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Grafting of poly(ethylene oxide) onto C_{60} fullerene using macroazo initiators

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Abstract

In order to improve the solubility of C_{60} fullerene in conventional solvents, grafting of hydrophilic poly(ethylene oxide) (PEO) by utilizing the radical-trapping nature of C_{60} fullerene was investigated. Macroazo initiators containing a poly(ethylene oxide) unit, known as Azo-PEO, were prepared at various molecular weights by the reaction of 4,4′-azobis(4-cyanopentanoyl chloride) with poly(ethylene glycol) methyl ether. PEO radicals formed by thermal decomposition of Azo-PEO were successfully trapped by C_{60} fullerene to give PEO-grafted C_{60} fullerene. Their structures were confirmed by FT-IR spectroscopy, size exclusion chromatography, UV–vis spectroscopy, and differential scanning calorimetry. When Azo-PEO with low-molecular weight was reacted with C_{60} fullerene, a bis-adduct, C_{60}-$(PEO)_2$, and a tetrakis-adduct, C_{60}-$(PEO)_4$, were formed. In contrast, in reactions with Azo-PEO of higher molecular weight, only the bis-adduct was formed, and no formation of the tetrakis-adduct was observed. The structure of bis-adduct was found to be 1,4-type. The solubility of C_{60} fullerene in water, THF, methanol, and other conventional organic solvents was remarkably improved by grafting of PEO. In addition, the thermal stability of PEO was dramatically increased by grafting onto C_{60} fullerene.

Keywords: C_{60} fullerene; Macroazo initiator; Radical trapping

1. Introduction

Since 1990, the fundamental physical properties of fullerene have been investigated extensively, and a variety of interesting properties, such as the ability to accept and release electrons [1], free-radical trapping [2], physiological activity [3], photoactivity [4], biocompatibility, and relatively high chemical reactivity allowing structural modification [5] have been reported. Moreover, derivatives of C_{60} fullerene have also been found to show interesting properties. For example, K_3C_{60} exhibits superconductivity at 18 K [6], and TDAE-C_{60} [TDAE: tetrakis(dimethylamino) ethylene] shows ferromagnetic properties [7]. C_{60} fullerene has recently begun production on a commercial scale at Frontier Carbon Corporation, a Japanese venture company, which is planning to expand its fullerene production capacity from 300 tons/year in 2005 to 1500 tons/year in 2007 [8]. It is expected that the introduction of large-scale production will lead to mass applications.

However, C_{60} fullerene is only slightly soluble in most solvents [9], which is a problem in terms of practical development of mass applications. To improve solubility in conventional solvents, various methods for chemical modification of C_{60} fullerene have been reported, not only in fundamental studies [5] but also for the practical applications [10]. Grafting of polymer chains onto C_{60} fullerene is one available method for overcoming this problem, and can provide polymeric materials with interesting properties and technological applications.

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C_{60} fullerene is known as a ''radical sponge'' because of its strong ability to trap free radicals. Theoretical calculations of the molecular orbital levels of C_{60} fullerene show that the LUMO exhibits a comparatively low energy and is triply degenerate. This is why C_{60} fullerene has an electron-accepting, radical-trapping nature.

Many reactions of C_{60} fullerene with low-molecular radicals have been reported; for example, methyl [11], benzyl [11], and *tert*-butylperoxy [12] radicals undergo multiple additions to C_{60} fullerene. Reactions of C_{60} fullerene with azo compounds have been also reported; for example, Ford and co-workers reported that thermal decomposition of 2,2′-azobisisobutyronitrile (AIBN) in a *o*-dichlorobenzene (*o*-DCB) solution of C_{60} fullerene gave three regioisomeric C_{60} fullerene derivatives, two of which were assigned as the 1,4- and 1,2-regioismers [13].

Studies have been conducted on reactions of C_{60} fullerene not only with low-molecular radicals but also with macromolecular radicals. Three approaches to polymerization in the presence of C_{60} fullerene have been reported so far. The first is the use of free-radical initiators for copolymerization of C_{60} fullerene with vinyl monomers such as styrene (St) [14] and methyl methacrylate (MMA) [15], the second is nitroxyl-mediated ''living'' radical polymerization (NMRP) [16], and the third is atom transfer radical polymerization (ATRP) [17]. The first method, in many cases, resulted in a mixture of poorly defined multi-adducts, but the second and third, employing the principle of equilibrium between a low concentration of active species and a large number of dormant compounds, produced polymers with well-defined and narrow molecular weight distributions.

Ederlé and co-workers reported the grafting of poly(ethylene oxide) (PEO) onto C_{60} fullerene by reacting the fullerene with living PEO anions formed by the reaction of poly(ethylene glycol) methyl ether with diphenyl methyl potassium [20]. In addition, Manolova et al. reported the reaction of amino-capped PEO with C_{60} fullerene [21].

In addition, we reported that polymer radicals formed by thermal decomposition of macroazo initiators were effectively trapped on the surface of multi-walled carbon nanotubes (MW-CNT) [18], cup-stacked carbon nanotubes (CS-CNT) [18], and carbon black (CB) [19] to give the corresponding polymer-grafted MW-CNT, CS-CNT, and CB.

In this paper, we report the reaction of C_{60} fullerene with poly(ethylene oxide) (PEO) radicals formed by thermal decomposition of the corresponding PEO-containing macroazo initiator (Scheme 1). In addition, the solubility and thermal stability of the PEO-grafted C_{60} fullerene is discussed. This is a new approach to the preparation of polymer-grafted C_{60} fullerene, which exploits the radical-trapping nature of the fullerene.

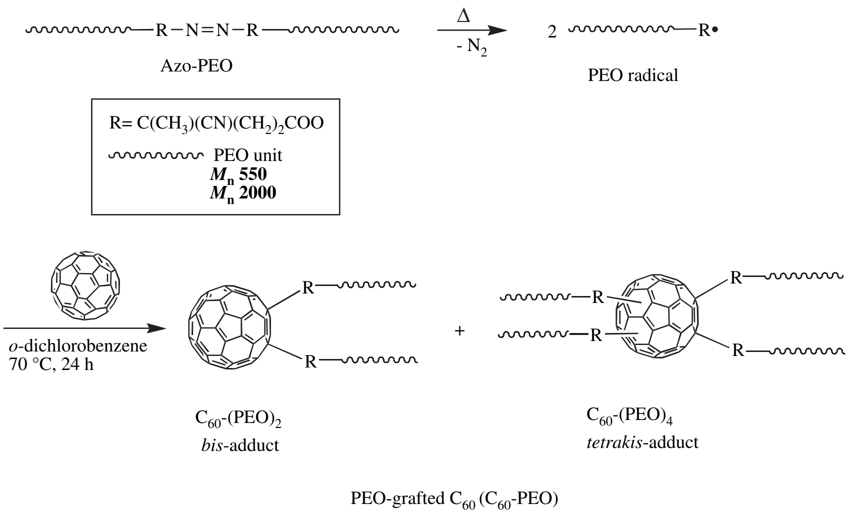
2. Experimental

2.1. Materials and reagents

The C_{60} fullerene used was ''nanom purple N60-S'', obtained from Frontier Carbon Co., Ltd., Japan, which was used without further purification. The purity and average particle size were >96% and 30−70 μm, respectively. The product was dried in vacuo at 50 °C before use.

4,4′-Azobis(4-cyanopentanoic acid) (ACPA) was obtained from Wako Pure Chemical Ind. Co., Ltd., Japan, and was recrystallized from methanol and dried in vacuo at room temperature. Poly(ethylene oxide) methyl ether (PEO-Me) ($M_n = 550$ and 2000), obtained from Aldrich Chemical Company, Inc., was dried in vacuo at 50 °C before use.

o-Dichlorobenzene (*o*-DCB) was dried over calcium hydride and then distilled under reduced pressure. Toluene and *n*-hexane were refluxed over sodium and distilled. Chloroform and trichloroethylene were dried over calcium chloride and distilled. Tetrahydrofuran (THF) and *n*-pentane, used for fractionation of the products, were used without further purification.



Scheme 1.

2.2. Preparation of Azo-PEO550 and Azo-PEO2000

Azo-PEOs were prepared by reaction of 4,4′-azobis(4-cyanopentanoyl chloride) (ACPC) with PEO-Me ($M_n = 550$ and 2000), according to a literature method [22]. ACPC was prepared by reaction of ACPA with phosphorous pentachloride.

2.3. Reaction of Azo-PEO with C_{60} fullerene

A typical experiment is as follows: 0.20 mmol of C_{60} fullerene, 0.20 mmol of Azo-PEO550 (Azo-PEO2000) containing a small amount of PEO-Me, and 15.0 ml (20.0 ml when Azo-PEO2000 was used) of *o*-DCB were placed in a glass tube, degassed with several freeze-thaw cycles, and sealed off under high vacuum. The sealed tube was heated at 70 °C for 24 h with stirring. After the reaction, *o*-DCB was removed from the reaction mixture at 50 °C and a pressure of 6.7 kPa by use of a centrifugal evaporator.

2.4. Isolation of C_{60}-PEO550 from reaction product

After the reaction, the product mixture contained PEO550-grafted C_{60} fullerene (C_{60}-PEO550), unreacted C_{60} fullerene, and ungrafted PEO. The mixture was separated and purified by the method shown in Fig. 1. A large excess of THF was added to the product mixture (*a*) and unreacted C_{60} (*b*) was removed as a precipitate (C_{60} fullerene is insoluble in THF). A mixture of C_{60}-PEO550 and ungrafted PEO (*c*) was then obtained from the supernatant solution by evaporation of THF and fractionated using a toluene/*n*-pentane solvent mixture as follows: 0.20 g of (*c*) was completely dissolved in 20 ml of toluene, and then 12 ml of *n*-pentane was added dropwise to the solution. The resulting precipitate (C_{60}-$(PEO550)_4$) (*d*) was recovered by decantation. Next, 20 ml of *n*-pentane was once again added to the supernatant solution, and the resulting precipitate (a mixture of the bis-adduct and the tetrakis-adduct) (*e*) was recovered by decantation. Another 5 ml of *n*-pentane was added to the supernatant solution, and the resulting precipitate (C_{60}-$(PEO550)_2$) (*f*) was recovered by decantation. Thus, the bis-adduct and the tetrakis-adduct were fractionated and purified. Yields: bis-adduct 53 mg, tetrakis-adduct 52 mg.

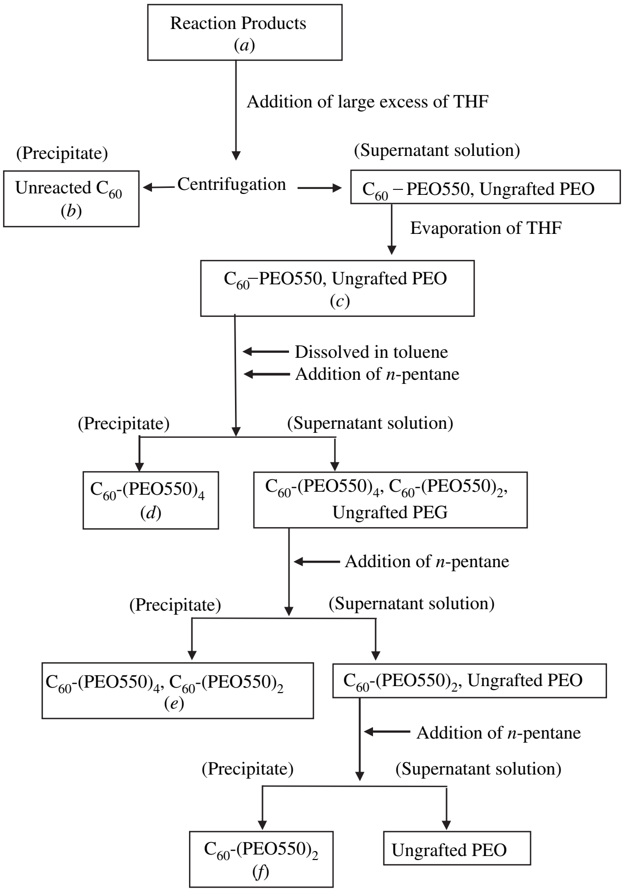


Fig. 1. Fractionation and purification of C_{60}-PEO550.

2.5. Isolation of C_{60}-PEO2000 from the reaction products

The mixture was separated and purified by the method shown in Fig. 2. A large excess of THF was added to the product mixture (*a*′), and unreacted C_{60} (*b*′) was removed as a precipitate. A mixture of C_{60}-PEO2000 and ungrafted PEO (*c*′) was obtained from the supernatant solution by evaporation of THF and fractionated using a toluene/*n*-pentane mixed solvent as follows: 0.30 g of the product mixture (*c*′) was completely dissolved in 20 ml of toluene, and 12 ml of *n*-pentane was added dropwise. The resulting precipitate (C_{60}-$(PEO2000)_2$) (*d*′) was recovered by decantation. Yield: 0.19 g.

2.6. Measurements

Thermogravimetric analysis (TGA) was performed under a nitrogen flow using a thermogravimetric analyzer (Shimadzu Manufacturing Co., Ltd., TGA-50) at a heating rate of 10 °C/min. Differential thermal analysis was performed under

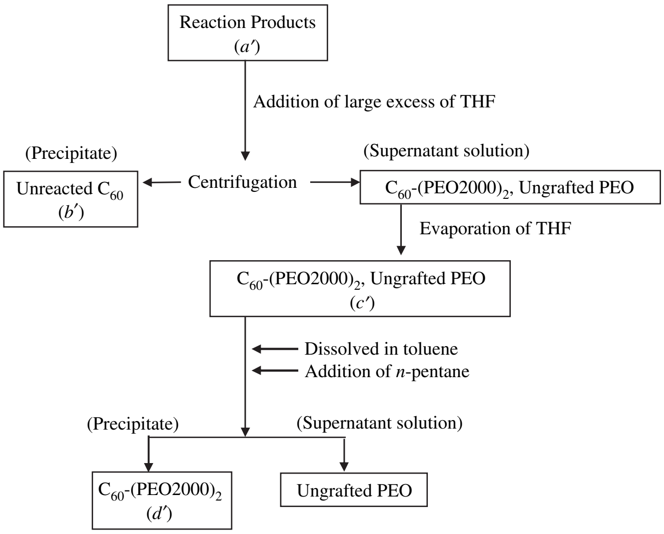


Fig. 2. Fractionation and purification of C_{60}-PEO2000.

a nitrogen flow using a differential scanning calorimeter (DSC) (Shimadzu Manufacturing Co., Ltd., DSC-50) at a heating rate of 10 °C/min. From the results, calorific values were determined.

UV–vis spectra were recorded on a UV-1600 spectrometer (Shimadzu Manufacturing Co., Ltd.). Infrared spectra were recorded on an FT-IR spectrophotometer (Shimadzu Manufacturing Co., Ltd., 8200A).

Size exclusion chromatograms (SEC) were recorded on a Tosoh chromatograph system equipped with gel columns (TSKgel G3000H_{XL}) and refractive index (RI-8010)/ultraviolet (UV-8010) dual-mode detectors using chloroform as an eluent at 40 °C. The system was calibrated using Shodex standard polystyrenes. From the SEC results, the number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were determined.

Thermal decomposition gas chromatograms and mass spectra (GC–MS) were recorded on a gas chromatograph mass spectrometer (Shimadzu Manufacturing Co., Ltd., GPMS-QP2010) equipped with a double-shot pyrolyzer (Frontier Laboratories, Ltd., PY-2020).

3. Results and discussion

3.1. Synthesis of Azo-PEO

Azo-PEO550 and Azo-PEO2000 were prepared via the reaction of ACPC with PEO-Me550 and PEO-Me2000, respectively [22]. Characterization of Azo-PEO was performed by FT-IR, SEC, and DSC.

Fig. 3 shows the SEC curves of Azo-PEO550 and Azo-PEO2000 using refractive index detection. It can be seen that the SEC curve of Azo-PEO550 is bimodal; the larger and smaller peaks corresponded to those of Azo-PEO550 and unreacted PEO-Me550, respectively. The M_n and M_w/M_n of Azo-PEO550 were determined as 1427 (calcd. 1344) and 1.06, respectively.

The SEC curve of Azo-PEO2000 also shows two peaks, as shown in Fig. 3, with the larger and smaller peaks corresponding to Azo-PEO2000 and unreacted PEO-Me2000, respectively. The M_n and M_w/M_n of the resulting Azo-PEO2000 were determined to be 3670 (calcd. 4244) and 1.05, respectively.

The Azo-PEO550 and Azo-PEO2000 thus obtained were used without further purification for the reaction with C_{60} fullerene, because unreacted PEO can be removed after the reaction.

3.2. Grafting reaction of Azo-PEO550 with C_{60} fullerene

Grafting of Azo-PEO onto C_{60} fullerene was carried out via trapping of PEO radicals formed by thermal decomposition, as shown in Scheme 1. The structures of PEO-grafted C_{60} species (C_{60}-PEOs) were confirmed by SEC and by FT-IR and UV-vis spectroscopy.

Fig. 4 shows SEC curves for the products (Fig. 1(a)) of the reaction of C_{60} fullerene with Azo-PEO550 before fractionation, detected by UV at 440 nm. Azo-PEO550 was not detected at this wavelength. SEC curves of products A–C show three peaks (*h*, *m*, *l*), as shown in Fig. 4. When the molar ratio of Azo-PEO550 to C_{60} fullerene in the feed was changed from 1.0 to 5.0, the third peak (*l*), which corresponds to unreacted C_{60} fullerene, decreased (Fig. 4).

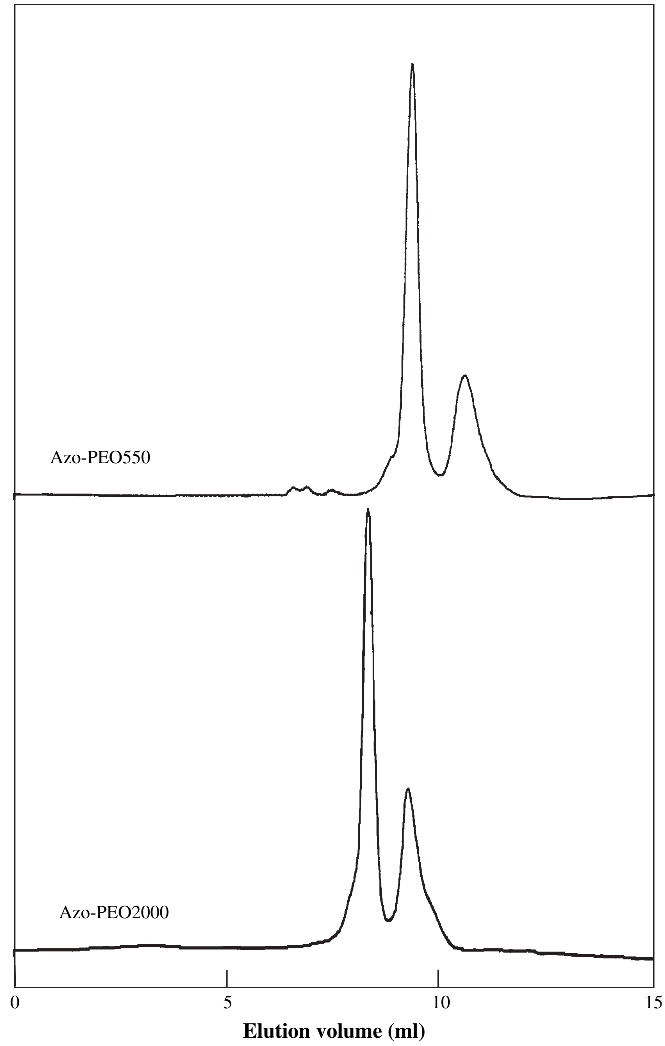


Fig. 3. SEC of Azo-PEO550 and Azo-PEO2000, detected by refractive index.

The reaction product of C_{60} fullerene with Azo-PEO550 was fractionated to give two fractions, fraction-A (Fig. 1(d)) and fraction-B (Fig. 1(f)). Fig. 5 shows SEC curves of fraction-A and fraction-B detected by refractive index; this confirms that fraction-A corresponds to peak *h* and fraction-B corresponds to peak *m* in Fig. 4. These results indicate that the reaction mixture was almost completely purified by fractionation using a toluene/*n*-pentane mixture.

The M_n values of fraction-A and fraction-B were determined to be 2900 and 1700, respectively, and the M_w/M_n values of fraction-A and fraction-B were determined to be 1.16 and 1.07, respectively, by SEC. The formula weights of C_{60}-$(PEO550)_4$ (tetrakis-adduct) and C_{60}-$(PEO550)_2$ (bis-adduct) were calculated to be 3352 and 2036, respectively. These results show that fraction-A and fraction-B correspond

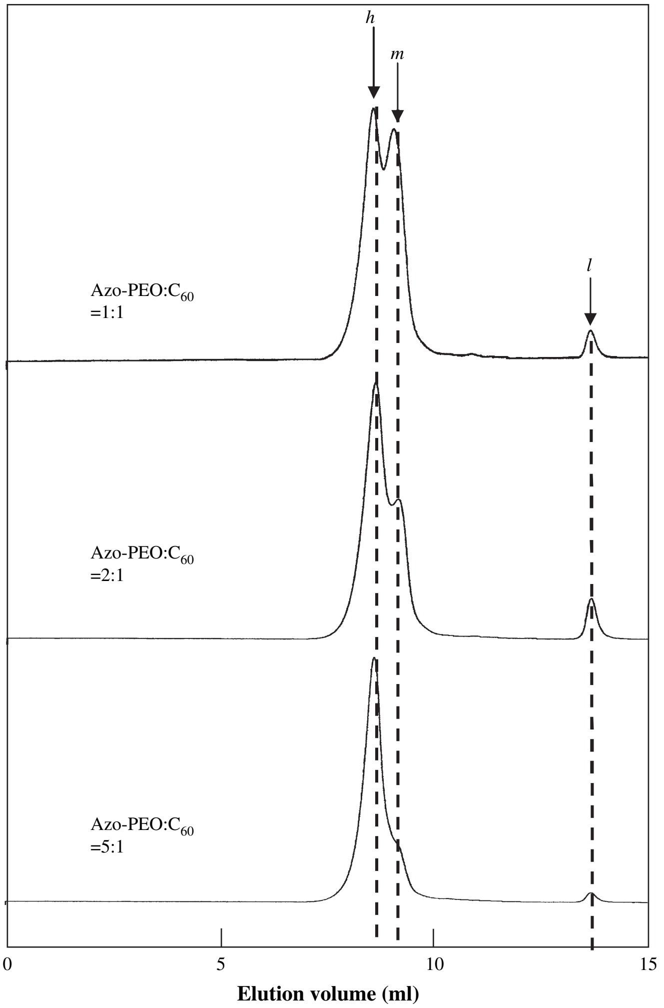


Fig. 4. SEC of reaction products of C_{60}/Azo-PEO550, detected by UV at 440 nm.

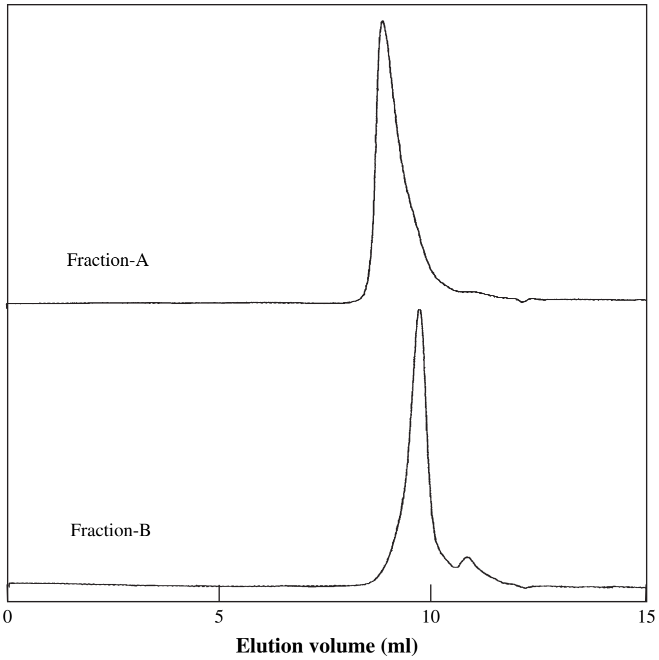


Fig. 5. SEC of fraction-A and fraction-B obtained from the reaction products of C_{60}/Azo-PEO550, detected by refractive index.

to the tetrakis-adduct and the bis-adduct, respectively. Moreover, Fig. 4 indicates that formation of the tetrakis-adduct proceeded preferentially with an increase in the molar ratio of Azo-PEO550 in the feed.

Fig. 6 shows FT-IR spectra of untreated C_{60} fullerene and C_{60}-PEO550. The same spectra were obtained for the bis-adduct and the tetrakis-adduct. FT-IR spectra of C_{60}-PEO show the characteristic adsorptions of PEO. Although untreated C_{60} fullerene shows four characteristic absorptions at 528, 577, 1183, and 1429 cm^{-1}, these signals disappeared completely after the grafting reaction. This shows that grafting of the PEO550 radicals altered the C_{60} fullerene cage.

Fig. 7 shows UV–vis spectra of (A) C_{60}-(PEO550)$_2$, (B) C_{60}-(PEO550)$_4$, and (C) untreated C_{60}. Some obvious changes were observed in the visible region of the C_{60}-(PEO550)$_2$ spectrum in comparison with that of C_{60} fullerene; a new characteristic broad peak appeared at approximately 443 nm.

It is well known that di-substituted C_{60} derivatives show characteristic UV–vis spectral features depending on the relative position of substitution—a sharp absorption at 430 nm for a 1,2-bis-adduct and a broad peak at 443 nm for a

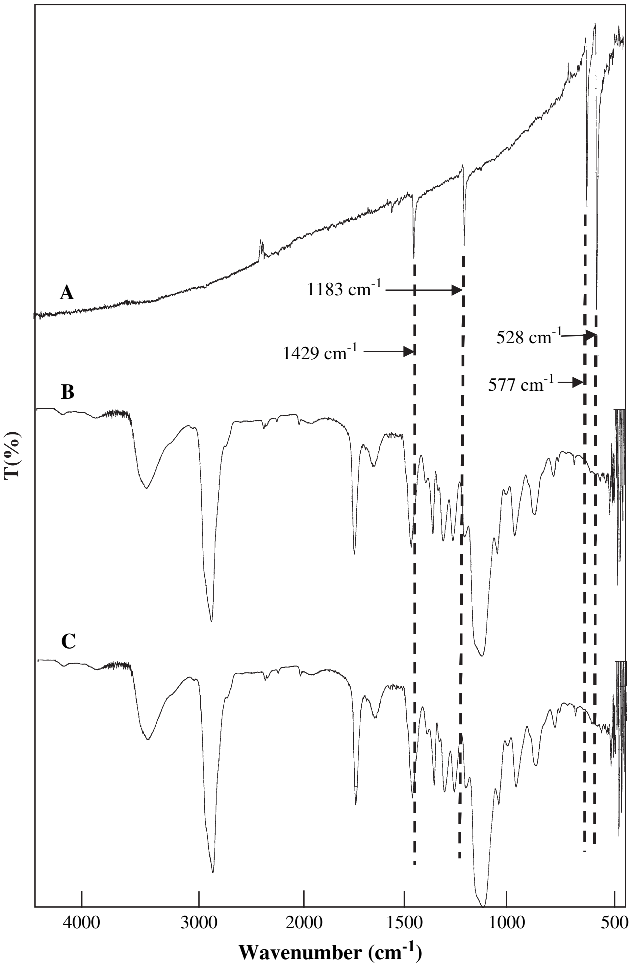


Fig. 6. FT-IR spectra of (A) untreated C_{60} (KBr pellet), (B) C_{60}-(PEO550)$_2$ (NaCl cell), and (C) C_{60}-(PEO550)$_4$ (NaCl cell).

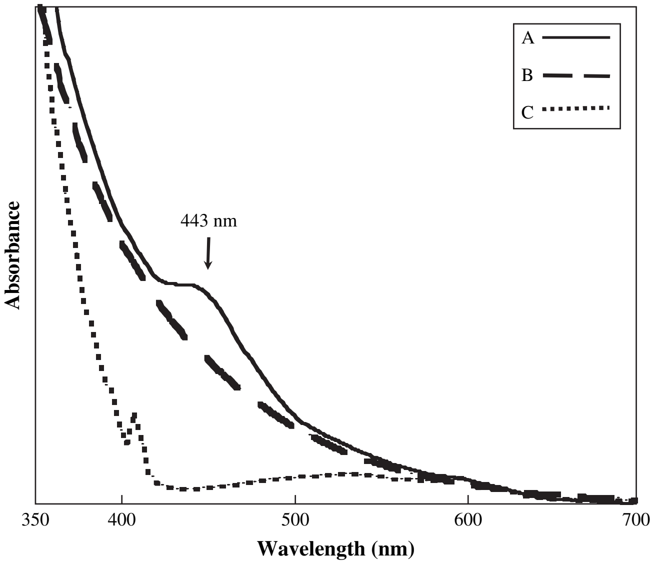


Fig. 7. UV–vis spectra of (A) C_{60}-$(PEO550)_2$ (solid line), (B) C_{60}-$(PEO550)_4$ (broken line), and (C) untreated C_{60} (dotted line) in $CHCl_3$.

1,4-bis-adduct [13,16,23,24]. The spectrum of C_{60}-$(PEO550)_2$ (Fig. 7(A)) indicates that it may be the 1,4-type.

When the spectrum of C_{60}-$(PEO550)_4$ (Fig. 7(B)) was compared with that of C_{60}-$(PEO550)_2$ (A), the broad peak at approximately 443 nm had disappeared. This result shows that further PEO chains were added to C_{60}-$(PEO550)_2$.

Fig. 8(A) shows the effect on conversion of the molar ratio of Azo-PEO550 to C_{60} fullerene in the feed. Conversion values were calculated using the following equation:

$$\text{Conversion}\ (\%) = [(A - B)/A] \times 100,$$

where A is the amount of C_{60} (g) used in the reaction, and B is unreacted C_{60}. Fig. 8 clearly shows that, as expected, the conversion increased with an increasing molar ratio of Azo-PEO550.

Based on the above results, it is concluded that PEO550 radicals formed by thermal decomposition of Azo-PEO550 were successfully trapped by C_{60} fullerene to give two types of PEO550-grafted C_{60} fullerene, the bis-adduct C_{60}-$(PEO550)_2$, and the tetrakis-adduct C_{60}-$(PEO550)_4$. In addition, it is likely that the structure of the bis-adduct is of the 1,4-type. Moreover, formation of the tetrakis-adduct increased with an increase in the molar ratio of Azo-PEO550 in the feed.

3.3. Grafting reaction of Azo-PEO2000 with C_{60} fullerene

Fig. 9 shows the SEC curve of fractionated C_{60}-PEO2000 (Fig. 2(d′)) detected by refractive index. Fig. 9 shows that fractionated C_{60}-PEO2000 was purified to a considerable extent but still contained slight amounts of ungrafted PEO2000. The molecular weight of the fractionated C_{60}-PEO2000 was determined to be 4600, and the formula weight of C_{60}-$(PEO2000)_2$ (bis-adduct) was calculated to be 4936. These results show that the large peak in the SEC curve corresponds to bis-adduct.

In contrast to the reaction with Azo-PEO550, formation of the tetrakis-adduct was not observed in this case even when the molar ratio of Azo-PEO2000 in the feed was increased. It is considered that the formation of tetrakis-adduct was inhibited due to steric hindrance of the high-molecular-weight PEO2000 species.

Fig. 10 shows UV–vis spectra of (A) C_{60}-$(PEO2000)_2$ and (B) untreated C_{60}. The spectrum of C_{60}-$(PEO2000)_2$ (A) is similar to that of C_{60}-$(PEO550)_2$, as shown in Fig. 7. Hence, the structure of C_{60}-$(PEO2000)_2$ may also be 1,4-type.

Fig. 8(B) shows the effect on conversion of the molar ratio of Azo-PEO2000 to C_{60} fullerene in the feed. It is clear that,

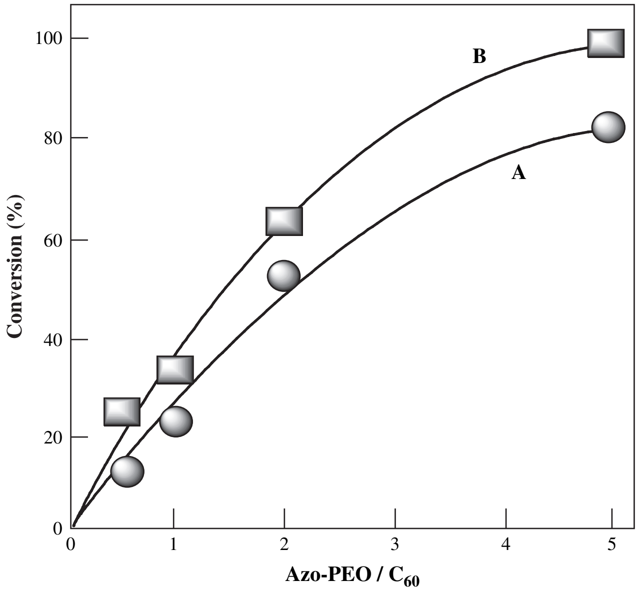


Fig. 8. Effect on conversion of molar ratio of (A) Azo-PEO550 and (B) Azo-PEO2000 to C_{60} fullerene in feed.

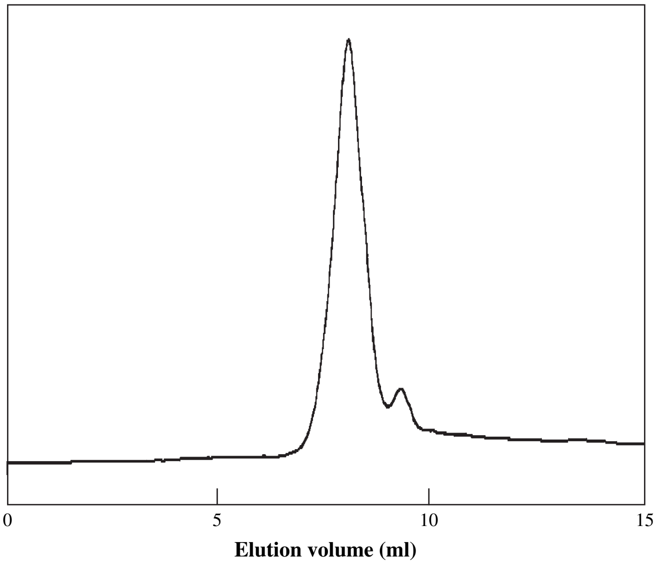


Fig. 9. SEC of fractionated products of C_{60} with Azo-PEO2000, detected by refractive index.

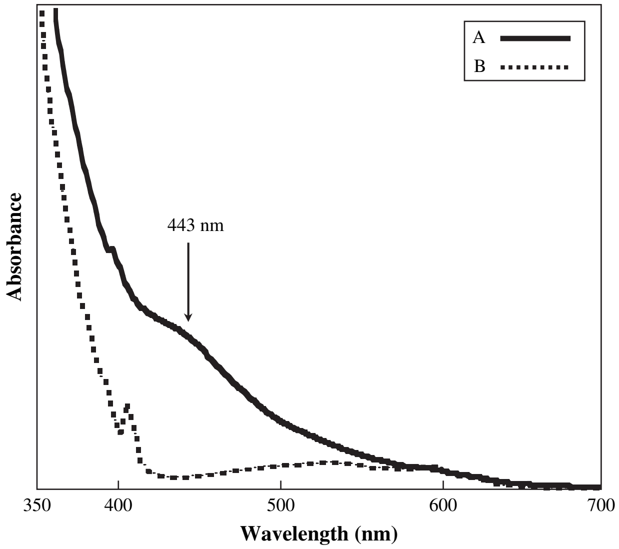


Fig. 10. UV–vis spectra of (A) C_{60}-PEO2000 (solid line) and (B) untreated C_{60} (dotted line) in $CHCl_3$.

as expected, conversion increased with an increase in Azo-PEO2000.

Based on the above results, it was concluded that PEO2000 radicals formed by thermal decomposition of Azo-PEO2000 were successfully trapped by C_{60} fullerene to give PEO2000-grafted C_{60} fullerene in the form of the bis-adduct C_{60}-$(PEO2000)_2$ only. In addition, the structure of the bis-adduct may be 1,4-type.

Ederlé et al. reported that in the reaction of C_{60} fullerene with PEO anions, the number of PEO chains ($M_n = 5000$) grafted onto C_{60} fullerene was more than six [20]. The difference between this result and the current results may be due to the fact that PEO anions, rather than PEO radicals, were used.

3.4. Solubility of PEO-grafted C_{60}

Fig. 11 shows the solubility of C_{60}-PEO in water, methanol, and THF. Each solution contained about 30 mg of C_{60}-$(PEO550)_2$ per 1 ml of solvent. It was found that more than 100 mg of C_{60}-$(PEO550)_2$ could be dissolved in 1 ml of water, which equates to at least 35 mg of C_{60} fullerene. C_{60}-$(PEO550)_4$ and C_{60}-$(PEO2000)_2$ were also highly soluble in these polar solvents.

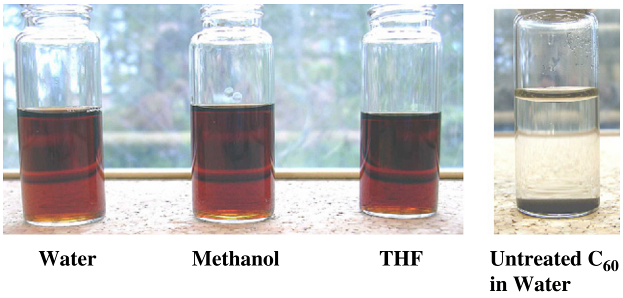


Fig. 11. Solubility of C_{60}-PEO in various polar solvents.

It was found that the solubility of C_{60} in these solvents increased significantly due to grafting of PEO onto C_{60} fullerene. In addition, solubility in conventional organic solvents such as acetone, chloroform, and toluene was also considerably improved. There was no appreciable difference in the solubilities of C_{60}-$(PEO550)_2$ and C_{60}-$(PEO550)_4$ in these polar solvents.

3.5. Thermal stability of PEO-grafted C_{60} (C_{60}-PEO)

Fig. 12 shows TGA curves of C_{60}-$(PEO550)_2$, C_{60}-$(PEO550)_4$, and Azo-PEO550. The intersection with the tangent line represents the thermal decomposition temperature (T_d) of each C_{60}-PEO species. The T_d of bis- and tetrakis-adduct C_{60}-PEO550 were increased by about 100 °C in comparison with that of Azo-PEO550. The T_d of C_{60}-PEO2000 was also increased by over 100 °C compared with that of Azo-PEO2000.

C_{60} fullerene has been reported to show retarding and inhibiting effects on the thermal decomposition of poly(methyl methacrylate) (PMMA), PSt [25,26], acrylic polymers [27], and poly(*N*-vinylcarbazole) [28]. Zuev et al. reported that the T_d of mixture of acrylic polymer such as poly-*n*-alkyl methacrylates (PAA-*n*) and poly-*n*-alkyl acrylates (PMA-*n*) with C_{60} fullerene was raised by about 20–30 °C compared with those of acrylic polymers [27]. Chen et al. also reported that the T_d of C_{60}-poly(*N*-vinylcarbazole) copolymer was raised by about 13 °C compared with that of poly(*N*-vinylcarbazole) [28].

The T_d of each C_{60}-PEO species seems to be dramatically increased in comparison with those of acrylic polymers, poly(*N*-vinylcarbazole). It is assumed that this is due to the ability of C_{60} fullerene to trap radicals formed by thermal decomposition of PEO to a greater extent than radicals of PMMA, PSt, acrylic polymers, and poly(*N*-vinylcarbazole), as the latter types are stabilized by conjugation.

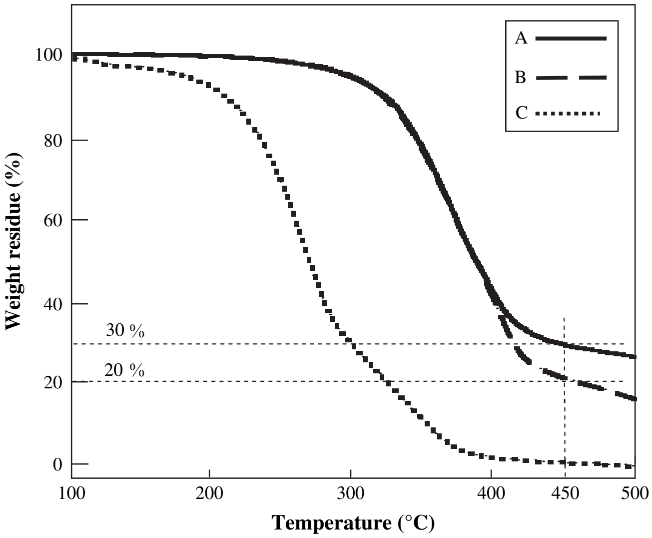


Fig. 12. TGA curves of various C_{60}-PEO. (A) C_{60}-$(PEO550)_2$ (solid line), (B) C_{60}-$(PEO550)_4$ (broken line) and (C) Azo-PEO550 (dotted line).

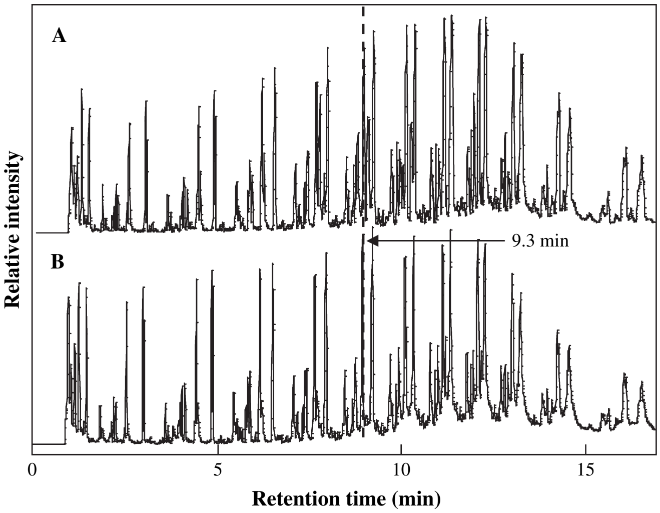


Fig. 13. Gas chromatograms of decomposed (A) Azo-PEO2000 and (B) C_{60}-(PEO2000)$_2$ gas.

The gas chromatogram (GC) of decomposed C_{60}-(PEO2000)$_2$ gas was clearly the same as that of Azo-PEO2000, as shown in Fig. 13. In addition, the mass spectrum of decomposed C_{60}-(PEO2000)$_2$ gas at retention time 9.3 min was the same as that of Azo-PEO2000, as shown in Fig. 14. It can be seen from Fig. 14 that C_{60}-(PEO2000)$_2$ produces ethylene oxide monomers, dimers, trimers, etc., on decomposition. It is well known that C_{60} fullerene reacts easily with low-molecular weight alkyl radicals [11]. It is thought that the C_{60} moiety of C_{60}-PEO actively trapped small radical species (monomers to trimers) on initial decomposition, and the trapping of C_{60} moiety suppressed weight loss to raise the T_d of each C_{60}-PEO species.

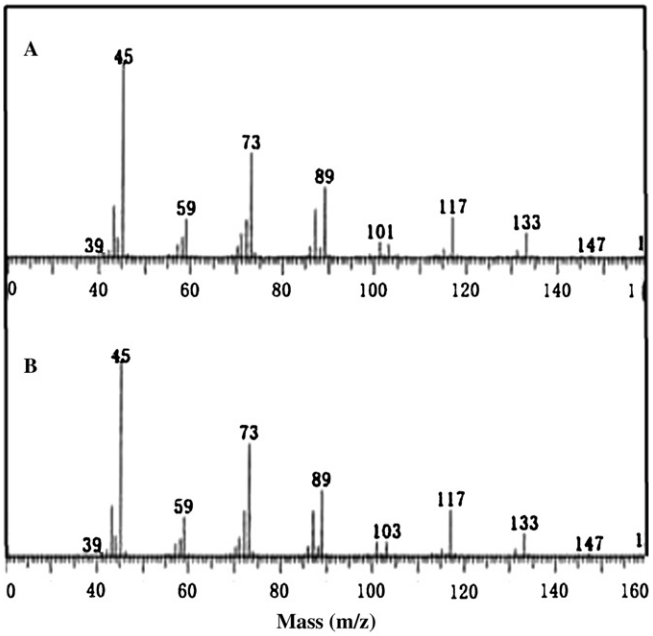


Fig. 14. Mass spectra of decomposed (A) Azo-PEO2000 and (B) C_{60}-(PEO2000)$_2$ gas shown in Fig. 13 at retention time 9.3 min.

Table 1
C_{60} content in C_{60}-PEO determined from TGA and molecular formula

	Measured by TGA (wt.%)	Calcd. (wt.%)
C_{60}-(PEO550)$_2$	30	35.4
C_{60}-(PEO550)$_4$	20	21.5
C_{60}-(PEO2000)$_2$	17	14.6

Based on the above results, it is concluded that the thermal stability of PEO is dramatically increased by grafting onto C_{60} fullerene.

Fig. 12 and Table 1 show further information on C_{60} fullerene content in PEO-grafted C_{60}, determined based on weight residue at 450 °C. At this temperature, Azo-PEO is fully decomposed, while C_{60} fullerene has not yet undergone much decomposition. C_{60} fullerene content in C_{60}-PEO can also be calculated based on formula weights. Table 1 shows that the C_{60} fullerene content determined from TGA was in agreement with that calculated from the molecular formula of PEO-grafted C_{60} fullerene.

4. Conclusions

1. PEO550 radicals formed by thermal decomposition of Azo-PEO550 were successfully trapped by C_{60} fullerene to give two types of PEO550-grafted C_{60} fullerene, a bis-adduct C_{60}-(PEO550)$_2$ and a tetrakis-adduct C_{60}-(PEO550)$_4$.
2. PEO2000 radicals formed by thermal decomposition of Azo-PEO2000 were also successfully trapped by C_{60} fullerene to give PEO2000-grafted C_{60} fullerene, bis-adduct C_{60}-(PEO550)$_2$ only.
3. The structure of the bis-adducts (C_{60}-(PEO550)$_2$ and C_{60}-(PEO2000)$_2$) was concluded to be 1,4-type.
4. The solubility of C_{60} fullerene in water, THF, methanol, and other conventional organic solvents was remarkably improved by grafting of PEO.
5. The thermal stability of PEO was dramatically increased by grafting onto C_{60} fullerene.

References

[1] Martin N, Sanchez L, Illescas B, Perez I. Chem Rev 1998;98:2527–47.
[2] Tumanskii B, Kalina O. Radical reactions of fullerene and their derivatives. Dordrecht: Kluwer Academic Publishers; 2001 [chapters 1, 2, and 7].
[3] Tokuyama H, Yamago S, Nakamura E. J Am Chem Soc 1993;115: 7918–9.
[4] Guldi DM, Prato M. Acc Chem Res 2000;33:695–703.
[5] Hirsch A, Brettreich M. In: Weinheim, editor. Fullerenes: chemistry and reactions. 2nd ed. Weinheim: Wiley-VCH; 2005.
[6] Hebard AF, Rosseinsky MJ, Haddon RC, Murphy DW, Glarum SH, Palstra TTM, et al. Nature 1991;350:600–1.
[7] Allemand PM, Khemani KC, Koch A, Wudi F, Holczer K, Donovan S, et al. Science 1991;253:301–3.
[8] Murayama H, Tomonoh S, Alford JM, Karpuk ME. Fullerenes, Nanotubes, Carbon Nanostruct 2004;12:1–9.
[9] Ruoff RS, Tse DS, Malhotra R, Lorents DC. J Phys Chem 1992;97: 3379–83.

[10] (a) Hinokuma K, Ata M. Chem Phys Lett 2001;341:442−6; Bravec CJ, Sariciftci NS, Hummelen JC. Adv Funct Mater 2001;11(1):15−26;
(b) Cha M, Sariciftci NS, Heeger AJ, Hummelen JC, Wudl F. Appl Phys Lett 1995;67:3850−2.

[11] (a) Krusic PT, Wasserman E, Parkinson BA, Malone B, Holler Jr ER, Keizer PN, et al. J Am Chem Soc 1991;113:6274−5;
(b) Krusic PT, Wasserman E, Keizer PN, Morton JR, Preston KF. Science 1991;254:1183.

[12] Gan L, Huang S, Zhang X, Zhang A, Cheng B, Cheng H, et al. J Am Chem Soc 2002;124:13384−5.

[13] Ford WT, Nishioka T, Qiu F, D'Souza F, Choi J, Kutner W, et al. J Org Chem 1999;64:6257−62.

[14] (a) Cao Ti, Webber SE. Macromolecules 1995;28:3741−3;
(b) Sun YP, Lawson GE, Bunker CE, Johnson RA, Ma B, Farmer C, et al. Macromolecules 1996;29:8441−8.

[15] Ford WT, Graham TD, Mourey TH. Macromolecules 1997;30:6422−9.

[16] Okamura H, Terauchi T, Minoda M, Fukuda T, Komatsu K. Macromolecules 1997;30:5279−84.

[17] (a) Zhou P, Chen GQ, Hong H, Du FS, Li ZC, Li FM. Macromolecules 2000;33:1948−54;
(b) Audouin F, Nuffer R, Mathis C. J Polym Sci Part A Polym Chem 2004;42:3456−63.

[18] Tsubokawa N. Polym J 2005;37:637−55.

[19] Tsubokawa N, Yanadori K. Kobunshi Ronbunshu 1992;49:865−70.

[20] Ederlé Y, Mathis C, Nuffer R. Synth Met 1997;2287−8.

[21] Manolova N, Rashkov I, Beguin F, Damme HV. J Chem Soc Chem Commun 1993;34:1725−7.

[22] Ueda A, Nagai S. J Polym Sci Part A Polym Chem 1987;25:3495−8.

[23] Schick G, Kampe KD, Hirsch A. J Chem Commun 1995;2023−4.

[24] D'Souza F, Caron C, Subramamian R, Kutner W, Jones MT, Kadisd KM. Recent advances in the chemistry and physics of fullerenes and related materials. Pennington, NJ: The Electrochemical Society; 1994. p. 768−78.

[25] Troitskii BB, Troitskaya LS, Yakhnov AS, Lopatin MA, Novikova MA. Eur Polym J 1997;33:1587.

[26] Troitskii BB, Troitskaya LS, Dmitriev AA, Yakhnov AS. Eur Polym J 2000;36:1073−84.

[27] Zuev VV, Bertini F, Audisio G. Polym Degrad Stab 2005;90:28−33.

[28] Chen Y, Huang Z, Cai RF. J Polym Sci Part B Polym Phys 1996;34:631−40.