrolysis of the ester unit. The ^{13}C NMR of C_{60}-oligo(VOEMNa) **9** in D_2O was shown in Figure 5. The signals for sp^2 carbons of the hydrophobic C_{60} moiety were fairly broadened but still observed in the 130–150 ppm region in D_2O.

The complete conversion of C_{60}-oligo(AcOVE) **6** into C_{60}-oligo(HOVE) was confirmed by ^{1}H and ^{13}C NMR measurements. Also in this case, in the ^{13}C NMR spectrum of the hydrolysis product in D_2O, the signals assignable to the carbons in the C_{60} moiety still appeared, indicating the hydrophobic C_{60} moiety and the hydrophilic oligo(HOVE) segment are tightly bound.

UV-vis spectrum of C_{60}-oligo(VOEMNa) **9** in water was shown in Figure 6. The spectrum appeared to be broadened and poorly resolved compared to those of the parent C_{60} and VE-based C_{60} derivatives shown in the preceding chapters. A similar structureless spectrum was observed for C_{60}-oligo(HOVE). As will be described in Chapter 5, the UV-vis spectral profiles of C_{60}-containing polymers in organic solvents are closely related to the dissolution states of the solute molecules. Namely, multimoleculer micelle formation of the C_{60} derivatives brings about characteristic changes in their UV-vis spectra. Due to the amphiphilic nature of the C_{60} end-capped VE oligomers in this study, these derivatives are expected to form some aggregates like micelles in aqueous solutions. Studies on the effects of the dissolution states on the spectroscopic features will be discussed elsewhere.

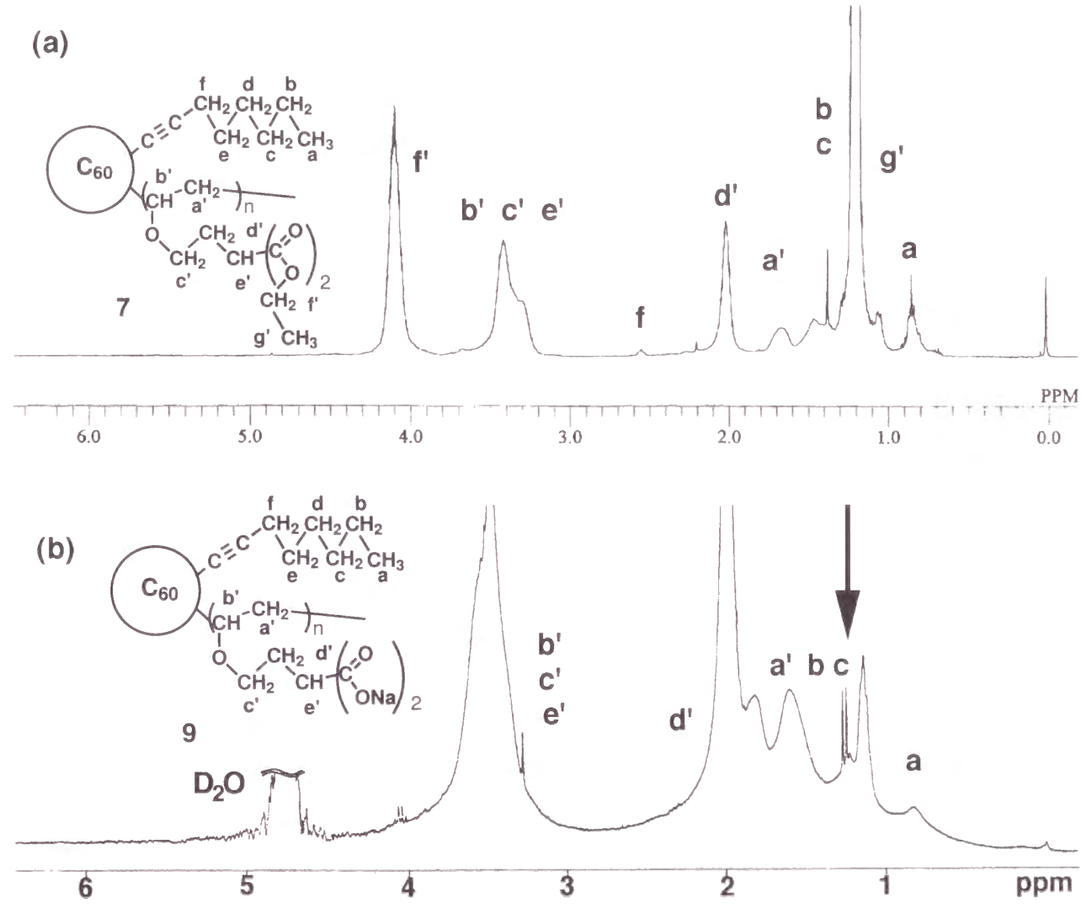


Figure 4. ^{1}H NMR spectra of (a) C_{60}-oligo(VOEM) **7** in $CDCl_3$ and (b) C_{60}-oligo(VOEMNa) **9** in D_2O.

Saturation Solubilities of C_{60}-Oligo(HOVE) 8 and C_{60}-Oligo(VOEMNa) 9

As already noted, C_{60} in itself does not dissolve in water. Moreover, most of the water-soluble C_{60} derivatives so far reported possess relatively low saturation solubility in water. Derivatization of C_{60} with oligomeric or polymeric addend(s) consisting of multiple hydrophilic groups is one of the most effective method to enhance the aqueous solubility

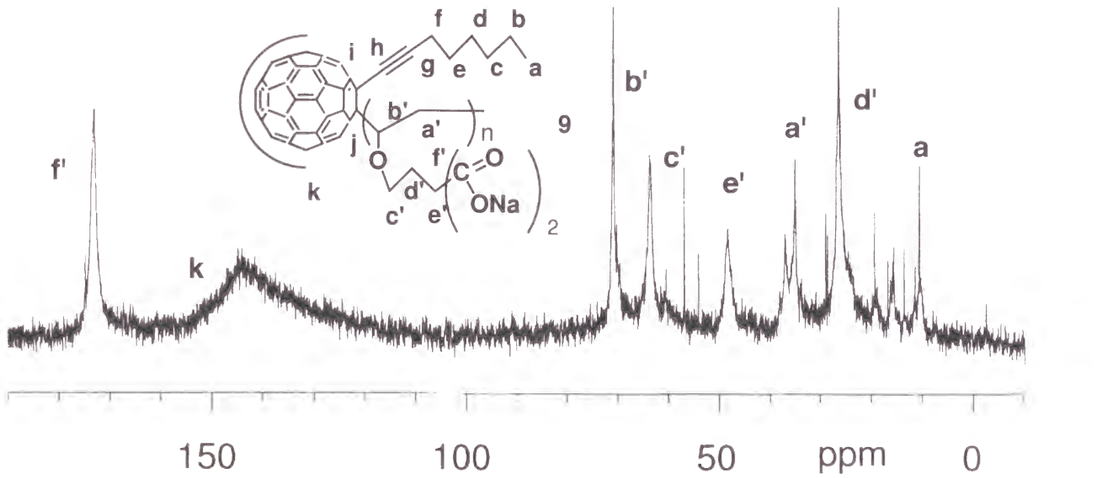


Figure 5. ^{13}C NMR spectrum of C_{60}-oligo(VOEMNa) **9** in D_2O.

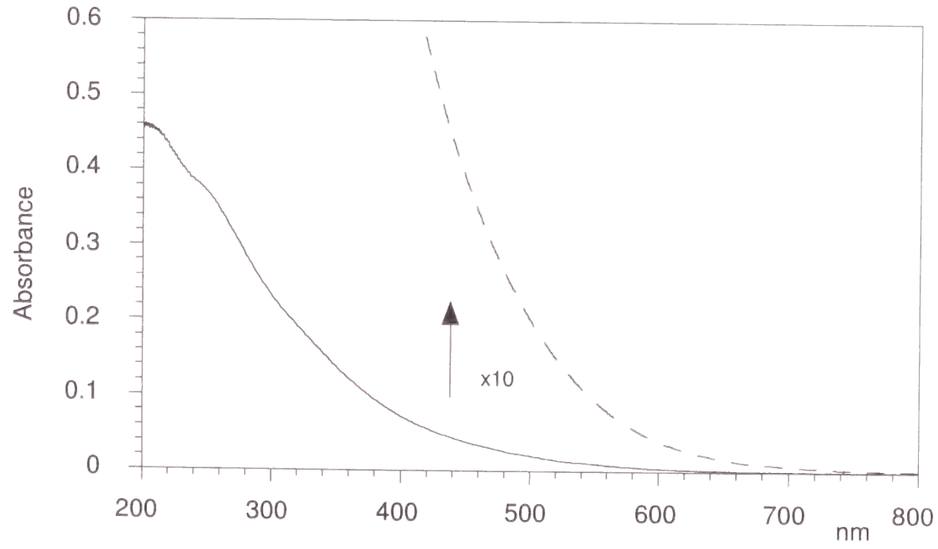


Figure 6. UV-vis spectrum of C_{60}-oligo(VOEMNa) **9** (1.95×10^{-2} mg mL^{-1}) in water.

of the derivatives. The saturation solubility of the C_{60} moiety in the derivatives would depend on the molecular weight of the hydrophilic substituent(s). Such a solubility-molecular weight relationship will be discussed elesewhere.[14] Another structural factor which determines the aqueous solubility of the C_{60} derivatives is the hydrophilicity of the incorporated substituent(s). In this Chapter, the aqueous solubility of two types of C_{60} end-capped oligomers is discussed in terms of the substituent's chemistry.

C_{60}-oligo(HOVE) **8** and C_{60}-oligo(VOEMNa) **9** are water-soluble and possess multiple hydroxyl and sodium carboxylate groups in the oligomer moieties, respectively. Saturation solubilities of **8** and **9** were estimated in water at 25 °C. Anionic oligomer **9** with a C_{60} content of 27% by weight exhibited an aqueous solubility of 96.6 mg mL^{-1} which corresponds to 25.9 mg mL^{-1} of the C_{60} moiety, showing the excellent aqueous solubility of **9** compared to those of the water-soluble C_{60} derivatives hitherto reported. Although the DP_n of the hydrophilic oligomer segment of **8** is about two times of that of anionic counterpart **9**, the aqueous solubility of the former was found to be about one-third (saturation solubility, 9.3 mg mL^{-1} of the C_{60} moiety) of that of the latter. These results indicate that carboxylate anion is more effective for dissolving the C_{60} moiety in water, and also that the derivatizing methodology established in this study is useful for the synthesis of a variety of water-soluble C_{60} derivatives.

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Part II

Synthesis and Properties of C_{60}-Containing Polymers by Nitroxide-Mediated 'Living' Radical Polymerization

Chapter 4

Synthesis and Characterization of C_{60} Fullerenes with Two Well-Defined Polystyrene Arms

ABSTRACT

This is the first report of the synthesis of well-defined disubstituted polymer derivatives of C_{60} by a radical mechanism. Narrow-polydispersity polystyryl adducts with TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy), prepared by the nitroxide-mediated "living" radical polymerization technique, were heated with a 4-fold excess (in molar ratio) of C_{60} in *o*-dichlorobenzene at 145 °C to give 1,4-dipolystyryldihydro[60]fullerenes (yields 60-80%). A low-mass model compound 2-benzoyloxy-1-phenylethyl adduct with TEMPO gave essentially the same result. These disubstituted derivatives retained the redox properties of C_{60} and gave UV-vis spectra characteristic of 1,4-bisadducts. A possible mechanism by which disubstituted derivatives are selectively produced was discussed.

INTRODUCTION

C_{60}, a representative of the fullerene family, has attracted much attention due to its unique physical and chemical properties.[1] Various methods for the chemical modification of C_{60} have been reported not only for fundamental studies[2] but also for applications.[3] In order to overcome the low solubility and poor processability of C_{60}, incorporation of C_{60} molecules into polymer chains is gaining particular interest.

Fullerene-containing polymers[4-8] reported so far can be classified into four types (see also the General Introduction). The first type is polymers with fullerene units incorporated into main chain (in-chain type).[4] The second is those bearing pendant fullerene (on-chain type).[5] The third is fullerene-incorporating polymer networks (cross-link type), where fullerene acts as a cross-linking site.[6] The fourth is fullerene-terminated telechelic polymers, i.e., polymers having one or two fullerene end groups (end-chain type).[7,8] In particular, many attempts have been made for the preparation of C_{60} end-capped polymers: Samulski et al.[7] reported the preparation of polystyrene-(PS-)multisubstituted fullerenes, which they designated "flagellenes", by the use of nucleophilic addition of C_{60} to living anionic polymer species. To regulate the addition number, an excess equivalent of C_{60} was effective. By this principle, PS-monosubstituted C_{60} with well-defined structure was prepared.[9] Frey et al.[10] also prepared PS-monosubstituted C_{60} by the reaction of C_{60} with the amino-functionalized polystyrene prepared by living anionic polymerization. The preparation of oligo(vinyl ether)-monosubstituted C_{60} by the addition of living cationic polymerization species to 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion[11] was described in Chapter 2 of this thesis.

On the other hand, the preparation of PS-C_{60} adducts by the radical mechanism[12–14] has been attempted by carrying out the copolymerization of C_{60} with styrene in bulk or in solution initiated spontaneously or with azobis(isobutyronitrile) or benzoyl peroxide. But the reaction products were, in many cases, a mixture of poorly defined multiadducts of PS,

and it seems very difficult to prepare PS-C_{60} adducts with a well-defined structure by the usual radical polymerization methods.

This chapter deals with the first synthesis of well-defined polymer derivatives of [60]fullerene by the addition reaction between C_{60} and the polystyryl radical derived from a PS-TEMPO adduct, where TEMPO is 2,2,6,6-tetramethylpiperidinyl-1-oxy. For this purpose, the author prepared several PS-TEMPO adducts with narrow-polydispersity PS[15] of varying lengths and also a low-mass model compound BS-TEMPO,[16,17] where BS is a 2-benzoyloxy-1-phenylethyl group. These adducts are expected to produce polystyryl (or benzoyloxystyryl) radicals at high temperatures by the cleavage of the C–ON bond. An independent experiment has confirmed that TEMPO does not add to C_{60}. So this system is much simpler than the conventional ones. A similar reaction was reported recently,[18] but the reaction products therein reported are quite different from those obtained here and poorly defined. Some discussion will be given about the reaction mechanism and the electric properties of the products.

EXPERIMENTAL

Materials

o-Dichlorobenzene (ODCB) was distilled over CaH_2. Benzonitrile was distilled over P_2O_5. Commercially obtained styrene and benzoyl peroxide (BPO; Nacalai Tesque, Japan) were purified by the standard methods described elsewhere.[19] TEMPO (Aldrich) was used as received.

Preparation of PS-TEMPO and BS-TEMPO

PS-TEMPO adducts were prepared as described previously.[20] In a typical run, a mixture of styrene, BPO (6.80×10^{-2} mol L^{-1}), and TEMPO (7.14×10^{-2} mol L^{-1}) was charged in a glass tube, degassed with several freeze-thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 95 °C for 3.5 h and at 125 °C for 4 h to yield a polymer.

The polymer was recovered as a precipitate from a large excess of methanol, purified by reprecipitation with a chloroform (solvent)/methanol (nonsolvent) system, and thoroughly dried (conversion: 14.5%), which, according to the PS-calibrated GPC, had a number-average molecular weight M_n of 2400 and a M_w/M_n ratio of 1.14. A chain-extension test[20] indicated that this sample contained a fraction of inactive species (without a TEMPO moiety at the chain end) in about 5%.

The BS-TEMPO adduct was prepared as reported previously.[16] BPO (0.80 mol L^{-1}) and TEMPO (0.96 mol L^{-1}) were dissolved in styrene and heated at 95 °C for 3.5 h after degassing. The crude product was purified by column chromatography, and BS-TEMPO was obtained in 42% yield.

Preparation of C_{60}-BS Adduct

The C_{60}-BS adduct was prepared as follows. BS-TEMPO (6.90 x 10^{-4} mol L^{-1}) and C_{60} (2.78 x 10^{-3} mol L^{-1}) were dissolved in ODCB, charged in a glass tube, degassed with several freeze-thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 125 °C for 24 h. The product was subjected to column chromatography to afford a C_{60}-BS adduct in 69% yield;[21] ^{1}H NMR (270 MHz, $(CD_3)_2CO/CS_2$ = 1:4) δ 8.52-7.35 (m, 6H, aromatic), 7.35-6.98 (m, 14H, aromatic), 5.44 (m, 4H, O-CH_2), 4.47 (m, 2H, CH-Ph); ^{13}C NMR (100 MHz, $(CD_3)_2CO/CS_2$ = 1:4) δ 168.34, 168.25, 168.14, 168.06 (CO in previous 4 peaks), 157.39, 157.30, 156.64, 156.50, 154.30, 153.92, 153.19, 152.82, 151.63, 151.60, 151.52, 151.25, 151.16, 151.18, 150.76, 150.60, 150.21, 150.18, 149.93, 149.88, 148.99, 148.65, 148.52, 148.27, 148.21, 148.16, 148.09, 148.04, 147.73, 147.67, 147.62, 147.53, 147.42, 147.38, 147.33, 147.31, 147.25, 147.18, 147.17, 147.11, 147.04, 146.91, 146.54, 146.44, 146.12, 146.37, 146.30, 146.28, 146.22, 146.16, 146.14, 146.08, 145.91, 145.87, 145.74, 148.67, 145.65, 146.62, 145.57, 145.56, 145.39, 145.31, 145.30, 145.18, 145.03, 144.68, 144.61, 144.28, 144.19, 143.76, 143.01, 142.36, 141.94, 141.85, 141.71, 141.61, 144.58, 141.56, 140.21, 140.07, 139.39, 139.29, 139.06, 137.11, 136.59, 136.47, 139.01, 135.98,

135.94, 135.72, 133.55, 133.46, 133.21, 133.17, 133.09, 133.01, 132.98, 132.64, 132.89, 132.80, 132.76, 132.72, 132.64, 132.61, 132.29, 131.96, 131.87, 131.92, 131.76, 131.71, 131.68, 131.59, 131.51, 131.48, 131.41, 131.39, 131.30, 131.24, 131.13, 130.99, 130.85, 130.44, 130.31, 129.30, 128.99, 128.96 (126 signals, sp^2-carbons in the C_{60} core and the phenyl group), 68.85, 68.63, 68.10, 67.76 (CH_2-O in the previous 4 peaks), 64.87, 64.86, 64.78, 64.75 (quaternary sp^3-C in the C_{60} core in previous 4 peaks), 58.93, 58.83, 58.66, 57.99 (CH-Ph in the previous 4 peaks); UV-vis (cyclohexane) λ_{max} 210 nm (log ε 5.40), 257 (5.02), 328 (4.53), 440 (3.70), 540 (sh, 3.06), 620 (sh, 2.77), 684 (2.42); Anal. Calcd. for $C_{90}H_{26}O_4$: C, 92.31; H, 2.24; N, 0.00. Found: C, 91.99; H, 2.10; N, 0.00; MS (+FAB) *m/z* 1194 ($M + Na^+$), 1172 ($M + H^+$), 720 (C_{60}^+).

Preparation and Purification of C_{60}-PS Adducts

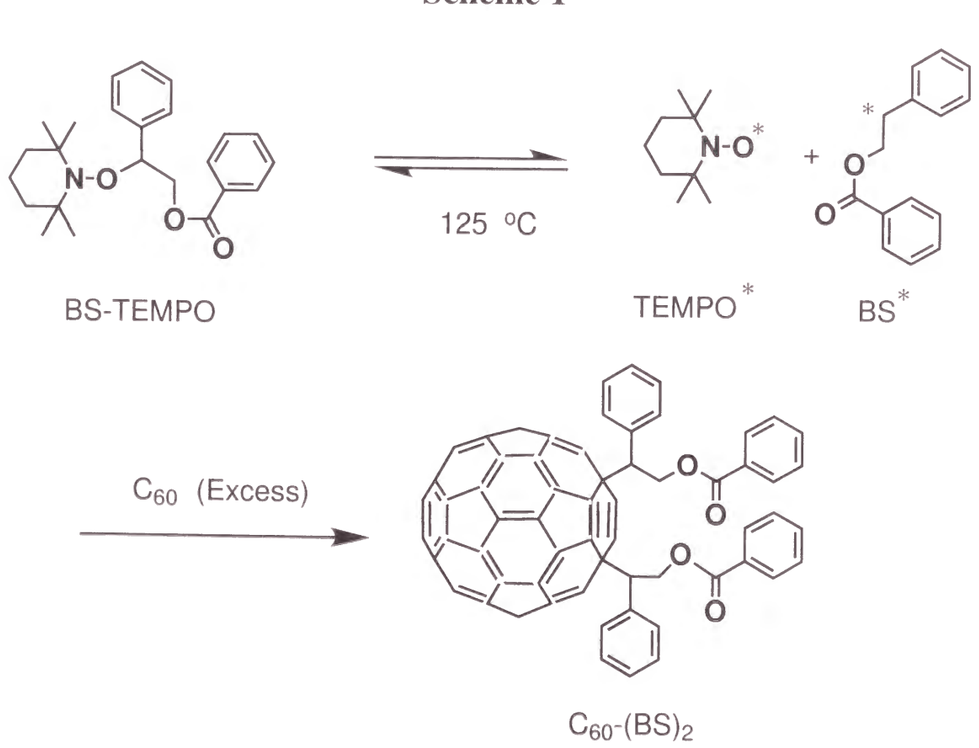
In a typical run, PS-TEMPO (6.90 x 10^{-4} mol L^{-1}) and C_{60} (2.78 x 10^{-3} mol L^{-1}) were dissolved in ODCB (5.00 mL), charged in a glass tube, degassed with several freeze-thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 145 °C for 24 h. The product was a mixture of C_{60}–PS adducts, unreacted PS and unreacted C_{60}. The following methods were used for purification of the samples: Since the solubility of C_{60} in THF is very low, virtually all (unreacted) C_{60} was removed as a precipitate by pouring the reaction mixture into THF (50 mL). The supernatant was dried by evaporation, to which 5.0 mL of benzene was added to dissolve the polymer. To this solution, 5.0 mL of methanol was slowly added and the precipitate was recovered by decantation. Since C_{60}-PS adducts and PS (or PS-TEMPO) have largely different solubilities in organic solvents, this process was effective enough to separate C_{60}-PS (precipitate) from PS (in solution). In fact, it was confirmed that the supernatant contained no C_{60} derivatives and that the PS-TEMPO adduct was perfectly soluble in the benzene/methanol mixture. All precipitate was carefully collected by centrifugation. The decanted solution was confirmed to contain only unreacted PS by ^{1}H NMR, UV and GPC.

RESULTS AND DISCUSSION

C_{60}-BS Adduct

The author investigated the reaction of BS-TEMPO with C_{60} at 125 °C in ODCB as a model reaction of PS-TEMPO with C_{60}. The ^1H NMR spectrum of the purified product was very different from that of BS-TEMPO, and indicated the structure of the product to be a bisadduct, C_{60}-$(BS)_2$ (Scheme 1). Each signal derived from the BS unit was broadened, and the signals relevant to TEMPO were absent. The result of elemental analysis was consistent with the bisadduct structure, i.e., C, 92.0% (92.3); H, 2.1% (2.2); N, 0% (0), where the values in parenthesis are theoretical. Mass spectrum also supported this structure, i.e., the molecular ion peak (M^+) appeared at 1171 in agreement to the theoretical value of 1171.2. Thus, the author can conclude that this C_{60} derivative has two BS units with no TEMPO moiety.

Scheme 1



It is known that disubstituted C_{60} derivatives show characteristic UV-vis absorption depending on the relative positions of substitution. Figure 1 shows the UV-vis spectrum of C_{60}-$(BS)_2$ in comparison to those of 1,4-difluorenyldihydro[60]fullerene (C_{60}-$(Flu)_2$)[22] and 1-(1-octynyl)-2-isobutoxyethyl-1,2-dihydro[60]-fullerene (C_{60}-IBVE)[23] described in Chapter 1. Clearly, the spectrum of C_{60}-$(BS)_2$ is very different from that of C_{60}-IBVE, and quite similar to that of C_{60}-$(Flu)_2$. Both C_{60}-$(BS)_2$ and C_{60}-$(Flu)_2$ exhibit a broad absorption at around 440 nm. This shows that C_{60}-$(BS)_2$ is a 1,4-disubstituted derivative, not a 1,2 type.

The ^{13}C NMR spectrum is shown in Figure 2. In addition to the four characteristic peaks (a–d), aromatic carbons derived from the C_{60} and phenyl moieties were observed between 110 ppm and 160 ppm. Interestingly, each of the peaks a through d splits into four peaks. Multiple peak-splitting is also seen for the aromatic carbons.

Most of the reported C_{60} derivatives carrying two identical substituents at the 1,4-positions have a C_{2v} symmetry. In contrast, the 1,4-C_{60}-$(BS)_2$ does not have this symmetry due to the two asymmetric carbons (c) of the 2-benzoyloxy-1-phenylethyl group directly attached to the C_{60} core, and therefore it should exhibit 116 signals for the sp^2 carbons of the C_{60} core. (Actually, 126 peaks including those derived from the phenyl group were discernible in the spectrum.) A similar phenomenon was observed for a C_{60} derivative having a chiral phosphine-borane moiety.[24] With all these data, the author concludes that the product is 1,4-bis(2-benzoyloxy-1-phenylethyl)dihydro[60]fullerene. As has been described, the preparation procedure is very simple, and should be practically useful as a method to functionalize C_{60}.

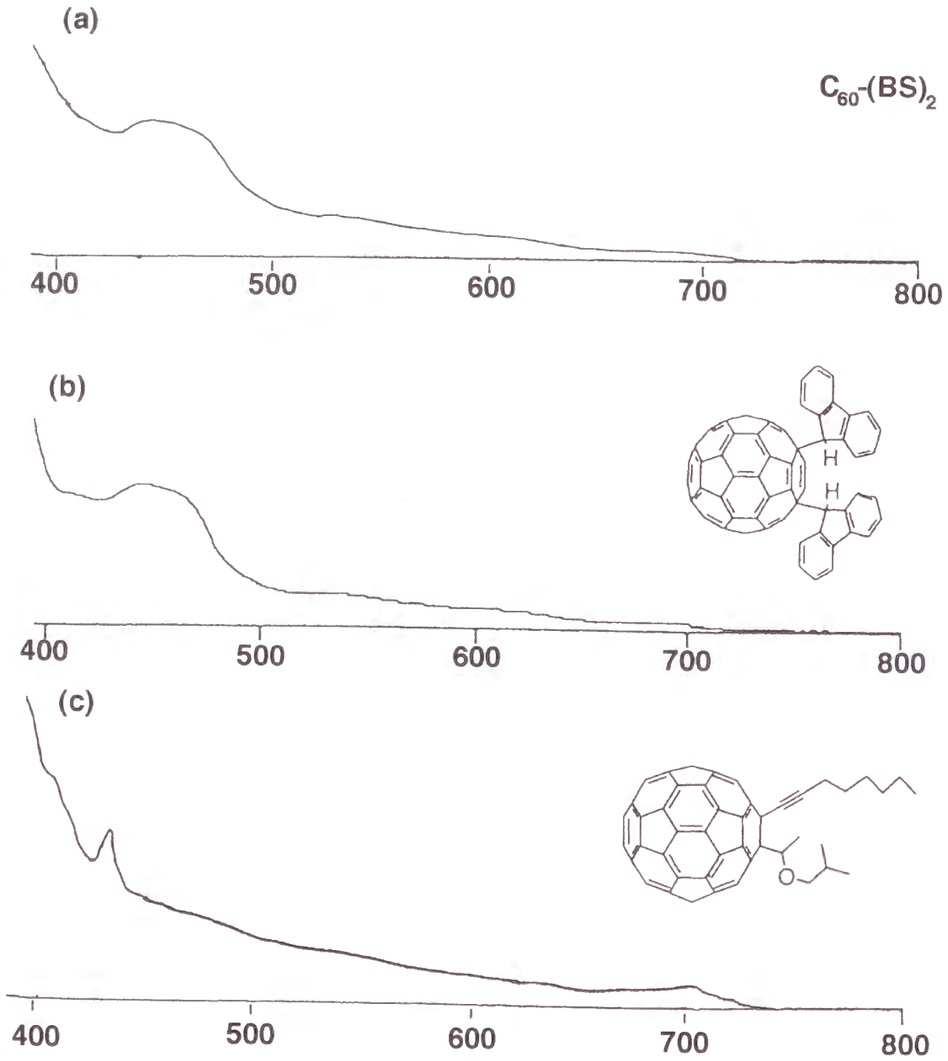


Figure 1. UV-vis spectra of (a) C_{60}-$(BS)_2$, (b) C_{60}-$(Flu)_2$ and (c) C_{60}-IBVE in cyclohexane.

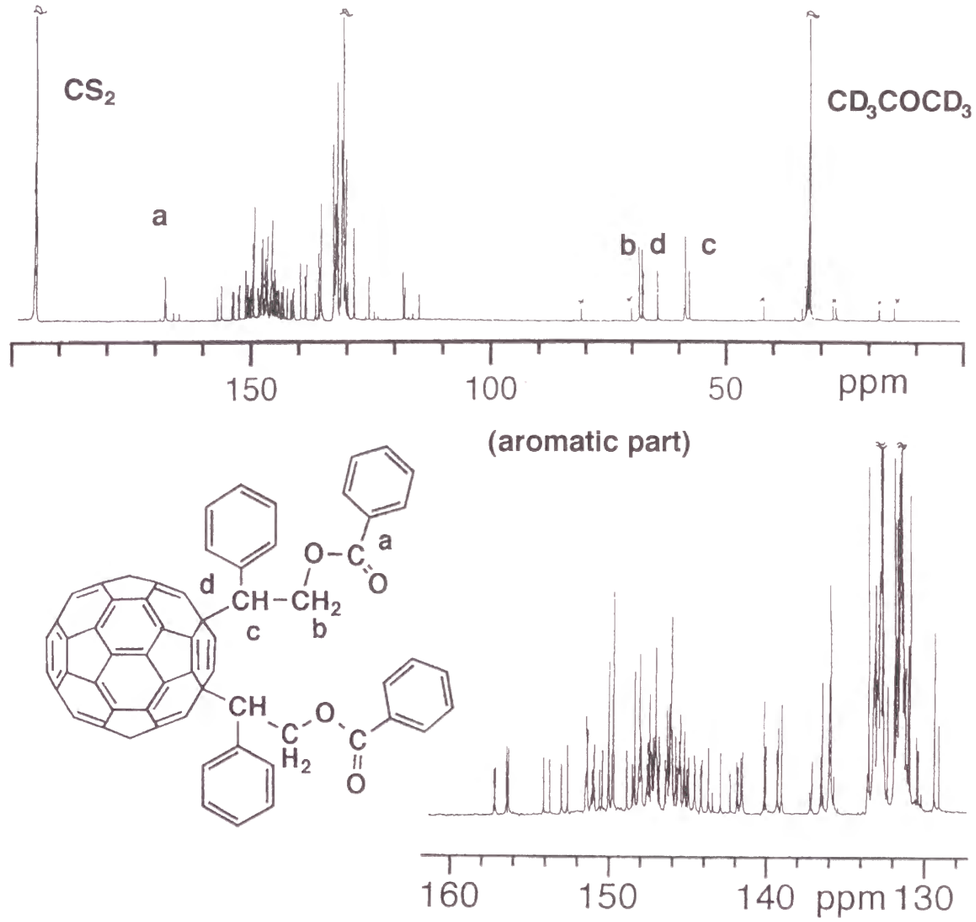


Figure 2. ^{13}C NMR spectrum of C_{60}-BS in $CS_2/(CD_3)_2CO$ = 4:1.

C_{60}-PS Adducts

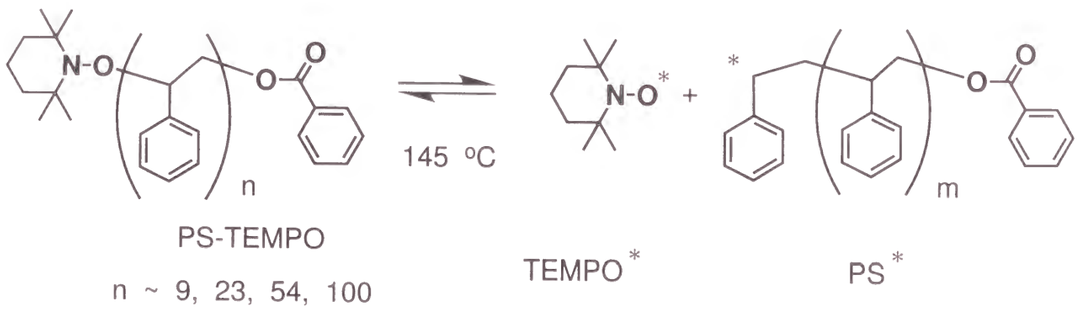
The author investigated the reaction of four PS-TEMPO samples with C_{60} according to Scheme 2. Table 1 shows the reaction conditions. The yield of the purified product, which is designated as C_{60}-PS, ranged from 60% to 80%, showing no appreciable dependence on the molecular weight of the PS moiety.

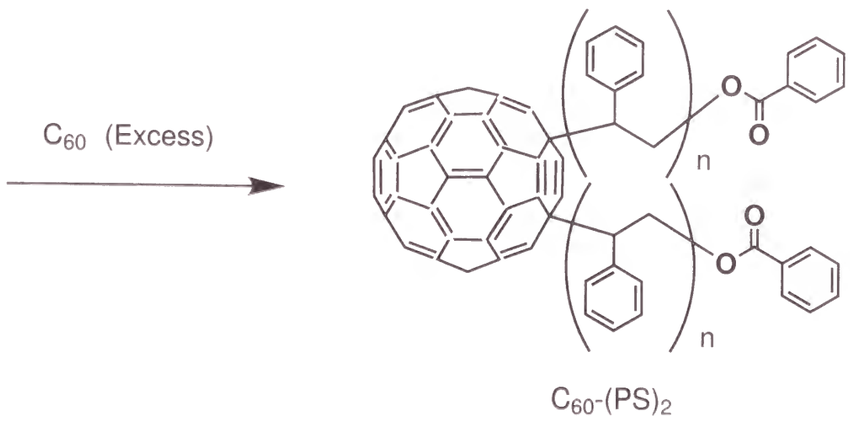
Table 1. Reaction of PS-TEMPO with C_{60}[a]

code	M_n (M_w/M_n)[b]	% Yield[c]
PS-TEMPO-1000	1040 (1.11)	56
PS-TEMPO-2400	2400 (1.14)	75
PS-TEMPO-5500	5500 (1.18)	67
PS-TEMPO-10000	10000 (1.14)	78

[a] In *o*-dichlorobezene (145 °C, 24 h); [PS-TEMPO] = 3.5×10^{-5} mol L^{-1} and $[C_{60}] = 1.4 \times 10^{-4}$ mol L^{-1} in all cases. [b] By PS-calibrated GPC. [c] 100 x (wt. of PS in C_{60}-PS) / (wt. of PS-TEMPO).

Scheme 2





The author characterized the samples of C_{60}-PS by ^1H and ^{13}C NMR, UV-vis, and GPC. Figure 3 shows the ^{13}C NMR spectra of C_{60}-PS-1000, where the attached number shows an approximate value of M_n of the PS moiety. In addition to the peaks derived from PS, aromatic carbons derived from C_{60} and the ipso carbon in PS are observed between 140 and 160 ppm.

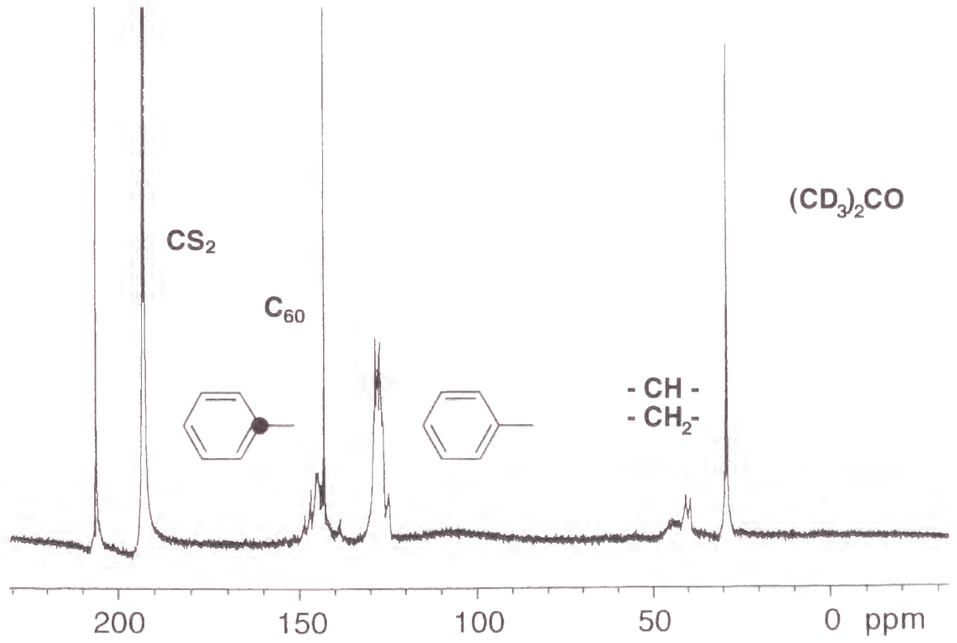


Figure 3. ^{13}C NMR spectrum of C_{60}-PS-1000 in $CS_2/(CD_3)_2CO$ = 4:1.

Figure 4 shows the GPC curves of C_{60}-PS-5500 recorded by different detectors. The PS moiety is detectable by both UV-270 nm and RI, but not by UV-430 nm, while the C_{60} moiety is detectable by all UV-430 nm, UV-270 nm and RI. The three GPC curves of C_{60}-PS-5500 are nearly identical with each other, which indicates a chemical uniformity of the polymer. Very interestingly, the three curves retain the narrow polydispersity and commonly show an M_n value of 11600, which is about twice that of the PS-TEMPO adduct. Similar results were obtained for all other samples (Table 2). This indicates that the reaction of PS-TEMPO with C_{60} also leads to a bisadduct.

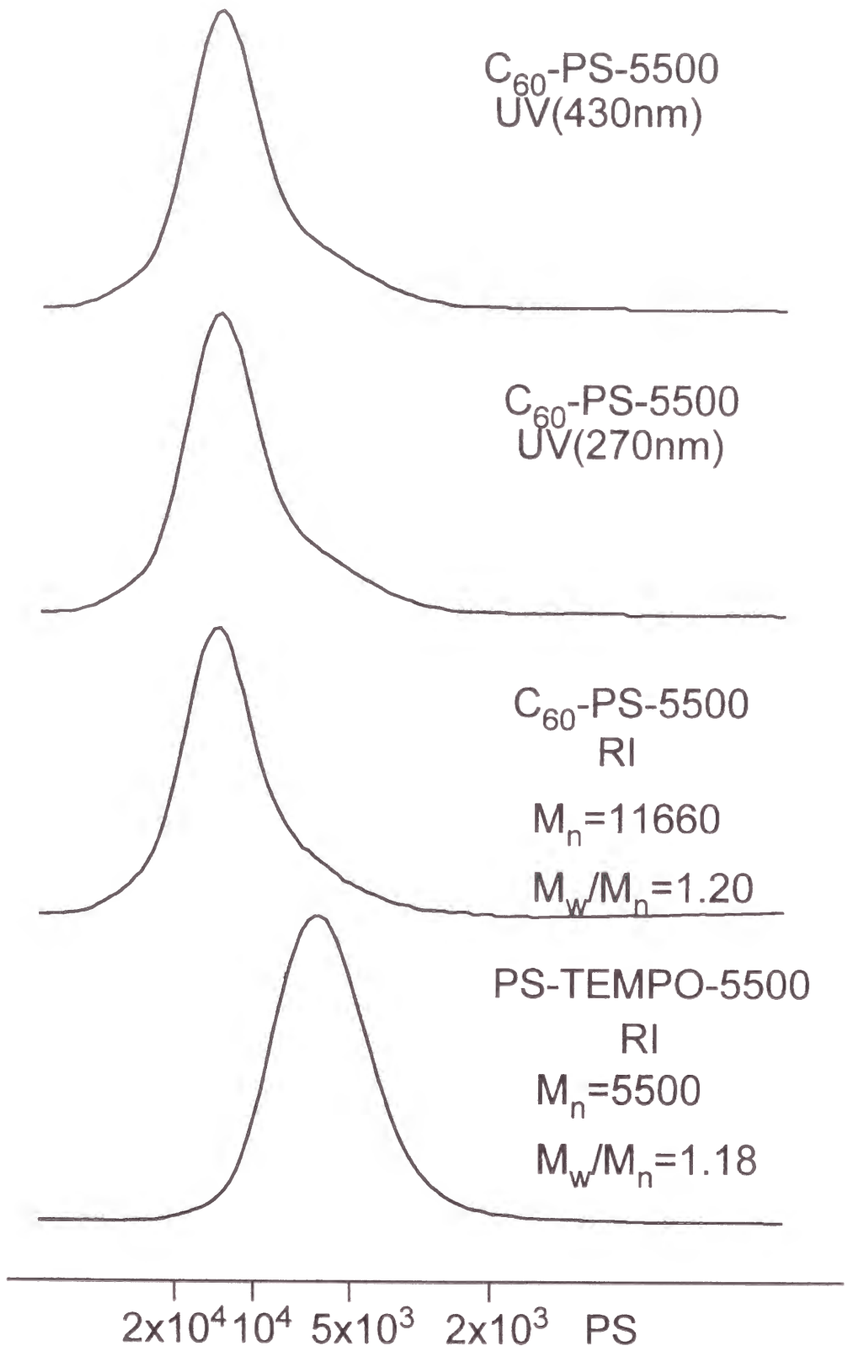


Figure 4. GPC curves of C_{60}-PS-5500 by UV (430 nm and 270 nm) and RI compared with the curve for PS-TEMPO-5500 by RI.

Figure 5 compares the UV-vis spectra from C_{60}-$(BS)_2$ and C_{60}-PS-1000 solutions of the same concentration. Clearly, the two spectra are very similar to each other. This means that the polymer derivative is also a 1,4-bisadduct, like C_{60}-$(BS)_2$. On the basis of the molar absorption coefficient of C_{60}-$(BS)_2$ at 440 nm, the M_n of the polymer derivatives was estimated (Table 2). Table 2 shows that the values of M_n by GPC and those by UV well agree with each other, and both are close, in most cases, to those calculated for the bisadduct structure. However, the GPC value for the lowest-M_n sample is significantly smaller than the UV and theoretical values. This implies that the C_{60} moiety contributes little to the hydrodynamic volume of the molecule because of its compact size and/or poor solubility, leading to an underestimation of M_n by the PS-calibrated GPC. As the size of the PS moiety increases, the relative importance of the C_{60} moiety should decrease and the GPC values will become more reliable, as is in fact observed (Table 2). The author thus concludes that the reaction of PS-TEMPOs with C_{60} produces well-defined PS-disubstituted 1,4-dihydro[60]fullerenes, selectively.

Table 2. Molecular Weights of PS-TEMPO and C_{60}-PS Estimated by GPC and UV Spectroscopy

M_n (M_w/M_n) by GPC		M_n by UV (440nm)[a]	M_n calcd.
PS-TEMPO	C_{60}-PS	C_{60}-PS	C_{60}-$(PS)_2$
1040 (1.11)	1410 (1.23)	2750	2800
2400 (1.14)	4600 (1.24)	7000	5500
5500 (1.18)	11600 (1.20)	10000	11700
10000 (1.14)	20100 (1.26)	20000	20700

[a] Calculated based on the molar absorption coefficient of C_{60}-$(BS)_2$ of 5.01×10^3 mol^{-1} mL cm^{-1}.

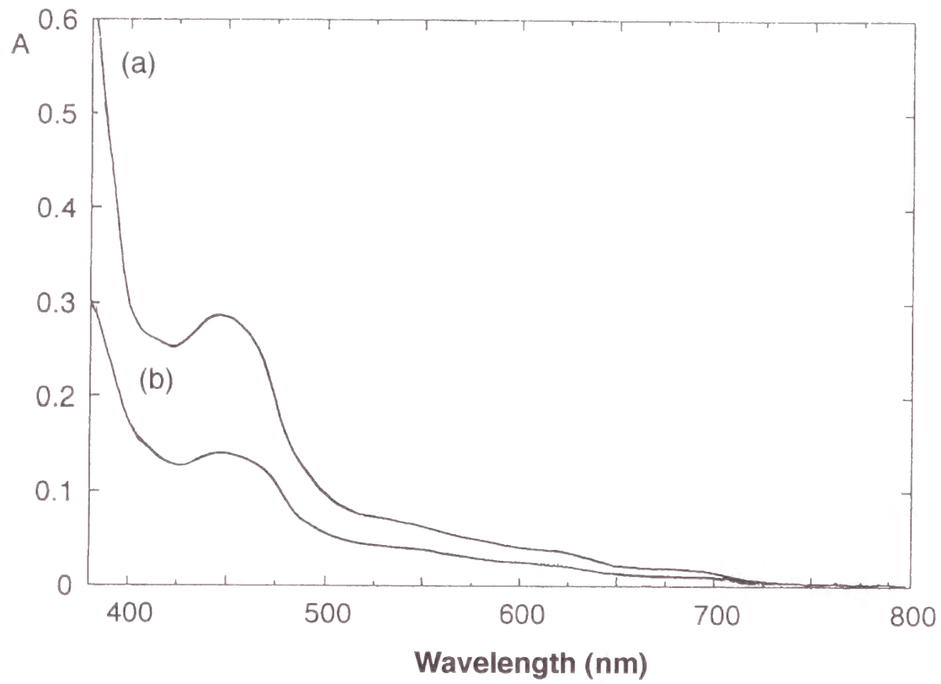


Figure 5. UV-vis spectra from (a) C_{60}-BS (5.8×10^{-5} mol L^{-1}) and (b) C_{60}-PS-1000 solutions of the same weight concentration in cyclohexane.

Reaction Mechanism

Possible reactions in a C_{60}/PS-TEMPO system at a high temperature may include

$$\text{PS-TEMPO} \rightleftharpoons \text{PS}^* + \text{TEMPO}^* \quad (1)$$

$$\text{PS}^* + C_{60} \longrightarrow \text{PS-}C_{60}^* \quad (2)$$

$$\text{PS-}C_{60}^* + \text{PS}^* \longrightarrow C_{60}\text{-(PS)}_2 \quad (3)$$

$$2\text{PS}^* \longrightarrow (\text{PS})_2 \text{ (mainly)} \quad (4)$$

$$2\text{PS-}C_{60}^* \rightleftharpoons \text{PS-}C_{60}\text{-}C_{60}\text{-PS} \quad (5)$$

$$\text{PS-}C_{60}^* + \text{TEMPO}^* \rightleftharpoons \text{PS-}C_{60}\text{-TEMPO} \quad (6)$$

An independent experiment has confirmed that TEMPO* does not add to C_{60}.

Reaction 1 is the reversible dissociation of the polystyroxyamine, whose dissociation and combination (association) rate constants are known.[20,25] The dissociation rate constant at 145 °C is fairly large (9.4×10^{-3} s^{-1}),[25] so that the concentrations of PS* and TEMPO* would reach their quasi-stationary values at an early stage of the heat treatment ($\leq$ 1 min) after the initial rapid increase from virtually zero values at time zero. Reaction 2 is the addition to C_{60}, and the C_{60} radical thus produced can be capped by another PS radical to produce a 1,4-bisadduct, reaction 3, as the author has seen above. Competitively to this can occur reactions 5 and 6. Reaction 5 is the dimerization reported by Morton et al.,[26] which actually is a reversible reaction (due to the steric instability) with the equilibrium more inclined towards the radical side at higher temperatures. Since reactions 5 and 6 are reversible ones and reaction 3 is an irreversible one, the C_{60} dimer and the C_{60}-TEMPO adduct would eventually become minor in population, even if they may be populated at some stage of the heat treatment. In fact, no TEMPO moiety was detected in the main product, and the molar ratio of the PS and C_{60} moieties in the main product was 2 to 1 in all cases (see above). Reaction 4, which can also occur competitively to section 3, would be unimportant when [PS*] is small enough and reaction 2 is much faster than 4, or [PS*] << [PS-C_{60}*]. This seems to be the case, since only a small amount of PS dimer (<10%) was detected in the (benzene/methanol)-soluble fraction which consisted predominantly of homo-PS chains.

An independent experiment suggests that, at 145 °C, the reaction seems to be completed within 1 h, and little increase in conversion is expectable with a longer heat

treatment. Fukuda recently observed that a TEMPO radical deactivates a PS radical by abstracting the β-proton producing a hydroxyamine and a terminally unsaturated PS.[27,28] The first-order decomposition rate constant of PS-TEMPO due to this mechanism is 4.2 x 10^{-5} s^{-1} at 145 °C.[28] This value means that after 5 h of the heat treatment at 145 °C, for example, about 50% of the PS-TEMPO adduct decomposes spontaneously. Thus a long heat treatment at a high temperature is not recommended.

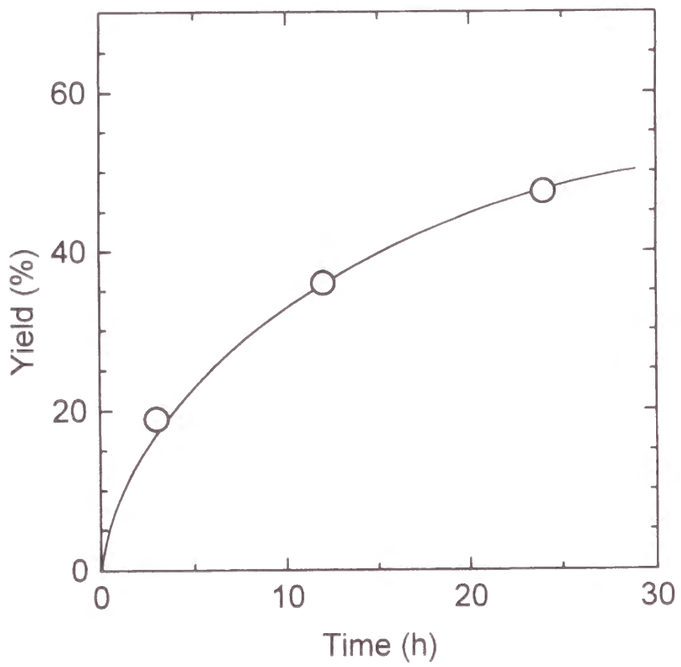


Figure 6. Time-conversion curve for the reaction of C_{60} with PS-TEMPO-3700 at 125 °C.

To examine the reactions more closely, the author has made a test run at a lower temperature, 125 °C, with other conditions unchanged. At this temperature, the decomposition rate is roughly 1/10 of that at 145 °C,[28] and all other reactions should also be slower. Figure 6 shows that the conversion gradually increases with time, suggesting that a maximum conversion is reached after several tens of hours. A GPC analysis showed that a main product is again a PS-bisadduct, independent of time. Namely, an increase in

reaction time increases the amount of the product but does not change its characteristics.

There are two possible reasons why bisadducts are selectively produced. One is the rather small molar ratio of PS-TEMPO to C_{60} in the feed (1:4, in the present experiments). However, if the addition of PS radicals to C_{60} occurs randomly in proportion to the number of the (unreacted) double bonds of the C_{60} moiety, one would expect to obtain, e.g., a tetrasubstituted compound, according to

$$C_{60}\text{-}(PS)_2 \quad + \quad 2PS^* \quad \longrightarrow \quad C_{60}\text{-}(PS)_4 \qquad (7)$$

with a molar ratio of about 1/4 (weight ratio of about 1/2) relative to the bisadduct. In the actual products, however, tetramers are hardly detectable or, if there are any, much less than expected for the random process (cf. Figure 4). It follows that the bisadducts have a rather high barrier against a further addition of PS*. This barrier may be an entropic (excluded-volume) or a chemical effect (or both) caused by the two PS substituents already attached to the C_{60} core. In any case, it is understandable that the addition of PS* to C_{60}-$(PS)_2$, which is a polymer-polymer reaction, is much slower than the addition of PS* to C_{60}, a reaction between a polymer and a low-mass compound. In this regard, the author expects that the decrease of the PS chain length would decrease the selectivity for disubstitution, increasing the chance of multiple additions.

In Figure 7, the author compares the GPC charts for the two runs carried out with the shortest PS-TEMPO available (M_n = 1040) with a feed molar ratio of PS-TEMPO to C_{60} of (a) 1:4 and (b) 1:2. Chart b exhibits an obvious shoulder in the molecular weight region corresponding to that of the tetramer, as expected. Thus, in order to obtain bisadducts with a high selectivity, the use is recommended of an excess amount of C_{60} and/or a high-molecular weight, and preferably, narrow-polydispersity PS-TEMPO or equivalent radical source.

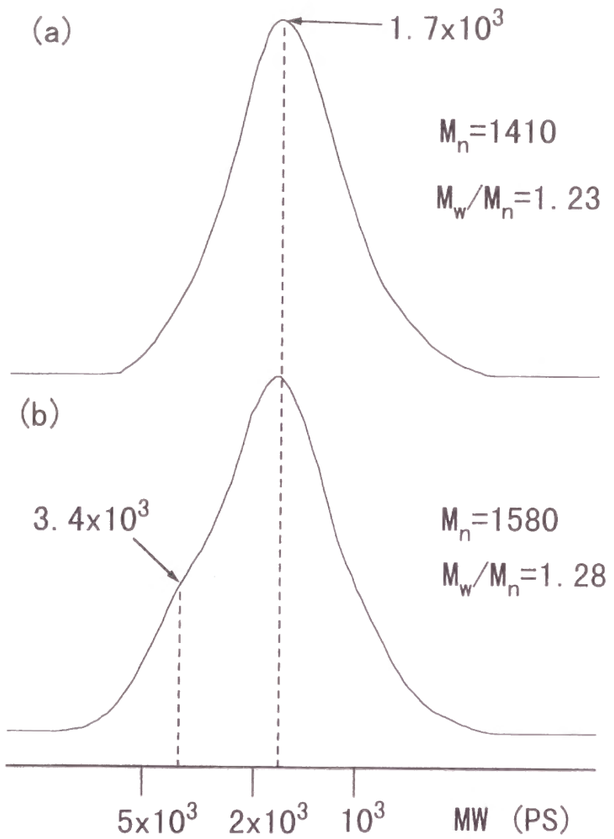


Figure 7. GPC curves for the main products obtained by the heat treatment (145 °C) of PS-TEMPO-1000/C_{60} mixtures with [PS-TEMPO]/[C_{60}] = 1/4 (a), and 1/2 (b).

Redox Properties

The redox properties of the new compounds C_{60}-$(PS)_2$ and C_{60}-$(BS)_2$ were examined by cyclic voltammetry. Figure 8 demonstrates an example of the voltammogram of C_{60}-$(BS)_2$. Although some weak bumps are observed with a wide sweeping range, the only reproducible waves were a single irreversible oxidation peak and three reversible waves as in the case of C_{60}. The numerical values obtained are summarized in Table 3. The reduction potentials of C_{60}-$(BS)_2$ and C_{60}-$(PS)_2$ were generally close to those of C_{60}, only about 0.1 V negatively larger than the latter, in agreement with the general tendency of disubstituted C_{60} derivatives.[29]

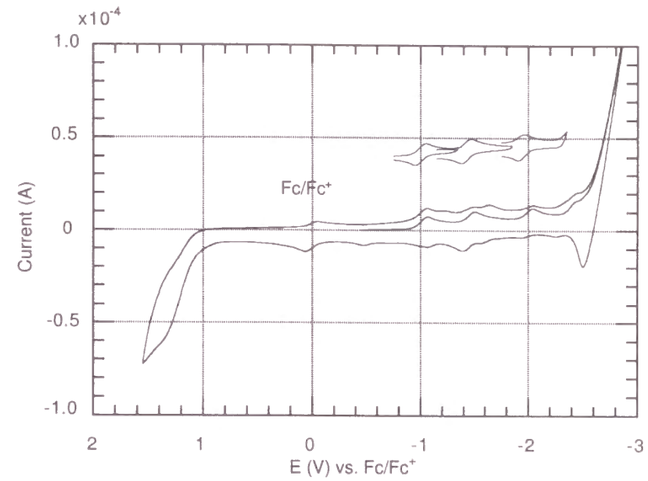


Figure 8. Cyclic voltammogram of C_{60}-$(BS)_2$. Insets show the individual reduction waves measured separately.

Table 3. Results of Cyclic Voltammetry[a]

compound	reversible, $E_{1/2}$ (V)		
	E_{red}^1 (V)	E_{red}^2 (V)	E_{red}^3 (V)
C_{60}	-0.93	-1.36	-1.85
C_{60}-$(BS)_2$	-1.00	-1.41	-1.94
C_{60}-$(PS\text{-}1000)_2$	-0.98	-1.40	-1.92
C_{60}-$(PS\text{-}2400)_2$	-1.00	-1.39	-1.95
C_{60}-$(PS\text{-}5500)_2$	-1.00	-1.44	-2.01
C_{60}-$(PS\text{-}10000)_2$	-0.99	-1.40	-2.03

[a] Potential in volts vs ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0.05 mol L^{-1}) as a supporting electrolyte; scan rate, 0.1 V s^{-1}.

CONCLUSIONS

Narrow-polydispersity polystyryl adducts with TEMPO (PS-TEMPOs), prepared by the nitroxide-mediated "living" radical polymerization technique, were heated with C_{60} in *o*-dichlorobenzene at 145 °C. The products consisted of three components: (1) unreacted C_{60}, which could readily be recovered as the only insoluble component in THF, (2) polystyryl adducts with C_{60} and (3) unreacted PS or PS-TEMPO. Owing to the large difference in solubility between C_{60} derivatives and PS or PS-TEMPO, components 2 and 3 were easily separable in a benzene/methanol mixture. The C_{60} derivatives thus obtained with a 60~80% yield were found to be 1,4-dipolystyryldihydro[60]fullerenes, predominantly. A low-mass model compound 2-benzoyloxy-1-phenylethyl adduct with TEMPO gave essentially the same result.

Main reasons for the selective production of the bisadducts in these systems were suggested to be an excess (4-fold excess) of C_{60} relative to PS-TEMPO (or BS-TEMPO) in the feed and/or the potential barrier of the PS moieties of the bisadducts that restricts a further addition of PS radicals to the C_{60} moiety. The instabilities of the C_{60}-TEMPO and C_{60} dimers at high temperatures might be another reason for the bisadduct selectivity.

The disubstituted derivatives thus synthesized retained the redox properties of C_{60} and gave UV-vis spectra characteristic of 1,4-bisadducts of C_{60}.

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Chapter 5

C_{60} Fullerenes with Two Well-Defined Styrene-Based Polymer Arms. 1. Solubility Characteristics in Organic Solvents

ABSTRACT

1,4-Disubstituted, low-polydispersity C_{60} derivatives of the types C_{60}-$(PS)_2$, C_{60}-$(PVP)_2$, and C_{60}-$(PS\text{-}PVP)_2$, where PS is polystyrene, PVP is poly(*p*-vinylphenol), and PS-PVP is a diblock copolymer of this sequence, were prepared by applying the nitroxide-controlled free radical polymerization technique and studied with their solubility behaviors in some organic solvents. The first clear experimental evidence was obtained for the formation of multimolecular micelles of C_{60}-bearing polymers under certain conditions: for example, light-scattering measurements showed that the C_{60}-$(PVP)_2$, C_{60}-$(PS\text{-}PVP)_2$, and C_{60}-$(PS)_2$ samples with a number-average molecular weight of a polymer arm roughly about 10000 formed stable micelles in dilute tetrahydrofuran (THF) solution with an association numbers of about 20, 6, and 1 (no micellization), respectively. The solvent power of THF for the mother polymers increases in this order. The saturation solubilities S_{C60} of the C_{60} moiety in C_{60}-$(PS)_2$ and C_{60}-$(PVP)_2$ were determined as a function of the PS and PVP chain length, showing that, in THF, the S_{C60} in the PS adduct is exceptionally large, much larger than that in the PVP adduct of the same chain length, in accord with the mentioned micellization tendency in dilute solution. On the other hand, C_{60}-$(PVP)_2$ showed a reasonable solubility in a polar solvent (methanol), in which C_{60}-$(PS)_2$ was little soluble. The micellization was found to be accompanied by characteristic changes in the UV-vis spectra, depending on micelle size.

INTRODUCTION

Despite its unique chemical and physical properties,[1] unfortunately, the fabrication of fullerene-based devices has been limited due to its poor solubility and processability. Polymer-bound fullerenes are particularly interesting because they can have the high solubility and processability of polymers as well as the unique properties of fullerene. Hence various kinds of C_{60}-containing polymers have been synthesized and studied with their optical, electrical, and solubility properties.[2-6] However, the information provided by these studies has often been limited.

As indicated above, C_{60} has very limited solubilities in solvents: no solvent is known that is miscible with C_{60} in all proportions. The maximum saturation solubility has been obtained with 1-chloronaphthalene at 51 mg/mL.[7] Although C_{60} is virtually insoluble in water, it can be solubilized in aqueous surfactant solutions via incorporation into the hydrophobic core.[8] Interestingly, the formation of colloidal forms of C_{60} in aqueous surfactant solutions drastically changes the UV-vis spectrum from that in a molecularly dispersed state.[8a] Another useful method to solubilize C_{60} is derivatization. The solubility of a C_{60}-containing polymer is, in a high-molecular weight limit of the polymer, expected to be essentially the same as that of the mother polymer, as in fact reported.[4d] However, the concentration of the C_{60} moiety itself in such a limit is small because of the small fraction of C_{60} in the polymer. The maximum saturation solubility of the C_{60} moiety in a solvent will be obtained when the C_{60} fraction in the polymer and the solubility of the mother polymer are optimized. Thus, it is required, in the discussion of C_{60} solubility by derivatization, to study the solubility of the derivatives as a function of the chain length of the polymer moiety as well as the solubility of the mother polymer itself. Such a systematic study has never been reported before this work. Here the author has prepared 1,4-disubstituted, low-polydispersity C_{60} derivatives of the types C_{60}-$(PS)_2$, C_{60}-$(PVP)_2$, and C_{60}-$(PS\text{-}PVP)_2$ by applying the nitroxide-controlled free radical polymerization technique,[9]

where PS, PVP, and PS-PVP denote polystyrene, poly(*p*-vinylphenol),[10] and PS-PVP type diblock copolymer,[10] respectively. This synthetic procedure was shown to be a simple and versatile one to yield well-defined C_{60} 1,4-bisadducts.[5]

Another important problem addressed in this work is the states of solution, i.e., the monomolecularly dispersed versus the multimolecularly associated state of the C_{60}-polymers in solution. The first direct experimental evidence will be presented showing that the C_{60} polymers form multimolecular micelles depending on the solubility and length of the polymer moiety and that the micellization accompanies characteristic changes in the UV-vis spectra, similar to those observed for pure C_{60} in aqueous surfactant solutions.[8a]

EXPERIMENTAL

Measurements

Static light-scattering measurements were made in tetrahydrofuran (THF) solvent at 25 °C by a DLS-7000 photometer (Otsuka Electronics, Japan), which was calibrated with benzene. The refractive index increment (dn/dc) in THF solution at 25 °C was measured by a DRM1030 differential refractometer (Otsuka Electronics).

Materials

p-tert-Butoxystyrene, kindly donated by Hokko Chemicals (Japan), was washed three times with 10 wt% aqueous NaOH solution and three times with distilled water, and dried over anhydrous sodium sulfate. The filtered dry monomer was stored at -15 °C in an ampule.[10]

Preparation of PS-TEMPO and PBOS-TEMPO

The polystyryl adduct with TEMPO (PS-TEMPO) was prepared as described previously.[2,9d] In a typical run to prepare a PBOS adduct with TEMPO,[10] a mixture of BOS, BPO (1.02×10^{-1} mol L^{-1}), and TEMPO (1.05×10^{-1} mol L^{-1}) was charged in a glass tube, degassed with several freeze-thaw cycles, and sealed off under vacuum. Then, the

mixture was heated at 95 °C for 3.5 h and at 125 °C for 3 h to yield a polymer. The polymer was recovered as a precipitate from a large excess of methanol, purified by reprecipitation with a chloroform (solvent)/methanol (nonsolvent) system, and thoroughly dried (conversion: 50.5%), which, according to the PS-calibrated GPC, had a number-average molecular weight M_n of 2600 and a M_w/M_n ratio of 1.12, where M_w is the weight-average molecular weight.

Preparation of PBOS-PS-TEMPO (Scheme 1)

A PBOS-TEMPO adduct (0.30 g, M_n = 6100, M_w/M_n = 1.08), obtained as above, was dissolved in styrene (0.92 mL) and heated at 125 °C for 2 h to obtain a PBOS-PS type block copolymer end-capped by TEMPO (PBOS-PS-TEMPO: 0.45 g, M_n = 13500, M_w/M_n = 1.15).

Preparation and Purification of C_{60}-$(PS)_2$, C_{60}-$(PBOS)_2$, and C_{60}-$(PS\text{-}PBOS)_2$

Preparation and purification of C_{60}-$(PS)_2$, C_{60}-$(PBOS)_2$, and C_{60}-$(PS\text{-}PBOS)_2$ were carried out on the basis of the same method described in Chapter 4. For example, PS-TEMPO (6.90×10^{-4} mol L^{-1}) and C_{60} (2.78×10^{-3} mol L^{-1}) were dissolved in ODCB (5.00 mL), charged in a glass tube, degassed with several freeze-thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 145 °C for 24 h. The product was a mixture of C_{60}–PS adducts, unreacted PS and unreacted C_{60}. Since the solubility of C_{60} in THF is very low, virtually all (unreacted) C_{60} was removed as a precipitate by pouring the reaction mixture into THF (50 mL). The supernatant was dried by evaporation, to which 5.0 mL of benzene was added to dissolve the polymer. To this solution, 5.0 mL of methanol was slowly added and the precipitate was recovered by decantation. Since C_{60}-PS adducts and PS (or PS-TEMPO) have largely different solubilities in organic solvents, this process was effective enough to separate C_{60}-PS (precipitate) from PS (in solution). In fact, it was confirmed that the supernatant contained no C_{60} derivatives and that the PS-TEMPO adduct was perfectly soluble in the benzene/methanol mixture. All precipitate

was carefully collected by centrifugation. The decanted solution was confirmed to contain only unreacted PS by ^{1}H NMR, UV and GPC. C_{60}-$(PBOS)_2$ and C_{60}-$(PS\text{-}PBOS)_2$ were prepared and purified similarly.

Hydrolysis of PBOS Moieties (Scheme 2)

Hydrolysis of PBOS and PBOS segments was carried out as described previously.[10,11] For example, 1 g of PBOS was dissolved in 1,4-dioxane (20 mL), and hydrobromic acid (8.6 N, 1.3 mL) was added. The solution was then stirred magnetically at room temperature for 24 h, and poured into water (200 mL). The precipitate was filtered off, again dissolved in 1,4-dioxane (15 mL), precipitated in hexane (180 mL), recovered by filtration, and finally freeze-dried twice from 1,4-dioxane to give poly(*p*-vinylphenol) (PVP) as a white powder with a quantitative yield.

Saturation Solubilities of C_{60}-$(PS)_2$ and C_{60}-$(PVP)_2$

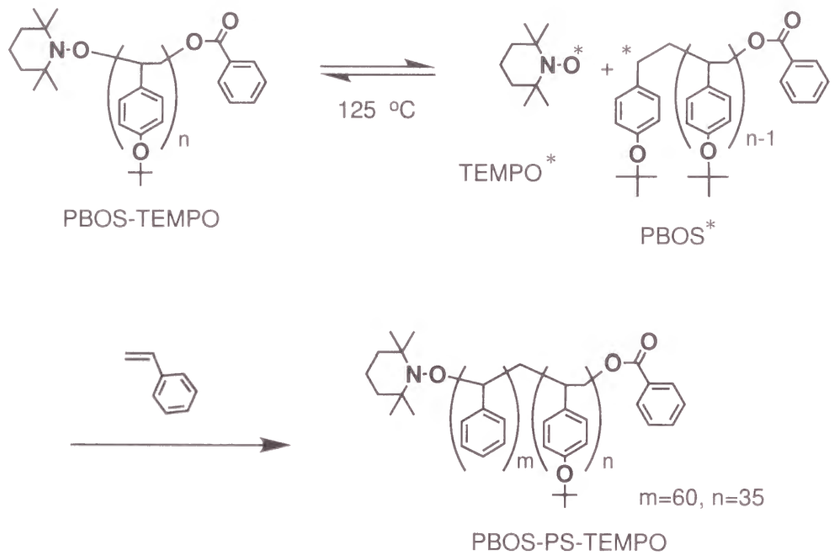
All operations were conducted in an air-conditioned room kept at 25 °C. A 40 mg quantity of each polymer sample was mixed with 0.1 mL of a test solvent in a centrifuge tube. After 1 min of sonication, the mixture was centrifuged for 20 min. The supernatant (10 μL, measured by microsyringe) was diluted to 100 or 500 times by the test solvent, and the concentration of the C_{60} moiety was determined by measuring the UV-vis absorption intensity at 440 nm and using the known molar absorption coefficient of C_{60}-$(BS)_2$ at 440 nm.[5]

RESULTS AND DISCUSSION

Synthesis and Characterization of C_{60}-$(PBOS)_2$ and C_{60}-$(PS\text{-}PBOS)_2$

From a synthetic viewpoint, this work is a simple extension of the previous one in which well-defined 1,4-bisadducts of C_{60} with PSs were prepared by the reaction of PS-TEMPO adducts with C_{60} at a high temperature, which was described in Chapter 4.

Scheme 1



Scheme 2

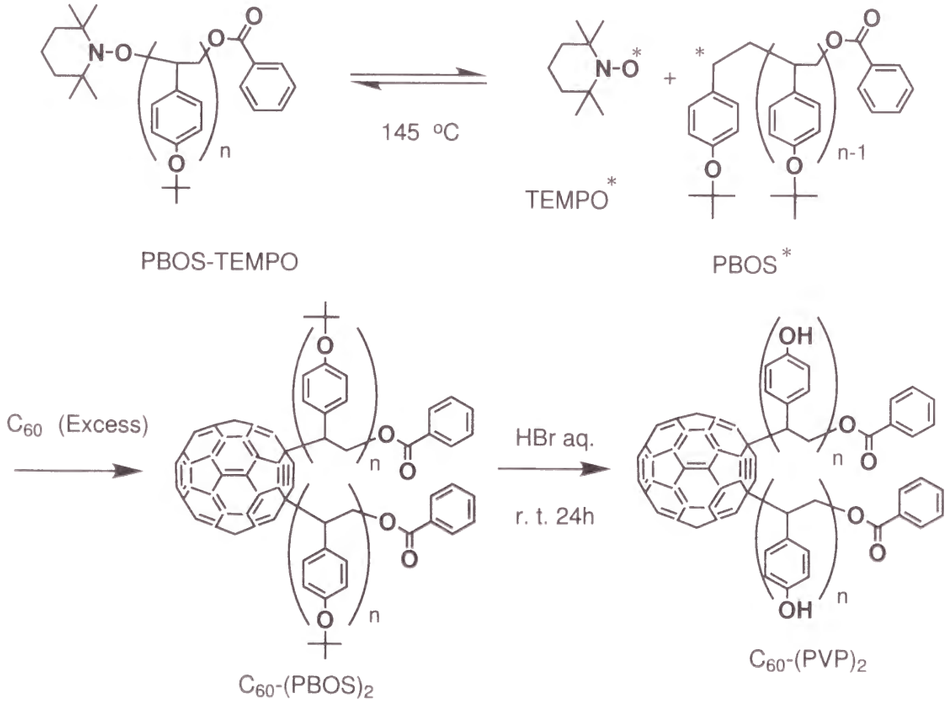


Table 1. Reaction of TEMPO Adducts with C_{60}[a]

precursor (TEMPO adduct)		product (C_{60} adduct)			
code	M_n (M_w/M_n) by GPC[b]	yield[c] (%)	M_n (M_w/M_n) by GPC[b]	M_n by UV[d]	M_n calcd[e]
PBOS-TEMPO-1	890 (1.16)	31	1320 (1.31)	1800	2300
PBOS-TEMPO-2	2600 (1.12)	44	4200 (1.27)	4600	5700
PBOS-TEMPO-3	5200 (1.13)	52	9300 (1.21)	10200	10900
PBOS-TEMPO-4	9800 (1.14)	42	17300 (1.24)	18800	20100
PBOS-PS-TEMPO-5[f]	13500 (1.15)	46	24600 (1.27)	26100	27500

[a] In *o*-dichlorobezene (145 °C, 24 h); [TEMPO-adduct] = 3.5 x 10^{-5} mol L^{-1} and [C_{60}] = 1.4 x 10^{-4} mol L^{-1} in all cases. [b] Calibrated by standard PSs. [c] 100 x (wt of PBOS in C_{60}-PBOS)/(wt of PBOS-TEMPO). [d] Calculated on the basis of the molar absorption coefficient of C_{60}-$(BS)_2$ of 5.01 x 10^3 mol^{-1} mL cm^{-1} (440 nm). [e] Caluclated for bisadduct structure. [f] $M_{n,\,PBOS}/M_{n,\,PS}$ = 6100/7400 (by GPC).

The preparation and characterization of the PBOS-TEMPO and PS-PBOS-TEMPO adducts used in this work were described in detail elsewhere.[10] A possible mechanism by which the PS bisadducts are selectively produced was proposed in Chapter 4, which should also apply to the PBOS and PS-PBOS systems.

Table 1 summarizes the result of the reaction of the TEMPO adducts with C_{60}. The yields (for definition, see footnote c to Table 1) of the purified products, which the author designates as C_{60}-$(PBOS)_2$ and C_{60}-$(PS\text{-}PBOS)_2$, ranged from 30% to 50%, showing no clear dependence on the molecular weight of the precursor alkoxyamine.

Figure 1 shows the ^{13}C NMR spectrum of C_{60}-$(PBOS)_2$-1, where the attached number shows the code number of the precursor alkoxyamine. In addition to the peaks derived from the PBOS moiety, the aromatic carbons derived from the C_{60} moiety and the ipso

carbon in the BOS unit attached to C_{60} are observed between 140 and 160 ppm.

Figure 2 shows the GPC curves of C_{60}-$(PBOS)_2$-3 recorded by different detectors. The PBOS moiety is detectable by both UV-270 nm and RI, but not by UV-440 nm, while the C_{60} moiety is detectable by all UV-440 nm, UV-270 nm and RI. The two GPC curves of C_{60}-$(PBOS)_2$-3 are nearly identical with each other, which indicates a chemical uniformity of the polymer. The two curves retain a narrow polydispersity and commonly show an M_n value of 9300, which is about twice that of the precursor PBOS-TEMPO-3. Similar results were obtained for all other samples (Table 1). This indicates that the reaction of PBOS-TEMPO with C_{60} leads predominantly to a bisadduct, as in the case of PS-TEMPO.

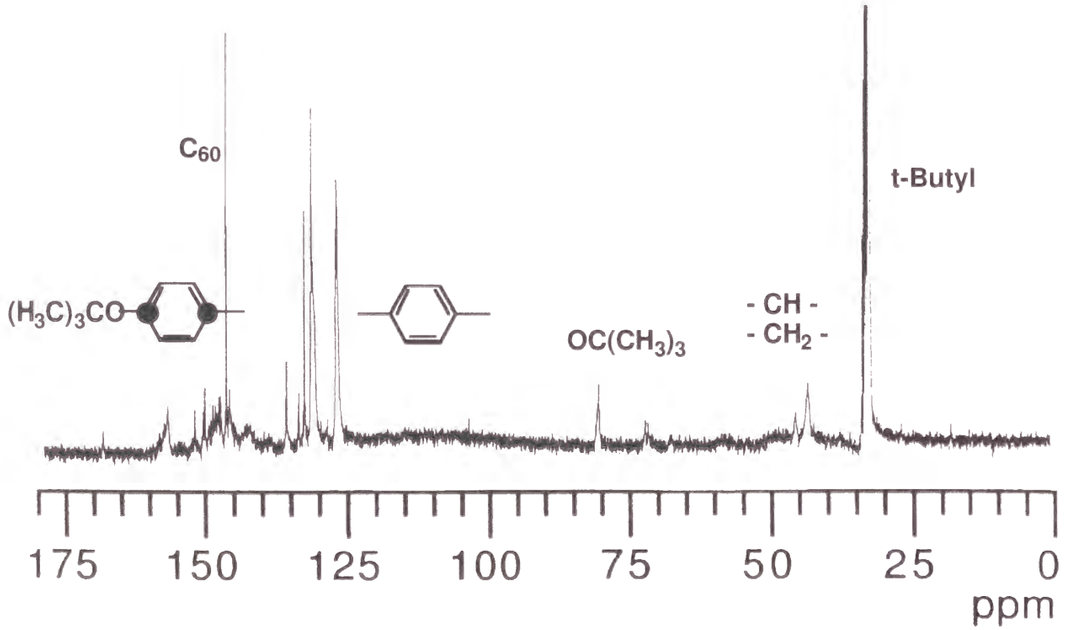


Figure 1. ^{13}C NMR spectrum of C_{60}-$(PBOS)_2$-1 in $CS_2/(CD_3)_2CO$ = 4:1.

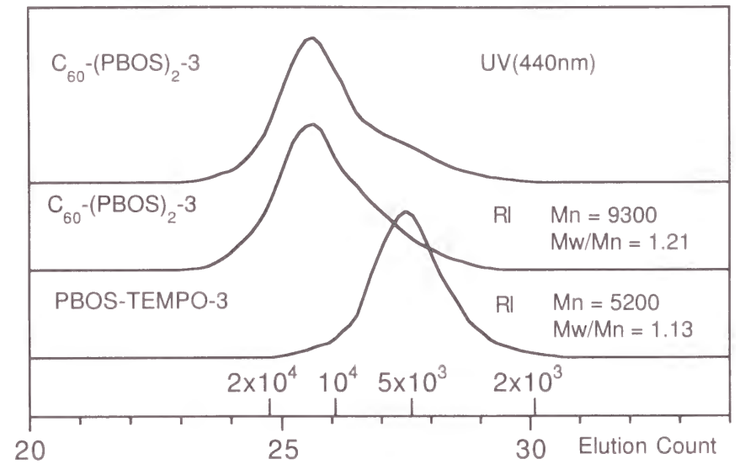


Figure 2. GPC curves for C_{60}-$(PBOS)_2$-3 by UV (440 nm) and RI compared with that for PBOS-TEMPO-3 by RI.

Figure 3 compares the UV-vis spectra from C_{60}-$(BS)_2$ and C_{60}-$(PBOS)_2$-1 solutions, where BS is the [2-(benzoyloxy)-1-phenyl]ethyl group.[5] The two spectra are very similar to each other. This means that the polymer derivative is also a 1,4-bisadduct, like C_{60}-$(BS)_2$ and C_{60}-$(PS)_2$.[5] On the basis of the molar absorption coefficient of C_{60}-$(BS)_2$ at 440 nm, the M_n of the polymer derivatives was estimated (Table 1). Generally, the values of M_n by GPC and those by UV well agree with each other, and both are close to those calculated for the bisadduct structure. (The GPC value for the lowest-molecular weight sample C_{60}-$(PBOS)_2$-1 is appreciably smaller than the UV and calculated values. This is ascribed to the C_{60} moiety contributing little to the hydrodynamic volume of the molecule. As the molecular weight of the PBOS moiety increases, this effect becomes less important.[5]) The author thus concludes that the reaction of PBOS-TEMPO or PBOS-PS-TEMPO with C_{60} provides well-defined PBOS- or PBOS-PS-disubstituted 1,4-dihydro[60]fullerenes, selectively.

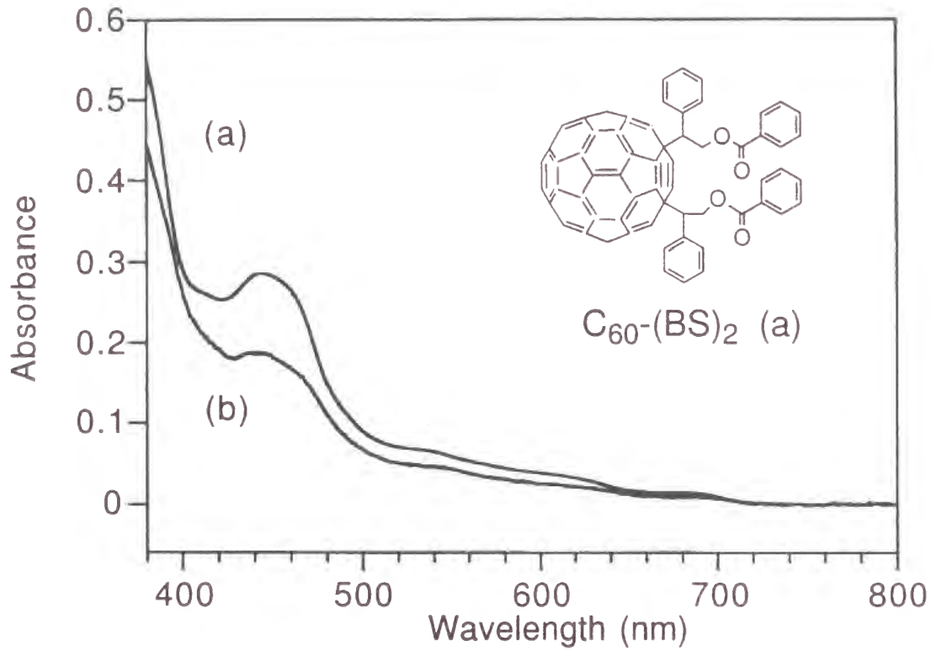


Figure 3. UV-vis spectra of (a) C_{60}-$(BS)_2$ and (b) C_{60}-$(PBOS)_2$-1 in cyclohexane (6.63 x 10^{-2} g mL^{-1}).

Hydrolysis of C_{60}-$(PBOS)_2$ and C_{60}-$(PS\text{-}PBOS)_2$

The hydrolysis of the BOS units of the above-mentioned C_{60} derivatives gave PVP polymers of the types C_{60}-$(PVP)_2$ and C_{60}-$(PS\text{-}PVP)_2$ (see the Experimental section). The ^{1}H NMR spectrum of C_{60}-$(PVP)_2$-1 is shown in Figure 4. The peak at 1.3 ppm ascribed to the *tert*-butyl group in BOS disappeared and the hydroxyl proton peak at 3.1 ppm newly appeared, which suggests a complete hydrolysis of the BOS unit. This was confirmed also by a ^{13}C NMR analysis.

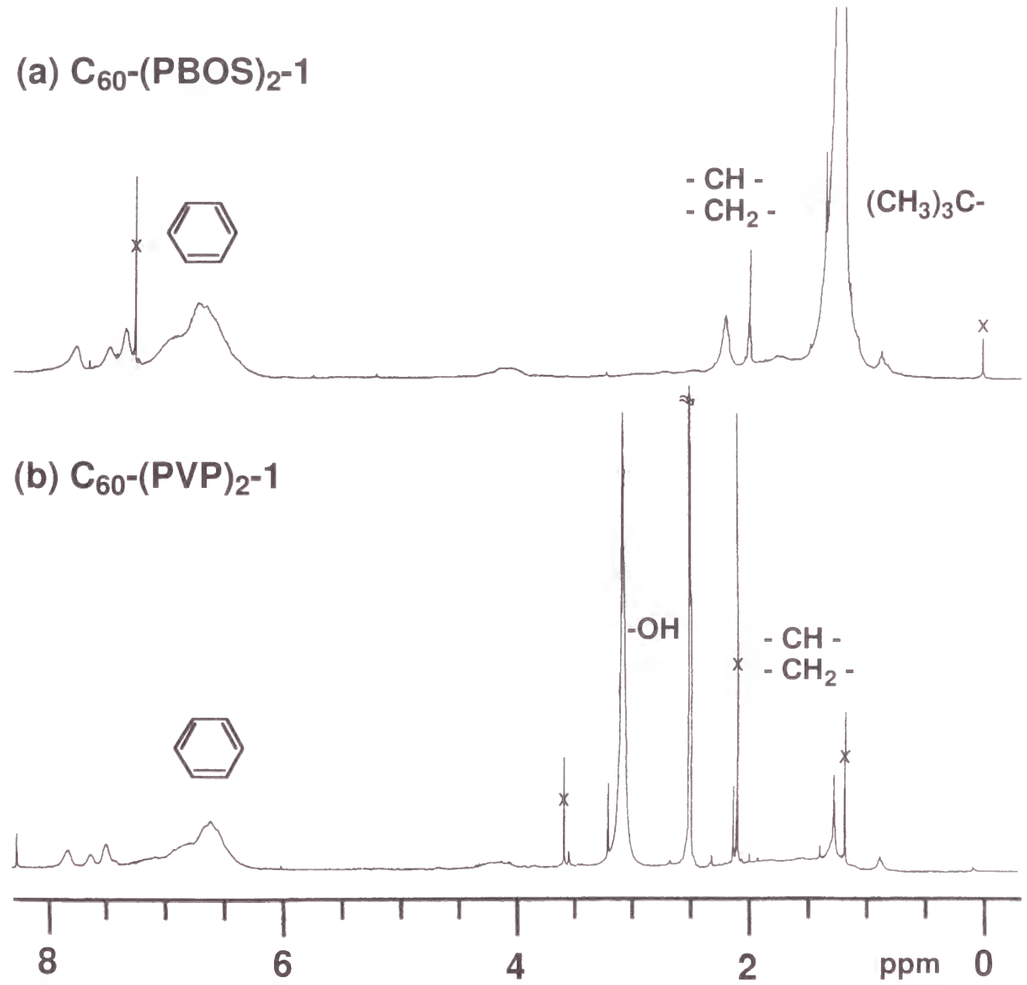


Figure 4. ^{1}H NMR spectra of (a) C_{60}-$(PBOS)_2$-1 in $CS_2/(CD_3)_2CO$ = 4:1 and (b) C_{60}-$(PVP)_2$-1 in DMSO.

Solute Dispersion State Viewed by GPC

Figure 5 compares the GPC curves of C_{60}-$(PS)_2$ (M_n = 10000, M_w/M_n = 1.14),[5] C_{60}-$(PVP)_2$-4, and C_{60}-$(PS\text{-}PVP)_2$-5 along with those of their precursor alkoxyamines. All these C_{60} derivatives (as well as their precursors) have nearly the same molecular weight and a low polydispersity ($M_w/M_n \leq 1.15$), according to the PS-calibrated GPC study made in THF

before removing the *tert*-butyl groups. This hydrolysis is unlikely to cause degradation of the main chain. Nevertheless, the GPC curves of the PVP-containing polymers are very different from those of the PS polymers in two main aspects, as Figure 5 shows. First, the elution time of PVP-TEMPO-4 is appreciably longer, and its elution profile is somewhat broader, than those of the PS-TEMPO counterpart. This suggests that PVP is less soluble and has a smaller hydrodynamic volume in THF than PS and/or that there is some attractive mean force between PVP and the stationary phase. This effect is still observable, though less markedly, for PVP-PS-TEMPO-5. Second and more notably, the elution curves for the PVP-containing C_{60} derivatives are composed of multiple peaks and strangely skewed, indicating the formation of multimolecular micelles of various sizes. Judging from the GPC curves, the micelle size of C_{60}-(PS-PVP)$_2$-5 may appear to be larger than that of C_{60}-(PVP)$_2$-4. However, this cannot be concluded since the micellar size is generally a function of concentration, and the concentration of the solutes migrating through the GPC column is not uniquely defined. Moreover, the possible solute-gel interaction suggested above would make it difficult to judge micellar sizes by GPC profiles. In fact, light scattering shows that C_{60}-(PVP)$_2$-4 forms a larger micelle in THF than the other derivative does (see below).

Micellization Behavior Studied by Light Scattering

Static light-scattering measurements were made for the THF solutions of C_{60}-(PVP)$_2$-4 and C_{60}-(PS-PVP)$_2$-5. In order to obtain an idea about the sizes of the micelles possibly formed by these polymers, the scattered light intensities (I) from their solutions with a fixed concentration (0.5 wt%) were measured at a fixed angle (90°) and compared with the intensities from the solutions of their precursors PVP-TEMPO-4 and PVP-PS-TEMPO-5, respectively, measured under the same conditions. The intensity ratios were found to be I[C_{60}-(PVP)$_2$-4]/I[PVP-TEMPO-4] = 15 and I[C_{60}-(PS-PVP)$_2$-5]/I[PVP-PS-TEMPO-5] = 6, respectively. This indicates that micelles formed by several molecules of the C_{60} polymer

exist in the THF solution in both cases, since the precursors can be assumed to be molecularly dispersed in THF.

To obtain more quantitative information, light-scattering measurements were made for the C_{60} polymers at varying angles and concentrations. An example of the Zimm diagram is given in Figure 6. The obtained values of M_w are compared with the theoretical (unimolecular) values in Table 2. Clearly, the C_{60} polymers form in THF micelles composed of about 21 and 6 molecules of C_{60}-(PVP)$_2$-4 and C_{60}-(PS-PVP)$_2$-5, respectively. Namely, the association number of the C_{60} polymer with the homo-PVP arms is larger than that with the PS-PVP block-copolymer arms. The derivatives of the type C_{60}-(PS)$_2$ are molecularly dispersed in THF, according to the previous GPC study.[5] Recalling that THF is a better solvent for PS than for PVP and that it will give an intermediate solubility to PVP-PS block copolymers, the author may tentatively suggest that the poorer is the solvent towards the

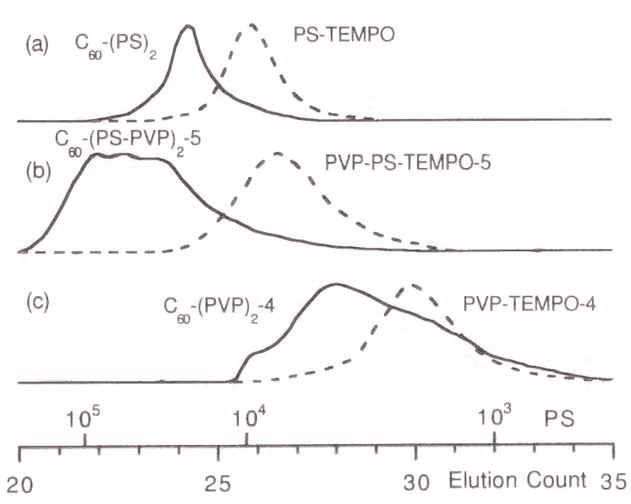


Figure 5. GPC curves of (a) C_{60}-(PS)$_2$ (M_n = 10000, M_w/M_n = 1.14), (b) C_{60}-(PS-PVP)$_2$-5, and (c) C_{60}-(PVP)$_2$-4 in THF by RI detector. The broken lines are for the respective precursor TEMPO adducts.

polymer moiety, the stronger is the association tendency of C_{60} polymer,[5] if compared at a common level of molecular weight. Since the C_{60} moiety is hardly soluble in THF, the micelles formed by a C_{60} polymer will have a core of the C_{60} moieties surrounded by the fringes of the polymer moieties, as illustrated in Figure 7. Such a core-fringes structure is somewhat similar to the one often observed for block copolymer micelles formed in dilute solution with a selective solvent.[12,13]

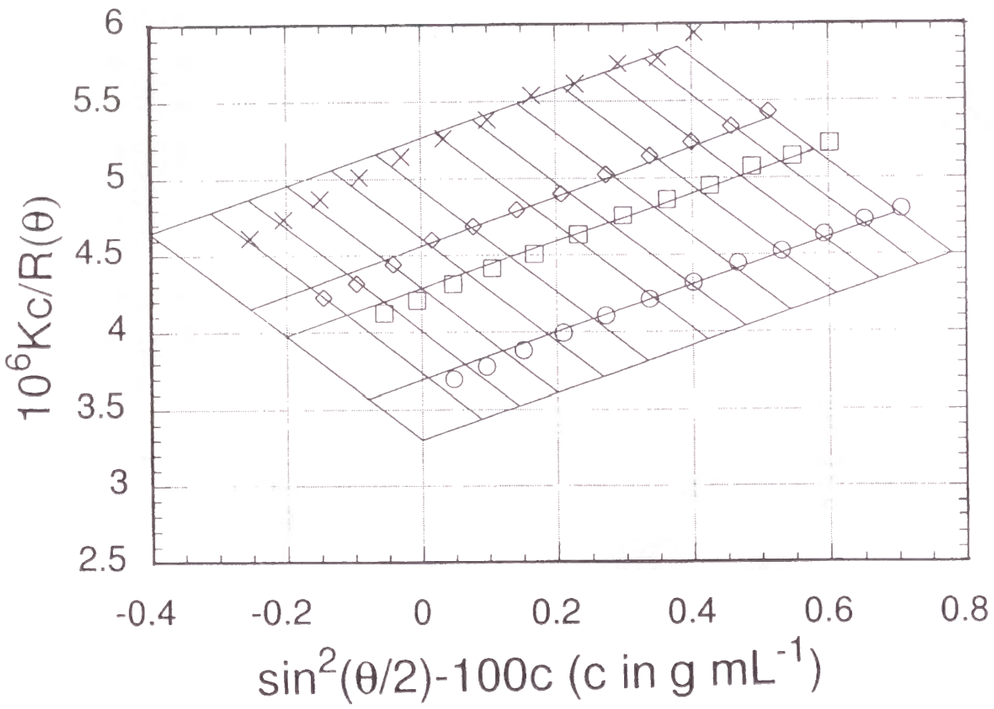


Figure 6. Zimm plot for C_{60}-$(PVP)_2$-4 in THF at 25.0 °C.

Table 2. Values of M_w of C_{60} Experimentally Observed in THF at 25 °C and Those Calculated

code	$M_{w,\,exp}$	$M_{w,\,calcd.}$	$M_{w,\,exp}/M_{w,\,calcd.}$
C_{60}-$(PVP)_2$-4	3.0×10^5 [a]	1.4×10^4 [c]	21
C_{60}-$(PS\text{-}PVP)_2$-5	1.5×10^5 [b]	2.4×10^4 [d]	6.3

[a] Determined by light scattering with dn/dc = 0.138 mL/g. [b] Determined by light scattering with dn/dc = 0.172 mL/g. [c] Calculated for the bisadduct structure using the GPC value for PBOS-TEMPO-4 (Table 1). [d] Calculated for the bisadduct structure using with GPC value for PBOS-PS-TEMPO-5 (Table 1).

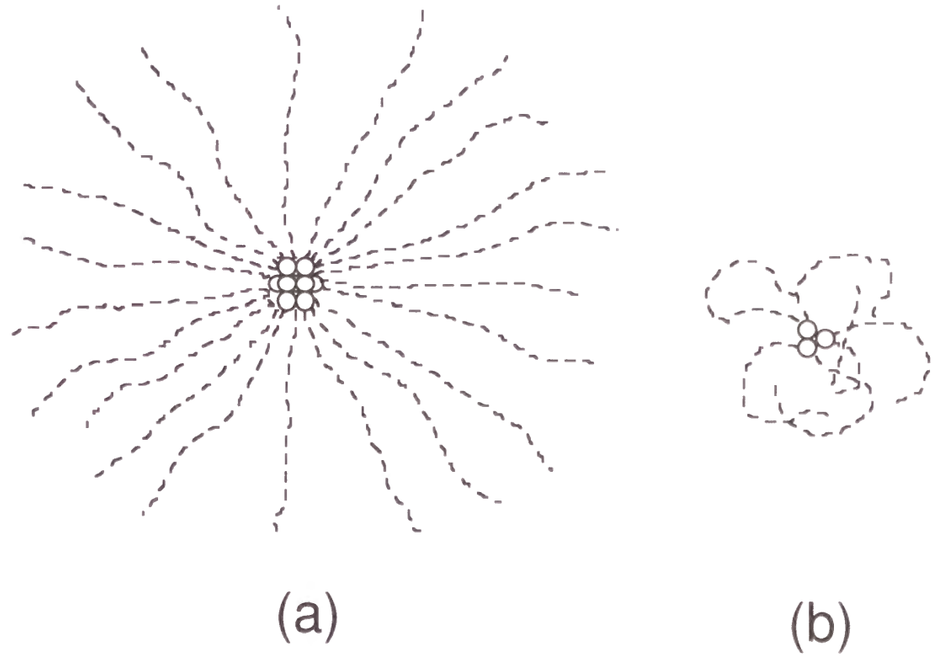


Figure 7. Schematic representation of multimolecular micelles formed by (a) C_{60}-$(PVP)_2$-4 and (b) C_{60}-$(PS\text{-}PVP)_2$-5 in THF at 25 °C.

It is also noted that the Zimm plot in Figure 6 seems quite normal, giving no indication of increasing association number with increasing concentration nor suggesting micelle dissociation at low concentrations. The straight concentration envelope with a positive slope (positive apparent second virial coefficient) implies that the micelles are stable in the studied range of concentration, $1 < 10^3 C$ (g/mL) < 4. In a strict sense, the light-scattering values of M_w given above are apparent ones, since the C_{60} polymers, particularly C_{60}-(PS-PVP)$_2$-5, are not uniform in the refractive index increment (dn/dc) along the chain, so that any distribution in the chain lengths of the PS and/or PVP moieties brings about a distribution of composition (hence dn/dc) among different molecules. This invalidates the simple light-scattering theory.[14] The effect of composition heterogeneity, however, should be rather minor in the present systems, since the polymers are fairly narrow in chain length distribution. Moreover, multimolecular micellization will effectively average out the composition heterogeneity, if there is any.[12a] The slope of the angular envelope in Figure 6 suggests a micelle radius of gyration, R_g, on the order of 40 nm. This value appears to be somewhat too large for the micellar structure suggested in Figure 7 and may not be very reliable. A possible cause for the overestimation of R_g may be the difficulty in preparing perfectly dust-free solutions (because of the limited amount of the C_{60}-polymer available). Nevertheless, the comparison of this R_g with the value of about 20 nm obtained for the C_{60}-(PS-PVP)$_2$-5 solutions, which were purified similarly, suggests that the polymer fringes in the C_{60}-(PVP)$_2$-4 micelles are appreciably more extended than those in the C_{60}-(PS-PVP)$_2$-5 micelles because of a higher steric hindrance in the former than in the latter, as illustrated in Figure 7.

Saturation Solubilities of C_{60}-(PS)$_2$ and C_{60}-(PVP)$_2$

As already noted, THF is a good solvent for PS and a nonsolvent for C_{60}. Thus it is expected that a C_{60}-(PS)$_2$ adduct with PS chains shorter than a critical length will have a limited solubility in THF depending on the PS chain length. Adducts with PS chains

longer than the critical length will be miscible with THF in all proportions. In fact, the adduct with a molecular weight of the PS chain, $M_{n,PS}$, of about 1000 showed a limited miscibility with THF, the saturation solubility being 190 mg/mL-solution. On the other hand, the adduct with $M_{n,PS} \cong 2400$ seems to be soluble in THF at all concentrations.

In view of the generally poor solubility of C_{60} in solvents and polymers, more interesting is the saturation solubility S_{C60} of the C_{60} moiety rather than that of the adduct as a whole. When the chain length of the PS moiety increases, the concentration of the C_{60} moiety within the bulk adduct decreases according to

$$S_{C60} = (M_{C60}/M_{adduct})d_{adduct} \qquad (1)$$

Here M_{C60} and M_{adduct} are the (number-average) molecular weights of the C_{60} moiety and the whole adduct, respectively, and d_{adduct} is the adduct density, which the author approximates here by the PS density of 1.06 g/mL. Equation 1 is shown by the dotted line in Figure 8, and it gives the maximum possible values of S_{C60} in any solvent. When a C_{60}-polymer adduct shows a limited solubility in a given solvent, its value of S_{C60} is necessarily smaller than the dotted line. Therefore the S_{C60} of the C_{60}-(PS)$_2$/THF system should behave like the dot-dash line in Figure 8, which is schematic to some extent because of the lack of a sufficient number of data points.

All the C_{60}-(PVP)$_2$ samples prepared in this work showed a limited solubility in THF. Figure 9 gives S_{C60} as a function of the molecular weight of the PVP chain, $M_{n,PVP}$. S_{C60} is considerably smaller than the maximum possible value for the bulk adduct, and seems to have a peak at around $M_{n,PVP} = 1000$, where about 16 mg of the C_{60} moiety can be solubilized in 1 mL of THF solution. This maximum value of S_{C60} is considerably smaller than the one attainable by the PS adduct (Figure 8). This is ascribed to the poorer solubility of PVP in THF than that of PS and is consistent with the micellization tendency described in previous sections.

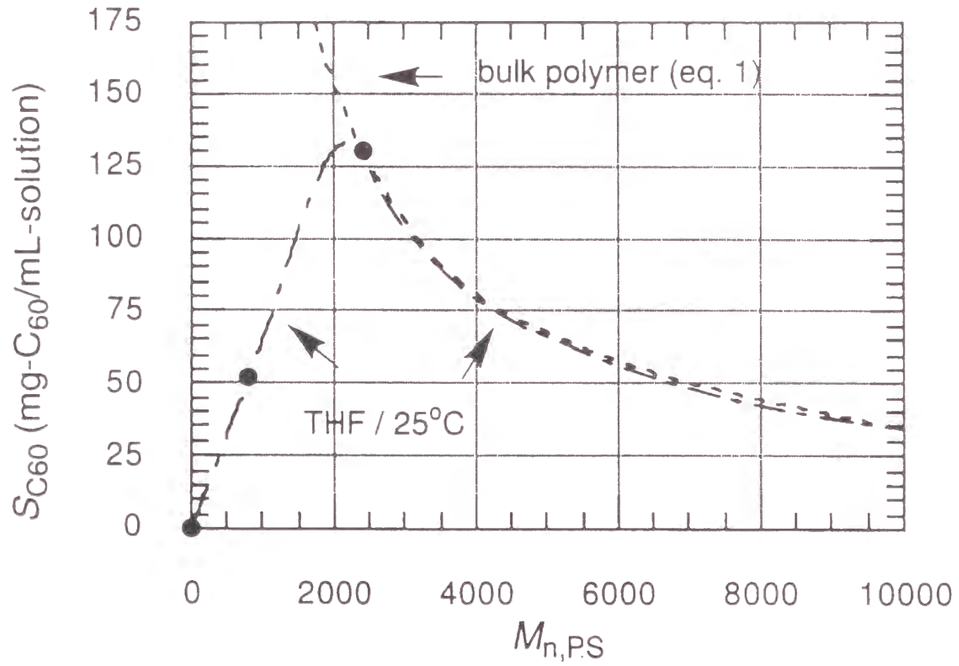


Figure 8. Saturation solubility S_{C60} of the C_{60} moiety in THF at 25 °C as a function of the M_n of the PS arm (dot-dash line). The dotted line shows eq 1.

In this connection, it should be remembered that both the GPC and light scattering studies on the micellization behavior were made at very low concentrations. For example, the highest concentration of C_{60}-$(PVP)_2$-4 studied by light scattering (Figure 6) is 4.0 mg/mL in the adduct concentration or about 0.04 mg/mL in the C_{60}-moiety concentration, which, of course, is far below the saturation-solubility line in Figure 9. Since micelles formed at low concentrations are unlikely to dissociate to single molecules at higher concentrations, it is indicated that C_{60}-$(PVP)_2$ adducts are solubilized in THF in a multimolecular micellar form in virtually the whole region below the S_{C60} line. On the other hand, all available C_{60}-$(PS)_2$ adducts ($M_{n,PS} \geq 1000$) are molecularly dispersed in dilute THF solution, as is judged from their GPC curves.[5] It is an interesting open question whether they remain in a molecularly dispersed state when the concentration is increased

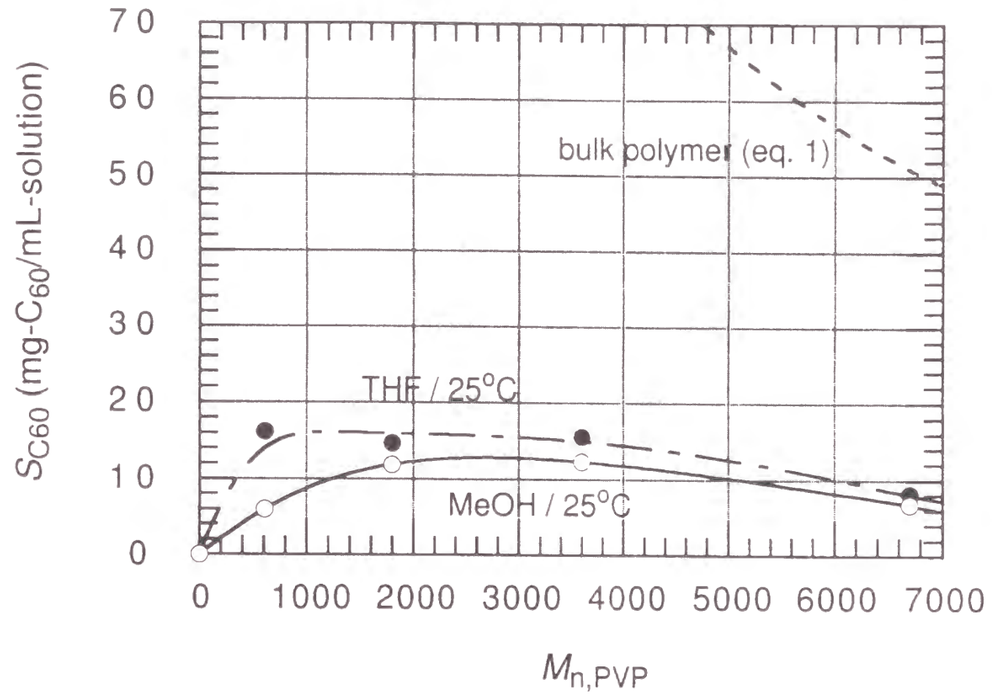


Figure 9. Saturation solubility S_{C60} of the C_{60} moiety in THF (dot-dash line) and in methanol (solid line) at 25 °C as a function of the M_n of the attached PVP chain.

towards the S_{C60} line in Figure 8. This question is somehow related to the likewise interesting and important one as to the molecular dispersion state in bulk C_{60}-polymers, which will be discussed in the next chapter.

Another interesting topic is the solubility of C_{60}-$(PVP)_2$ adducts in polar solvents. The author has determined the saturation solubilities of the PVP adducts in methanol, which seemingly is a good solvent for PVP. As in THF, however, all the C_{60}-$(PVP)_2$ adducts showed a limited solubility in methanol. Figure 9 gives S_{C60} as a function of $M_{n,PVP}$. This S_{C60} curve is similar in shape and magnitude to that in THF, and suggests that methanol is not a strong enough solvent to disperse the adduct mono-molecularly:

namely, it is highly likely that the molecules are dissolved in methanol forming multimolecular micelles, again. At this time, it is not possible to confirm this by light scattering due to the technical difficulty of conducting measurements in methanol. In any case, it should be stressed that the C_{60} moiety can be made soluble in the polar solvent in concentrations over 1 wt% by the PVP derivatization.

Micellization Behavior Studied by UV-vis Spectra

The electronic properties of C_{60} are affected by its environment. Estoe[8a] reported that the UV-vis spectrum of the C_{60} molecules solubilized in water in a colloidal form by use of a surfactant is markedly different from that of the molecules in a monomeric dispersion state. Figure 10 shows the UV-vis spectra of three derivatives of nearly the same size (in THF): C_{60}-$(PS)_2$ (solid line; $M_{n,PS} = 5500$, $M_w/M_n = 1.18$), C_{60}-$(PS\text{-}PVP)_2$-5 (broken line), and C_{60}-$(PVP)_2$-4 (dotted line). C_{60}-$(PS)_2$ shows the spectrum characteristic of 1,4-disubstituted

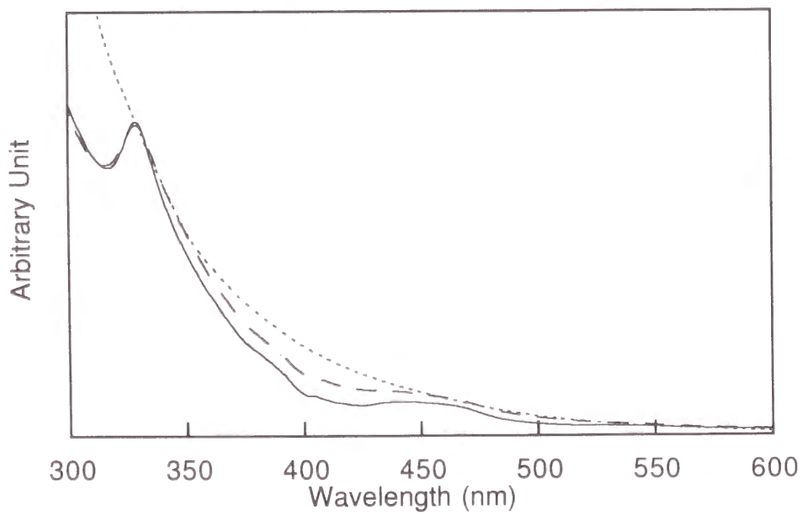


Figure 10. UV-vis spectra of C_{60}-$(PS)_2$ (solid line; $M_n = 5500$, $M_w/M_n = 1.18$), C_{60}-$(PS\text{-}PVP)_2$-5 (broken line), and C_{60}-$(PVP)_2$-4 (dotted line) in THF.

C_{60}, while C_{60}-$(PVP)_2$ gives a spectrum with no absorption maxima, which is rather similar to the one observed for the pure C_{60} in water in a colloidal form.[8a] On the other hand, the 440 nm peak of C_{60}-$(PS\text{-}PVP)_2$ is somewhat broadened and appears between the spectra of C_{60}-$(PS)_2$ and C_{60}-$(PVP)_2$. Remembering that the association numbers of the PVP, PS-PVP, and PS derivatives observed in this solvent are 21, 6, and 1 (no association), respectively, and that the colloidal micelles of C_{60} observed in water are of a macroscopic size, the author may conclude that UV-vis spectroscopy offers a quick and convenient means to study the dispersion state of C_{60} compounds. It can even inform us of the approximate micellar size, if the association number is not too large, say, < 10 - 20.

CONCLUSIONS

Low-polydispersity 1,4-disubstituted C_{60} derivatives of the types C_{60}-$(PVP)_2$ and C_{60}-$(PS\text{-}PVP)_2$ were prepared by applying the nitroxide-controlled free radical polymerization technique, and studied with their solubility behaviors in comparison with those of the C_{60}-$(PS)_2$ adducts prepared by the similar procedure described in Chapter 4.

Both GPC and light-scattering studies showed that C_{60}-$(PVP)_2$ and C_{60}-$(PS\text{-}PVP)_2$ form multimolecular micelles in THF at 25 °C. More specifically, the light-scattering study showed that C_{60}-$(PVP)_2$ and C_{60}-$(PS\text{-}PVP)_2$ with M_n roughly about 10^4 form stable micelles in dilute solution ($10^{-3} < C < 10^{-2}$ g/mL) with association numbers of about 20 and 6, respectively. On the other hand, C_{60}-$(PS)_2$ showed no indication of association in this solvent at least in dilute solution.

Except for the sample with the shortest (available) PS chain ($M_{n,PS} \cong 1000$), C_{60}-$(PS)_2$ seemed miscible with THF in all proportions, while all the available C_{60}-$(PVP)_2$ samples ($M_{n,PVP} < 10000$) showed a limited solubility in THF. Thus the solvent power towards the polymer moiety in a C_{60}-polymer adduct is reflected on both the saturation solubility and the micellization behavior in a consistent manner.

The maximum solubility of the C_{60} moiety in THF was found to exceed 100 mg/mL with C_{60}-$(PS)_2$ and about 18 mg/mL with C_{60}-$(PVP)_2$. The C_{60} moiety in C_{60}-$(PVP)_2$ can be made soluble even in a polar solvent (methanol) as much as 18 mg/mL. These maximum solubilities of the C_{60} moiety are commonly achieved with a polymer chain length in the range 1000-3000 in M_n.

The 440 nm absorption peak can be used as a measure of the dispersion state and micellar size of C_{60} derivatives in solution.

The experimental data given in this chapter were limited to those C_{60}-polymers with relatively low molecular weights. With an increase in the molecular weight of the polymer moiety, the solubility behaviors of the C_{60}-polymers should approach to those of the polymer moieties with the effects of the C_{60} moiety becoming less and less important. In this context, the conclusions given in this work can be regarded as general.

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Chapter 6

C_{60} Fullerenes with Two Well-Defined Styrene-Based Polymer Arms. 2. Solubility Characteristics in a Polystyrene Matrix

ABSTRACT

Four samples of C_{60}-$(PS)_2$, i.e., C_{60} fullerenes with two low-polydispersity PS arms at the 1,4-positions, were studied with their solubility in a PS (polystyrene) matrix with a number-average molecular weight M_n of 240000. The M_n of a PS arm ranged from about 1000 to 10000. (Because of the large differences in M_n between the arm and matrix PSs, the solubility behavior may be considered as approximately independent of the matrix M_n if it is larger than that of the PS used here.) The macroscopic miscibility of the two components was judged from the clarity and homogeneity of the blend film by optical microscopic observation. The dispersion state of the solute C_{60}-$(PS)_2$ in a "miscible" blend was studied by the previously proposed spectroscopic method, which is based on the characteristic changes in the UV-vis spectrum of the C_{60} polymers accompanying the formation of multimolecular micelles in solution (Chapter 5). In this way, a phase diagram showing the miscibility and dispersion state of the C_{60} polymers as a function of the M_n of the PS arm was obtained. It was confirmed for the first time that a C_{60}-bearing polymer is dispersed, in a blend film or a bulk film of itself, either monomolecularly or in a multimolecular micellar state, depending on the chain length of the polymer moiety and the blend composition.

INTRODUCTION

In Chapter 4, C_{60} fullerenes with two well-defined polymer arms were synthesized by applying the nitroxide-controlled free radical polymerization technique.[1] Solutions of those C_{60}-polymer adducts in organic solvents were studied in Chapter 5. It was shown that the maximum solubility of the C_{60} moiety, which, without the polymer arms, was extremely low in every known solvent, was drastically enhanced, especially when the solvent power was strong for the arm polymer. Light scattering measurement revealed that when the solvent power was moderate and the arm length was intermediate, the C_{60}-polymer was dissolved in the solvent by forming multimolecular micelles, presumably with a core of the C_{60} moieties and fringes of the polymer moieties. This micellization was accompanied by characteristic changes in the UV-vis spectra of solutions: the structured spectrum for a solution with monomolecularly dispersed C_{60}-polymer became less structured with increasing micellar size. Thus, UV-vis spectroscopy offers a quick and convenient means to study the dispersion state of C_{60} compounds.

In this chapter, the author studies the solubility and dispersion state of C_{60}-$(PS)_2$ adducts in a PS matrix, where PS is polystyrene, and C_{60}-$(PS)_2$ denotes a C_{60} fullerene with two PS arms at the 1,4-positions. The macroscopic miscibility of the two components can be judged by the clarity and homogeneity of the film. The microscopic dispersion state of the C_{60} polymers can be deduced by the mentioned spectroscopic method. In principle, the solute dispersion state in such a bulk blend can be studied by costly and highly specialized methods such as small-angle neutron scattering and X-ray scattering. However, the optical method is quick, economical, and accessible to everyone, even though obtainable information is qualitative in most cases. The following is the first report showing that a C_{60}-bearing polymer is either monomolecularly dispersed or forms a multimolecular micelle in the bulk or blend film, depending on the chain length of the polymer moiety and the blend composition.

EXPERIMENTAL

C_{60}-Bearing Polymer Samples

C_{60} derivatives with two well-defined polystyrene or poly(*p*-vinylphenol) arms at the 1,4-positions, which are denoted C_{60}-$(PS)_2$ and C_{60}-$(PVP)_2$, respectively, were synthesized as described in Chapter 5. A polystyrene (PS) sample with $M_n \cong 2.4 \times 10^5$ was commercially obtained (Aldrich) and used as a matrix polymer.

Preparation of C_{60}-$(PS)_2$/PS Blend Films

Thin films of C_{60}-$(PS)_2$ and C_{60}-$(PS)_2$/PS blends were prepared by applying a toluene solution (5 % by weight) onto a glass plate and allowing it to air-dry at room temperature. The films were then dried under vacuum for 24 h at 100 °C. The thickness of the films was about 10 μm in all cases.

RESULTS AND DISCUSSION

Four C_{60}-$(PS)_2$ samples designated C_{60}-$(PS)_2$-1 through C_{60}-$(PS)_2$-4 were used. The number-average molecular weight, $M_{n,PS}$, of the PS arm in those derivatives ranged from 1000 to 10000. Each derivative was mixed with the PS with M_n = 240000 in different proportions, and their thin films cast from a toluene solution were inspected by optical microscopy and also by the naked eye to examine the clarity and homogeneity of them. Results are summarized in Table 1. All the C_{60}-$(PS)_2$ samples with $M_{n,PS} \geq 2400$ were judged to be miscible with the PS in all proportions, since the blend films were clear and homogeneous in all cases. On the other hand, the sample C_{60}-$(PS)_2$-1 ($M_{n,PS}$ = 1000) showed limited miscibility with the PS. Namely, when the weight fraction of the C_{60} polymer was low, the mixture gave a transparent and homogeneous film, while at a high fraction (56%) of the C_{60} polymer, the film turned out to be inhomogeneous. Incidentally, this derivative in the bulk (without blending the PS) did not give a well-defined film, indicating that the PS moiety of this derivative is too short to give a homogeneous film.

Table 1. Characteristics of C_{60}-$(PS)_2$ Films[a]

code	$M_{n,PS}$[b]	content (wt%)		clarity of film[c]
		C_{60}-$(PS)_2$	C_{60} moiety	
C_{60}-$(PS)_2$-1-1	1000	15.4	4.44	H
C_{60}-$(PS)_2$-1-2		17.8	5.12	H
C_{60}-$(PS)_2$-1-3		37.8	10.9	H
C_{60}-$(PS)_2$-1-4		56.1	16.1	I
C_{60}-$(PS)_2$-1-b		100	28.8	(I)
C_{60}-$(PS)_2$-2-1	2400	28.9	3.99	H
C_{60}-$(PS)_2$-2-2		44.0	6.07	H
C_{60}-$(PS)_2$-2-3		74.8	10.3	H
C_{60}-$(PS)_2$-2-b		100	13.8	H
C_{60}-$(PS)_2$-3-1	5500	44.6	2.74	H
C_{60}-$(PS)_2$-3-b		100	6.31	H
C_{60}-$(PS)_2$-4-b	10000	100	3.52	H

[a]PS with M_n of 240000 (Aldrich) was used as a matrix polymer. [b]See Chapter 4 of this thesis for the polymer synthesis and characterization. [c]I, the film is opaque and optico-microscopically inhomogeneous; H, the film is transparent and optico-microscopically homogeneous.

The clarity and homogeneity of the film indicate the miscibility of the two components on a macroscopic scale but not necessarily the miscibility on a molecular scale. It was demonstrated in Chapter 5 that multimolecular micellization of C_{60} polymers in solution can occur in certain cases and it is accompanied by characteristic changes in the UV-vis spectra from the solutions. It was deduced that the micelles formed by a C_{60}-polymer have a core of the C_{60} moieties (surrounded by the fringes of the polymer moieties), thus making the electronic environment of the C_{60} moieties different from that in a monomolecularly dispersed system. We may reasonably assume that this is also the case

with a C_{60}-polymer in the bulk or dissolved in a polymer matrix. Namely, if the UV-vis spectrum from a sample film resembles that from a solution in which the C_{60}-bearing molecules are monomolecularly dispersed, then one may deduce that this is also the case with the bulk or blend system in question. On the other hand, if the spectrum is more like that from a micellar solution, it indicates that the C_{60}-polymer is dispersed in the film by forming multimolecular micelles.

The UV-vis spectra from the C_{60}-$(PS)_2$/PS blends, which are macroscopically homogeneous, are presented in Figures 1 through 3. Figures 1a, 2a, and 3a show the spectra in a wide wavelength range, while Figures 1b, 2b, and 3b show those in a limited range, normalized at a wavelength of 450 nm, around which 1,4-disubstituted C_{60} derivatives give a characteristic absorption band (when monomolecularly dispersed in solution).[2] For comparison, each figure includes the spectra from a tetrahydrofuran (THF) solution of C_{60}-$(PS)_2$-1 or -2 (monomolecularly dispersed system) and a THF solution of C_{60}-$(PVP)_2$-4 (micellar solution with an association number about 21[3]).

Figure 1 gives the spectra from C_{60}-$(PS)_2$-1 blended with the PS in different proportions. As Figure 1b shows, all the spectra from the blend films are more like that for the micellar solution rather than that for the same derivative in dilute THF solution (a monomolecularly dispersed system). This indicates that the C_{60}-polymer forms multimolecular micelles in the PS matrix in all studied cases, even though the films are apparently clear and homogeneous.

Figure 2 gives the spectra for C_{60}-$(PS)_2$-3-1, -3-b, and -4-b. All these spectra are similar to that for the monomolecularly dispersed systems (Figure 2b), suggesting that the C_{60} moieties in these films are molecularly dispersed without forming clusters.

Figure 3 gives the spectra for C_{60}-$(PS)_2$-2 blended with the PS in different proportions. As Figure 3b shows, all the curves for the blends lie between those for the micellar and the monomolecularly dispersed system. They are more like the spectrum for the THF

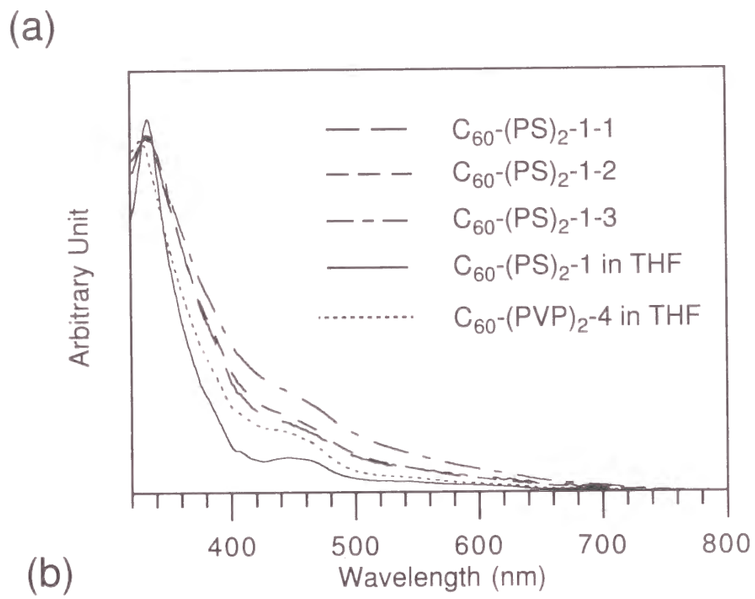

Figure 1. UV-vis spectra of C_{60}-$(PS)_2$-1-x (x = 1,2,3) normalized at (a) 330 nm and (b) 450 nm, respectively. For comparison, the UV-vis spectra of C_{60}-$(PS)_2$-1 and C_{60}-$(PVP)_2$-4 in THF were shown in both figures.

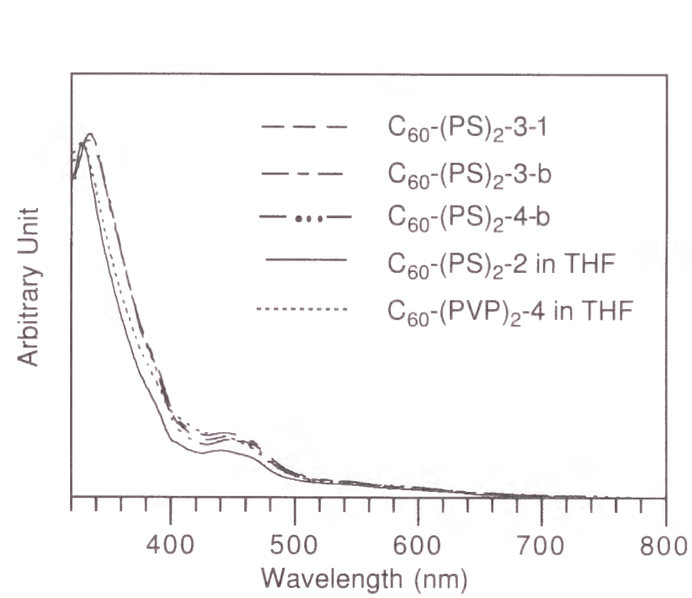

Figure 2. UV-vis spectra of C_{60}-$(PS)_2$-3-1, -3-b, and -4-b normalized at (a) 330 nm and (b) 450 nm, respectively. For comparison, the UV-vis spectra of C_{60}-$(PS)_2$-1 and C_{60}-$(PVP)_2$-4 in THF were shown in both figures.

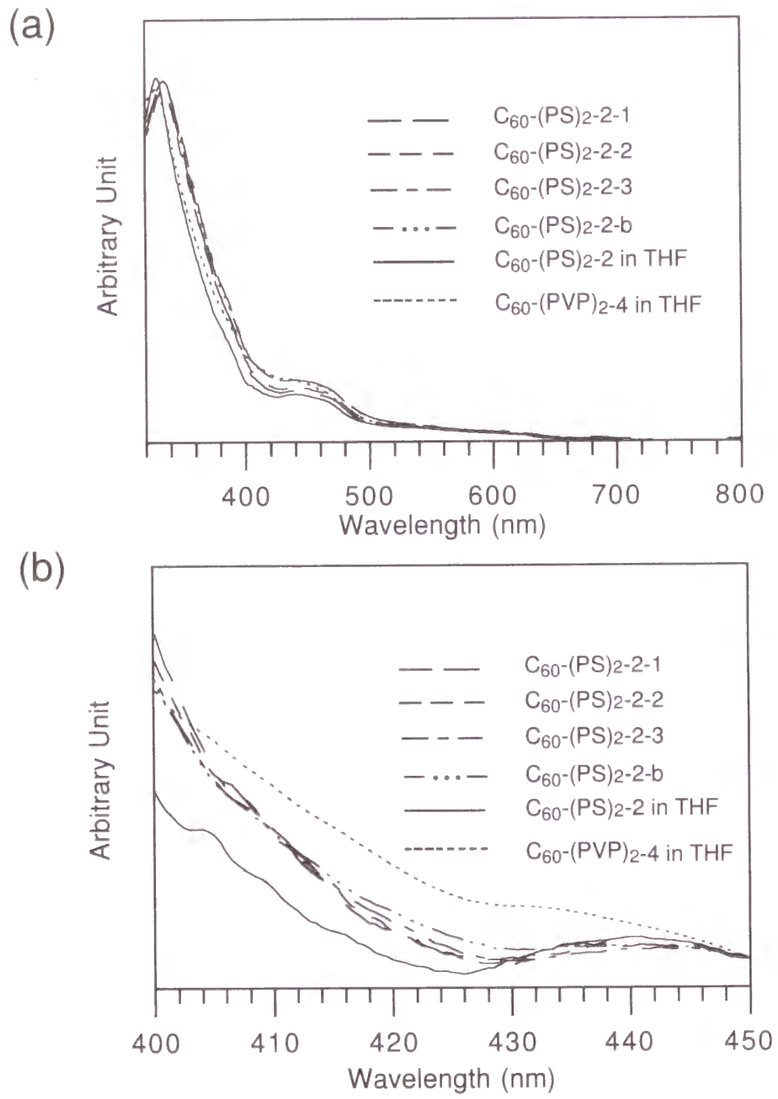

Figure 3. UV-vis spectra of C_{60}-$(PS)_2$-2-x (x = 1,2,3,b) normalized at (a) 330 nm and (b) 450 nm, respectively. For comparison, the UV-vis spectra of C_{60}-$(PS)_2$-2 and C_{60}-$(PVP)_2$-4 in THF were shown in both figures.

solution containing micelles composed of about 6 C_{60}-polymer molecules.[3] This indicates that C_{60}-$(PS)_2$-2 in the blend films form micelles of a relatively small size, smaller than those formed by C_{60}-$(PS)_2$-1 in the PS matrix (Figure 1).

All these results are summarized in Figure 4, where the miscibility and dispersion state of C_{60}-$(PS)_2$ molecules in the PS matrix are depicted in the W_{C60} vs. $M_{n,PS}$ plane, where W_{C60} is the weight fraction of the C_{60} moiety in the blend. The maximum possible value of W_{C60} is that for the pure C_{60}-$(PS)_2$ polymer, which is represented by the broken curve in the figure. The dot-dash line shows an approximate miscibility threshold between C_{60}-$(PS)_2$ and the PS. This line is numerically similar to the saturation solubility line for C_{60}-$(PS)_2$ in THF (cf. Figure 8 in ref 2), which means that PS is nearly as good a "solvent" for C_{60}-$(PS)_2$ as THF is. However, when $M_{n,PS}$ is 2400 or smaller, a C_{60}-$(PS)_2$ polymer in the PS matrix forms multimolecular micelles, whose size appears to increase with decreasing $M_{n,PS}$. Sample C_{60}-$(PS)_2$-2 ($M_{n,PS}$ = 2400) forms multimolecular micelles also in its bulk, while sample C_{60}-$(PS)_2$-1 ($M_{n,PS}$ = 1000) does not give a homogeneous film without blending with the PS. When $M_{n,PS}$ is 5500 or larger, a C_{60}-$(PS)_2$ polymer exists in a monomolecularly dispersed state in the bulk and blend with the PS. There would be a critical value of C_{60}-$(PS)_2$ concentration below which no micelles are formed in the PS matrix. This "critical micellization concentration" line, which is expected to be situated very close to the abscissa axis of the $W_{C60} - M_{n,PS}$ diagram, remains to be established.

This work has confirmed that the maximum amount of C_{60} moieties that can be monomolecularly dispersed in a polymer matrix is not smaller than about 6.3 wt%, which is the W_{C60} value for pure C_{60}-$(PS)_2$-3. It is expected that the properties of C_{60}-polymer hybrids depend not only on the macroscopic homogeneity of the system but also on the microscopic dispersion state of the C_{60} moieties. In this regard, the spectroscopic method and results presented in this Chapter will hopefully make an important contribution to the relevant field.

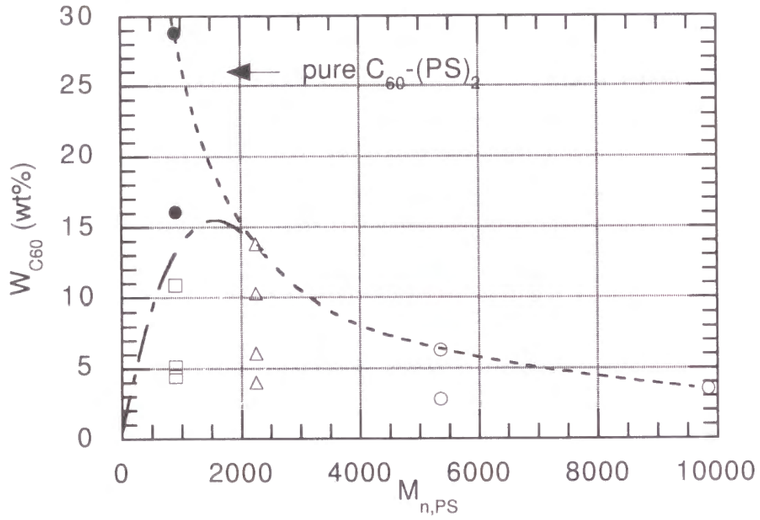

Figure 4. Diagram showing the miscibility and dispersion state in blends of C_{60}-$(PS)_2$ and PS (M_n = 240000): (●), inhomogeneous film; (□), homogenous film with multimolecular micelles of relatively large size; (△), homogenous film with multimolecular micelles of relatively small size; (○), homogenous film with monomolecular dispersion.

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Part III

Synthesis and Properties of Water-Soluble Polysaccharides Bearing Pendant C_{60} by Regioselective Reaction

Chapter 7

Preparation of Water-Soluble Pullulans Bearing Pendant C_{60} and Their Water Solubility

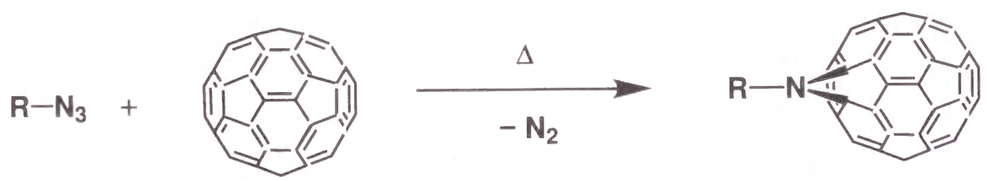
ABSTRACT

Water-soluble fullerene-bearing pullulans were successfully prepared by the addition reaction of azide-substituted pullulans with fullerene C_{60}. The chemical structure of the products was characterized by IR, UV, and NMR spectroscopy. It was found that the saturation solubility of the C_{60} moiety strongly depends on the degree of substitution (DS) of the sample, indicating that an optimum DS value of the C_{60} moiety exists for its water solubility.

INTRODUCTION

Recently Hawker et al.[1] reported a versatile method for the preparation of C_{60}-containing polymers with well-defined structure. The main reaction is the addition reaction of azides with fullerene C_{60}.[1-3] The characteristic of this reaction is that the reaction proceeds primarily through monoaddition according to Scheme 1.

Scheme 1



Thus, the fullerene's electronic properties remain unchanged after the addition reaction. This is very attractive as a method for the preparation of water-soluble polymers bearing pendant C_{60} with well-defined structure.[4] As already described in Chapter 3, biochemical and medicinal applications are expected for water-soluble polymers bearing C_{60} because of their biological activities.[5]

In this chapter, the author examined to prepare water-soluble C_{60}-bearing pullulan with well-defined structure using the cycloaddition reaction of azide-substituted pullulans with C_{60}. Pullulan is a linear polysaccharide produced by the fungus *Aureobasidium pullulans* and a non-ionic water-soluble polymer which undergoes no gelation in an aqueous solution.[6] The azide-substituted pullulans with well-defined structures can be prepared from pullulan which was chlorinated regioselectively at C-6 position.[7,8] Thus, pullulan is suitable for preparing non-ionic water-soluble polymers bearing pendant C_{60}.

EXPERIMENTAL

Measurements

Infrared (IR) spectra were obtained from KBr pellets with a Jasco FT/IR spectrometer Model 8000. Size exclusion chromatography (SEC) in tetrahydrofuran (THF) was carried out on a TOSOH HLC-802UR chromatograph equipped with polystyrene gel columns (TOSOH G2500H6 + G3000H6 + G4000H6; exclusion limit = 1.0 x 10^6; 8.0 mm i.d. x 60 cm each) and refractive index/ultraviolet dual-mode detectors. SEC columns (Tosoh TSK4000PW_{XL} and TSK6000PW_{XL}, Tokyo, Japan, flow rate 0.6 mL/min) were used with 0.3 M CH_3COONa in water as eluent and calibrated with polyethylene glycols.

Materials

THF, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), pyridine, and chlorobenzene were of reagent grade and distilled over calcium hydride prior to use. Methylsulfonyl chloride (mesyl chloride), sodium azide, acetic anhydride and pullulan (Nacalai Tesque, Japan) were used without further purification.

6-Chloro-6-deoxypullulans

Regioselective chlorination of pullulan was carried out according to the method of Mocanu et al.[7] Pullulan was dissolved in DMF (50 mL) under sonication for several hours at room temperature. The solution was cooled to -30 °C, and a known amount of mesyl chloride (MsCl) was added dropwise over 30 min under stirring and heated to room temperature. After the reaction of 24 h, the resulting solution was poured into methanol to precipitate a tan powder. The crude product was centrifuged, redissolved in water, dialyzed against deionized water for 3 days, and freeze-dried to give 6-chloro-6-deoxy pullulan (P-Cl) with > 80% yield.

6-Azide-6-deoxypullulans

Azidation of P-Cl was carried out in DMSO according to the method of Ball et al.[8] The sample P-Cl was dissolved in DMSO and NaN_3 (30 equiv for Cl units in P-Cl) was added and heated at 100 °C for 24 h. The resulting solution was poured into methanol to precipitate a tan powder. The precipitate was redissolved in water and dialyzed against deionized water for 2 days and freeze-dried to yield 6-azide-6-deoxypullulan (P-N_3) with > 70% yield.

Acetylation of P-N_3

Acetylation of the remaining hydroxyl groups in the P-N_3 samples was carried out according to the method of Teshirogi et al.[9] Acetic anhydride (4 mL, ca. 10 equiv for the hydroxyl group) was added to a solution of P-N_3 (0.25 g) in anhydrous pyridine (6 mL), and the mixture was stirred for 30 h at 80 °C. The resulting solution was poured into deionized water, condensed by evaporation, dialyzed against THF to remove acetic acid. The acetylated P-N_3 (P-Ac-N_3) was recovered by freeze-drying from the benzene solution.

Addition Reaction of C_{60} with P-Ac-N_3

Addition reaction of C_{60} with P-Ac-N_3 was carried out in refluxing chlorobenzene according to the method of Wudl.[2] C_{60} (5 equiv for the N_3 groups in P-Ac-N_3) was dissolved in chlorobenzene. A solution of P-Ac-N_3 in chlorobenzene (50 mL) was added dropwise into the refluxing C_{60} solution in chlorobenzene. Heating was continued for 48 h. The resulting solution was condensed by evaporation and poured into THF to remove any unreacted C_{60}. The supernatant was evaporated to dryness to afford the C_{60}-bearing product (P-Ac-C_{60}).

Deacetylation of P-Ac-C_{60}

Deacetylation of P-Ac-C_{60} was carried out by base-catalyzed hydrolysis. A solution of P-Ac-C_{60} in 1,4-dioxane was mixed with 20% aqueous sodium hydroxide

(3 equiv to the ester units in P-Ac-C_{60}) and the mixture was stirred at room temperature for 3 h. During the reaction, partially hydrolyzed polymers precipitated in the solution. After 1,4-dioxane was removed by evaporation, the precipitate was dissolved in a large amount of water. The solution was further stirred for 24 h at room temperature to complete the hydrolysis and concentrated by evaporation to a small volume. The concentrated solution was dialyzed against deionized water for 3 days. Finally the solution was concentrated and lyophilized to give the C_{60}-bearing pullulan (P-C_{60}).

Saturation Solubility of P-C_{60} in Water

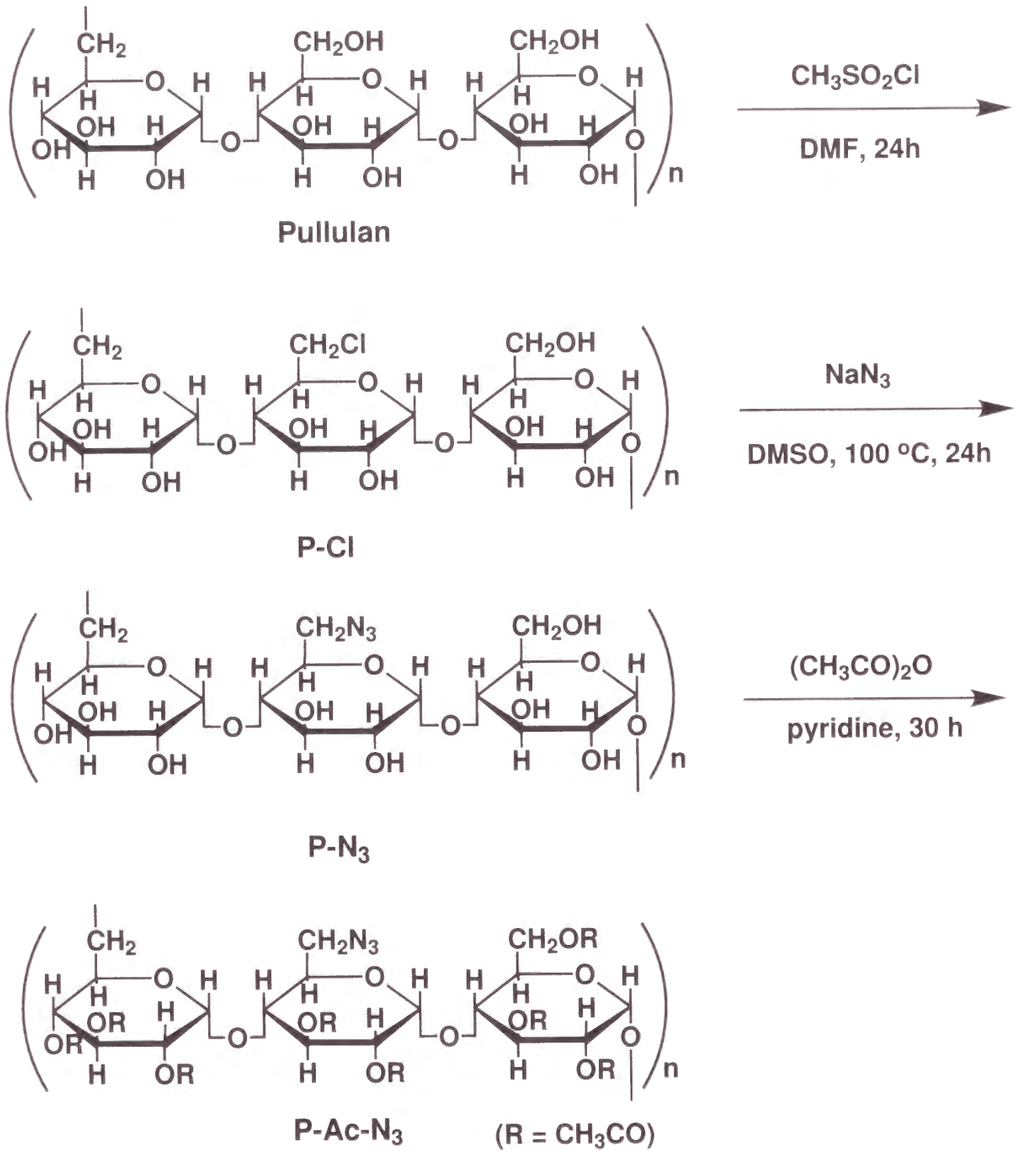
All operations were conducted in an air-conditioned room kept at 25 °C. 40 mg of each polymer sample was mixed with 0.1 mL of water in a centrifuge tube. After 1 min of sonication, the mixture was centrifuged. The supernatant (10 μL, measured by microsyringe) was diluted with water and the concentration of the C_{60} moiety was determined by measuring the UV absorption intensity at 430 nm.

RESULTS AND DISCUSSION

Preparation of 6-Azide-6-deoxypullulans (Scheme 2)

Pullulan is composed of α-1,6-linked maltotriose units. Hence, only two of the three glucoses in the repeating maltotriose unit have primary hydroxyl groups at C-6 position because the third is linked through C-6, that is, the maximum degree of substitution (DS) at C-6 position is not 1.0 but 0.67. Here DS = 3 indicates that all three hydroxyl groups of a glucose unit have been substituted, as in pullulan triacetate.

Scheme 2



Chlorination of polysaccharides with mesyl chloride (MsCl) in DMF is one of the regioselective reactions for polysaccharides.[7,9] The primary hydroxyl groups at C-6 position are selectively chlorinated by the method employed here. One of the important factors in the chemical modification of polysaccharides is the distribution of substituents along the main chain. For the present purpose, the uniform distribution

Table 1. Chlorination of pullulan

sample code	MsCl/ OH groups in pullulan (mol/mol)	chlorine (%)	DS[a]	color of product
P-Cl-1	0.5	1.05	0.048	Tan
P-Cl-2	1.0	2.99	0.14	Tan

[a] From elemental analysis of chlorine.

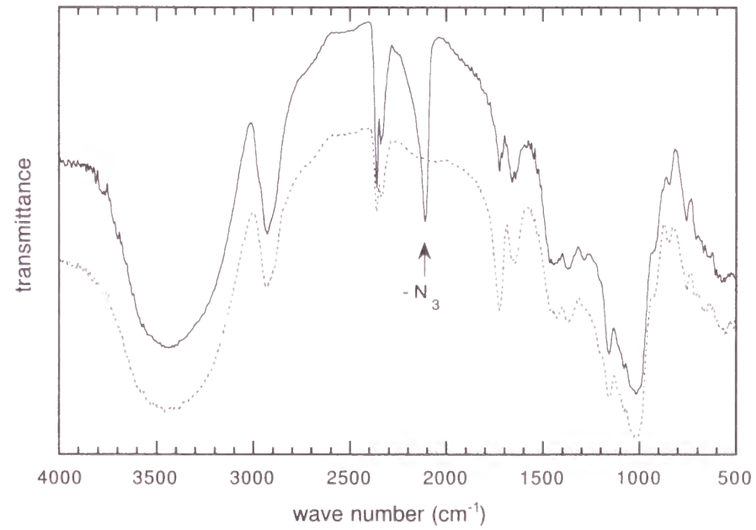


Figure 1. IR spectra of P-Cl-2 (broken line) and P-N_3-2 (solid line).

of substituents is important.[10] Taking into consideration the aqueous solubility of the target polymers, in this study, we examined to prepare 6-chloro-6-deoxypullulans (P-Cl) having a relatively low DS by the homogeneous reaction.

Table 1 shows the reaction conditions and the DS values of the samples prepared. The samples having different DS values were prepared by changing the amount of MsCl added. The DS values were estimated by elemental analysis. The regioselective chlorination of the primary hydroxyl groups at C-6 position was confirmed by ^{13}C NMR spectroscopy. For instance, the spectrum of the chlorinated

product exhibited a new C-6 resonance assignable to CH_2Cl at δ = 44 ppm, in addition to the signals of pullulan.

The P-Cl samples were converted into the corresponding 6-azide-6-deoxypullulans (P-N_3) by treating with sodium azide in DMSO. The results are shown in Table 2. It can be seen that the transformation of chlorine to azide groups is almost quantitative. Here DS values of 0.05 for P-N_3-1 and 0.11 for P-N_3-2 correspond to those for the samples which contain one azide group per 20 and 9 glucose units, respectively. Figure 1 shows the IR spectrum of the sample P-N_3-2 together with that of P-Cl-2. A strong absorption peak at 2100 cm^{-1} by azide groups appears in P-N_3-2.

The obtained P-N_3 samples were soluble in water and in some polar organic solvents such as THF, DMF, and DMSO, but insoluble in aromatic solvents such as chlorobenzene which is a good solvent for C_{60}. Hence, the P-N_3 samples were acetylated not only to protect the remaining hydroxyl groups but also to provide the solubility of polymers in chlorobenzene. Complete acetylation was confirmed by IR spectra. The IR spectra of acetylated P-N_3 samples (P-Ac-N_3) showed strong absorption peaks at 1760 cm^{-1} and 2100 cm^{-1} by ester and azide groups, respectively, while a broad absorption peak at around 3500 cm^{-1} by hydroxyl groups disappeared.

Table 2. Characterization of 6-azido-6-deoxypullulans

sample code	elemental analysis		DS[a]
	N (%)	Cl remaining (%)	
P-N_3-1	1.36	0	0.05
P-N_3-2	2.45	0.7	0.11

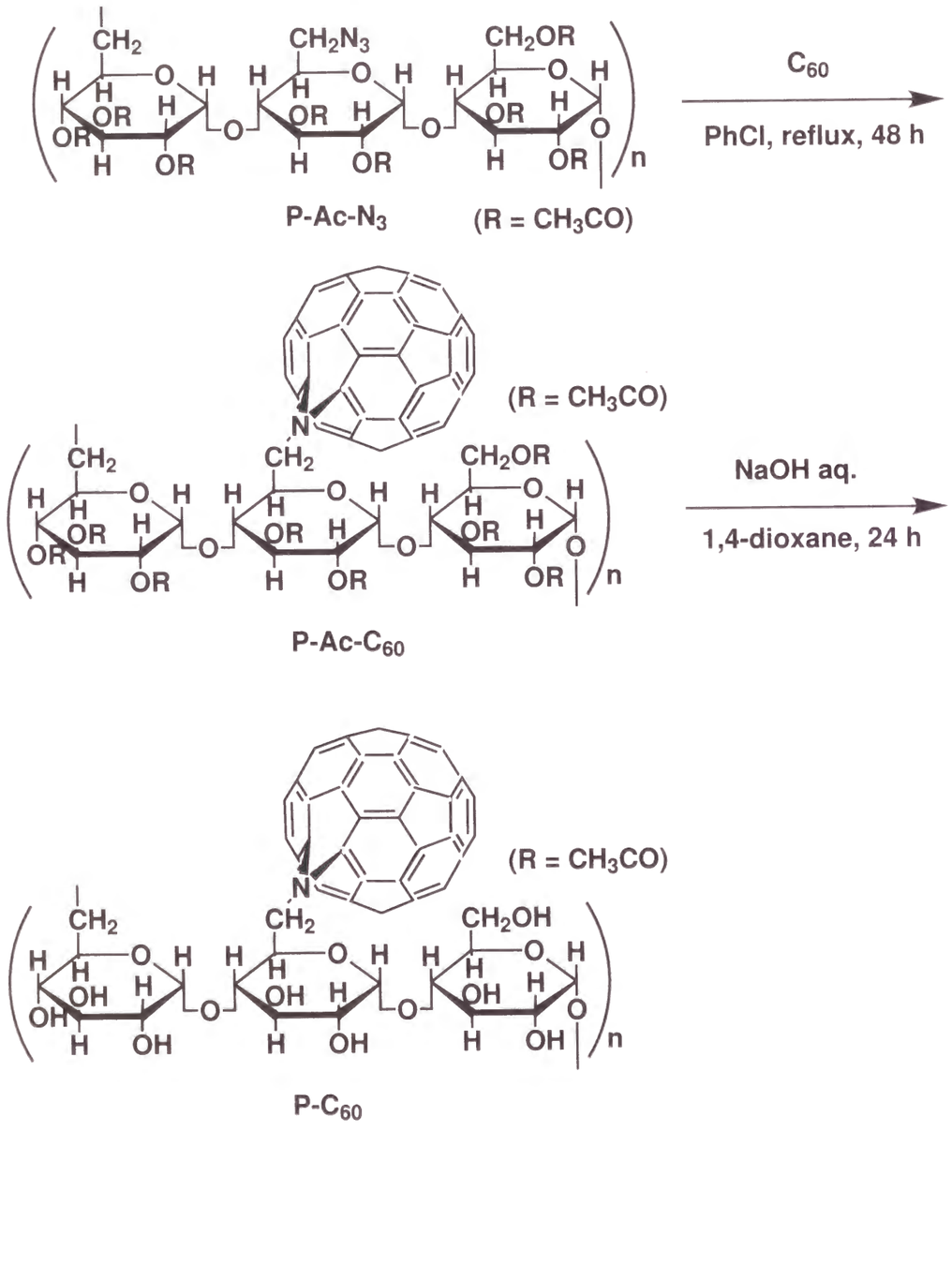
[a] From elemental analysis of nitrogen.

Addition Reaction of P-Ac-N_3 with C_{60} (Scheme 3)

The reaction of P-Ac-N_3 samples with C_{60} was carried out in refluxing chlorobenzene for 24 h. During the reaction, the color of the reaction solution gradually turned from purple to brown, as the addition reaction proceeded. The resulting solution was poured into THF. The C_{60}-bearing acetylated pullulans (P-Ac-C_{60}) were recovered by evaporating the supernatant. The crude products were redissolved in THF and filtered to remove any unreacted C_{60}. The pure products P-Ac-C_{60}-1 and P-Ac-C_{60}-2 were obtained as brown powders in high yields (> 80%). The reaction of P-Ac-N_3 with C_{60} was followed by IR spectroscopy. After 24 h, the absorption peak at 2100 cm^{-1} for the azide groups showed a decrease of about 70%, but did not completely disappear. These results mean that the transformation of azide groups to C_{60} was not completed under the reaction conditions employed here. The optimum reaction conditions of the addition reaction of P-Ac-N_3 with C_{60} are currently under investigation.

The covalent attachment of C_{60} to the pullulan backbone was confirmed by two methods. One is the ^{13}C NMR method. In the ^{13}C NMR spectra a broad set of resonances by the aromatic carbons of the substituted C_{60} moiety was observed between 130 and 150 ppm with the characteristic resonance at 143 ppm for pure C_{60} being absent. The other is the GPC method. Figure 2 shows the GPC curves of P-Ac-C_{60}-1 and P-Ac-N_3-1 recorded by different detectors. The pullulan moiety is detectable by RI, but not by UV (700 nm), while the C_{60} moiety is detectable by both UV (700 nm) and RI. The two GPC curves of P-Ac-C_{60}-1 are nearly identical, indicating that the chemical uniformity of the polymer was attained. In addition, the GPC curves of P-Ac-C_{60}-1 and P-Ac-N_3-1, detected by RI are almost identical, so that no degradation of the pullulan chain occurred during the reaction. Similar results were obtained for the sample P-Ac-C_{60}-2.

Scheme 3



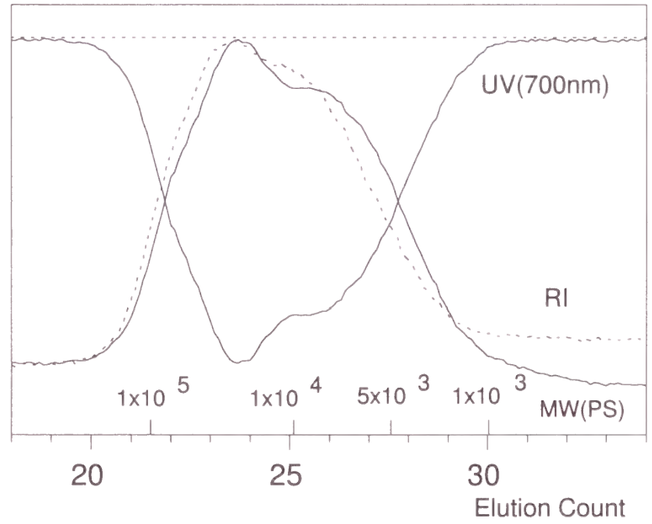


Figure 2. GPC curves of P-Ac-C_{60}-1 (solid line) by UV (700 nm) (upper) and RI (lower) compared with the curve for P-Ac-N_3-1 (broken line) by UV (700 nm) (upper) and RI (lower).

Hydrolysis of P-Ac-C_{60}

The hydrolysis of the acetyl groups of P-Ac-C_{60} samples yielded water-soluble C_{60}-bearing pullulan derivatives P-C_{60} (see the Experimental section). Complete conversion of P-Ac-C_{60} to P-C_{60} was confirmed by IR and ^{1}H NMR spectra. In the IR spectra of the hydrolysis products, a broad peak by hydroxyl groups at around 3500 cm^{-1} newly appeared as the absorption peak by ester groups at 1750 cm^{-1} disappeared. In the ^{1}H NMR spectra, the peak ascribed to acetoxy protons at 2.1 ppm completely disappeared.

Water Solubility of P-C_{60}

Saturation solubilities of P-C_{60} samples were estimated in water at 25 °C, and found to be 216 mg/mL for P-C_{60}-1 and 5.6 mg/mL for P-C_{60}-2, respectively. To be

noted here is that the saturation solubility of the C_{60}moiety in the pullulan derivatives prepared here strongly depends on the DS value of the C_{60} moiety introduced. In other words, an optimum DS value of the C_{60} moiety exists for its water solubility.

Here the saturation solubility of the C_{60} moiety was estimated from DS values of P-N_3 derivatives. If we assume that the degree of transformation of azide groups to C_{60} was approximately 60% as already described, the weight percent of the C_{60} moiety in P-C_{60}-1 and P-C_{60}-2 becomes 12% and 23%, respectively. The saturation solubility of the C_{60} moiety can be estimated to be 26 mg/mL for the sample P-C_{60}-1 and 1.3 mg/mL for the sample P-C_{60}-2. The results may indicate that C_{60}-bearing pullulans are applied practically in the field of medicinal materials. A detailed study on the DS dependence of C_{60}-bearing pullulans on their water solubility is in progress.

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List of Publications

Part I

Chapter 1

1) Synthesis of Disubstituted 1,2-Dihydro[60]fullerenes with Well-Defined Structure by Addition of 1-Alkoxy-1-chloroethanes to 2-(1-Octynyl)-1,2-dihydro[60]fulleren-1-ide Ion

H. Okamura, Y. Murata, M. Minoda, K. Komatsu, T. Miyamoto, and T. S. M. Wan

J. Org. Chem., **1996**, *61*, 8500-8502.

Chapter 2

2) Synthesis of C_{60}-capped vinyl ether oligomers by living cationic polymerization technique

H. Okamura, M. Minoda, K. Komatsu, and T. Miyamoto

Macromol. Chem. Phys., **1997**, *198*, 777-786.

Chapter 3

3) Synthesis of Water-Soluble C_{60} Vinyl Ether Oligomers with Well-Defined Polymer Arms

H. Okamura, K. Miyazono, M. Minoda, T. Fukuda, K. Komatsu, and T. Miyamoto

Macromolecules, in press.

Part II

Chapter 4

4) Synthesis of 1,4-Dipolystyryldihydro[60]fullerenes by Using 2,2,6,6-Tetramethyl-1-polystyroxypiperidine as a Radical Source

H. Okamura, T. Terauchi, M. Minoda, T. Fukuda, and K. Komatsu

Macromolecules, **1997**, *30*, 5279-5284.

Chapter 5

5) Solubility and Micellization Behavior of C_{60} Fullerenes with Two Well-Defined Polymer Arms

H. Okamura, N. Ide, M. Minoda, K. Komatsu, and T. Fukuda

Macromolecules, **1998**, *31*, 1859-1864.

Chapter 6

6) Solubility characteristics of C_{60} fullerenes with two well-defined polymer arms in a polystyrene matrix

H. Okamura, M. Minoda, T. Fukuda, T. Miyamoto, and K. Komatsu

Macromol. Rapid Commun., submitted.

Part III

Chapter 7

7) Preparation of water-soluble pullulans bearing pendant C_{60} and their aqueous solubility

H. Okamura, K. Miyazono, M. Minoda, and T. Miyamoto

Macromol. Rapid Commun., submitted.

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Haruyuki Okamura