REGULAR ARTICLE

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A Simple Preparation of C_{60}-Poly(ethylene glycol) Gel and its Properties

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Poly(ethylene glycol) (PEG) biradicals formed by thermal decomposition of macroazo-initiator, $(Azo\text{-}PEG)_n$, which were prepared by the polycondensation of 4,4′-azobis(4-cyanopentanoyl chloride) with PEG, were successfully trapped by C_{60} fullerene to give C_{60}-PEG gel containing C_{60} fullerene at cross-linked point. It was found that when the feed ratio (PEG/C_{60}) was less than 3, PEG-grafted C_{60} fullerene was formed, but the gelation does not proceed. On the contrary, when the feed ratio exceeded 4, the gelation of PEG successfully proceeded. In the case of the feed ratio is 4, the gel fraction was about 80%, and it was gradually decreased with an increase in the feed ratio. The gel fraction increased with increasing reaction temperature and reached to 80% at 80 °C. It is concluded that the reaction conditions to give highest gel fraction is summarized as follows: the feed molar ratio, 5 (mol/mol); concentration of C_{60}, 3.5 mmol/L; 70 °C; 24 h. The thermal stability of C_{60}-PEG gel was dramatically increased in comparison with that of $(Azo\text{-}PEG)_n$. C_{60}-PEG gel was swelled in solvents, such as water, methanol, and THF and degree of swelling was about 5.1 to 7.8. Breaking strength decreased with increasing the feed molar ratio.

KEY WORDS: C_{60} Fullerene / Poly(ethylene glycol) / Macroazo-initiator / Gelation / Radical Trapping / Biradical / C_{60}-PEG Gel /

After 1990, the fundamental physical properties of fullerenes were extensively investigated, and a variety of interesting properties, such as ability to accept and release electrons,[1] ability to trap free radicals,[2] physiological activity,[3] photo activity,[4] biocompatibility, and relatively high chemical reactivity that allows structural modification,[5] have been reported. The derivatives of C_{60} fullerene have also interesting properties. For example, K_3C_{60} has superconductivity at 18 K,[6] and TDAE-C_{60} [TDAE: *tetrakis*-(dimethylamino) ethylene] has ferromagnetism.[7]

On the other hand, C_{60} fullerene is known as "radical scavenger" because of its strong ability to trap free radicals as well as other nanocarbon materials, such as multi-walled carbon nanotubes (MW-CNT), cup-stacked carbon nanotubes (CS-CNT), and carbon blacks (CB). We have reported that polymer radicals formed by the thermal decomposition of macroazo-initiator, Azo-polymer, were readily trapped by these nanocarbon surfaces to give the corresponding polymer-grafted MW-CNT,[8] CS-CNT,[8] and CB.[9]

In addition, we have also reported that poly(ethylene glycol) (PEG) radicals formed by the thermal decomposition of macroazo-initiator, Azo-$(PEG)_2$, which was prepared by the reaction of 4,4′-azobis(4-cyanopentanoyl chloride) (ACPC) with poly(ethylene glycol) methyl ether, were successfully trapped by C_{60} fullerene surface to give PEG-grafted C_{60} *bis*-adduct, C_{60}-$(PEG)_2$, and *tetrakis*-adduct, C_{60}-$(PEG)_4$, as shown in Scheme 1:[10] when Azo-$(PEG)_2$ with low molecular weight was reacted with C_{60} fullerene, C_{60}-$(PEG)_2$, and C_{60}-$(PEG)_4$, were formed, but only *bis*-adduct was formed and no formation of *tetrakis*-adduct was observed, when Azo-$(PEG)_2$ with higher molecular weight was reacted.

On the other hand, it has been reported that macroazo-initiator, $(Azo\text{-}PEG)_n$, was prepared by the polycondensation of ACPC with PEG. Therefore, the formation of C_{60}-PEG gel, which have C_{60} fullerene at cross-linked point was expected by the reaction of C_{60} fullerene with $(Azo\text{-}PEG)_n$, because C_{60} fullerene traps PEG biradicals formed by the thermal decomposition of $(Azo\text{-}PEG)_n$ as shown in Scheme 2 (1) and/or the grafted chains of Azo-$(PEG)_x$ ($x < n$) on C_{60} fullerene produces terminal radicals, which react with other C_{60} fullerene as shown in Scheme 2 (2) to give C_{60}-PEG gel having C_{60} fullerene at cross-linked point.

In this present paper, we report a novel and simple preparation of C_{60}-PEG gel by the reaction of C_{60} fullerene with $(Azo\text{-}PEG)_n$. The properties of C_{60}-PEG gel having C_{60} fullerene at cross-linked point will be discussed.

EXPERIMENTAL

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 >99.5% and 30–70 μm, respectively. The **C_{60}** fullerene was dried *in vacuo* at 50 °C before use.

Macroazo-initiator, $(Azo\text{-}PEG)_n$, was commercially obtained from Wako Pure Chemical Ind. Co., Ltd., Japan (commercially name of the $(Azo\text{-}PEG)_n$ was VPE-0401). Molecular weight of PEG unit was 4.0×10^3 and it contains several azo groups, which can form polymer radical.

Toluene was refluxed over sodium and distilled. Tetrahydrofuran (THF) used for extraction from the reaction

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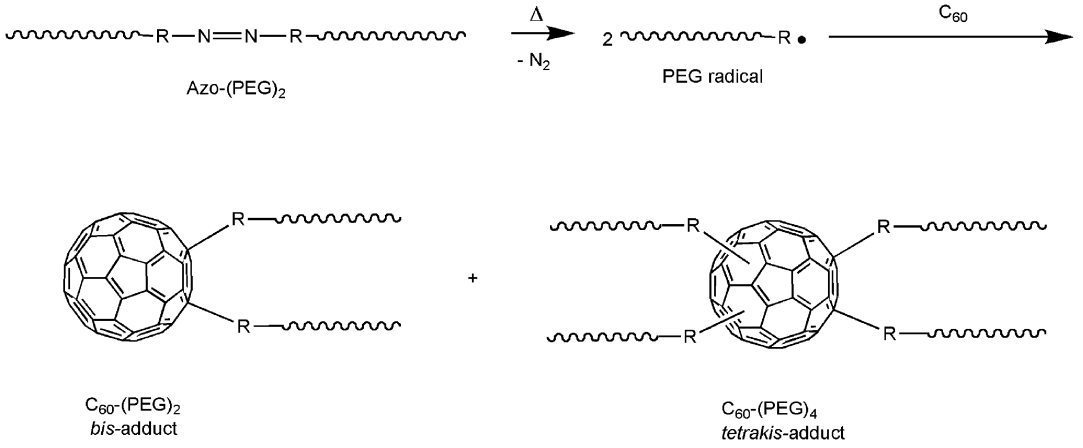
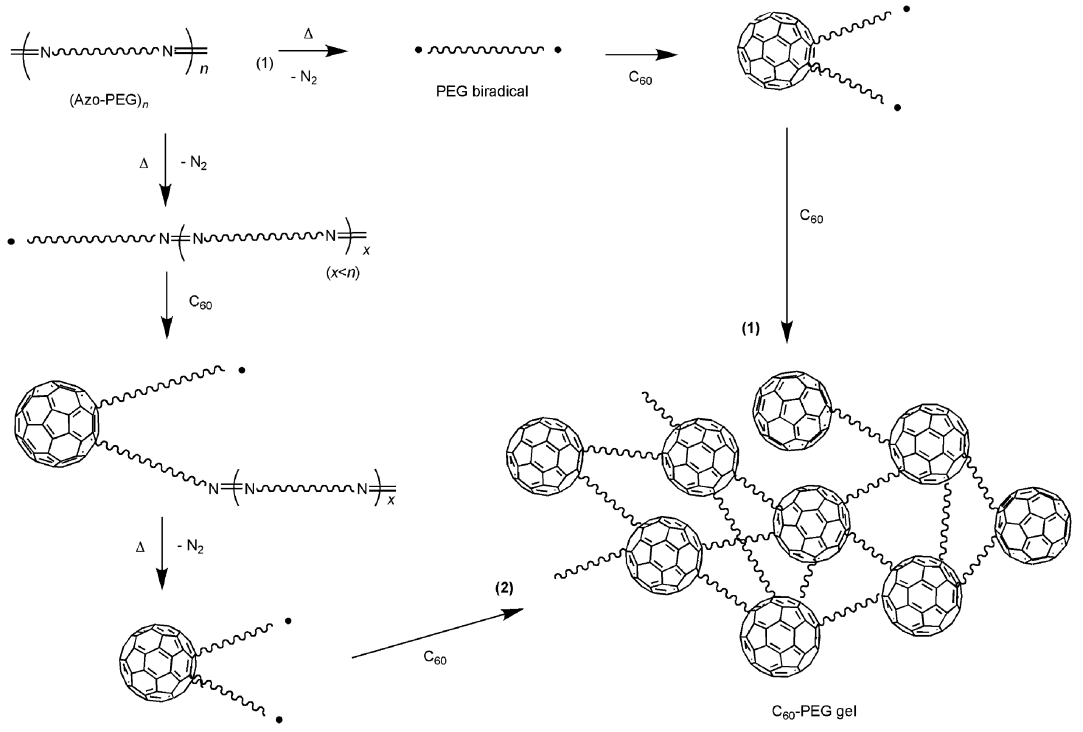


Scheme 1. Grafting of PEG onto C_{60} fullerene by the reaction with Azo-$(PEG)_2$.



Scheme 2. Preparation of C_{60}-PEG gel by reaction of $(Azo\text{-}PEG)_n$ with C_{60} fullerene.

products was used without further purification. Ion-exchange water, methanol, THF, *n*-hexane used for compression test and swelling test were used without further purification.

Preparation of C_{60}-PEG Gel

A typical experiment is as follows: 5.0×10^{-2} g (6.9×10^{-5} mol) of C_{60} fullerene, 1.4 g (PEG unit 3.5×10^{-4} mol) of $(Azo\text{-}PEG)_n$, and 20.0 mL of toluene were placed in a glass tube, degassed with several freeze-thaw cycles, and sealed off under high vacuum. The sealed tube was heated with stirring. The reaction conditions, reaction temperature, the molar ratio of C_{60} to $(Azo\text{-}PEG)_n$ in the feed, reaction time, were changed to investigate the effect of reaction condition on the gelation.

After the reaction, toluene was removed from the reaction mixture by use of a centrifugal evaporator. Then, the reaction product was extracted with THF (non-solvent for C_{60} fullerene but good solvent for PEG) using a Soxhlet extractor for 48 h. After the extraction, soluble part was obtained by evaporation of THF under reduced pressure. On the other hand, insoluble part was dried under 50 °C. Gel fraction (%) of C_{60}-PEG gel was calculated by the following equation:

$$\text{Gel fraction (\%)} = (A/B) \times 100$$

where A is insoluble part (C_{60} gel) after Soxhlet extraction (g), B is total quantities of reactants in the feed.

Measurement of Degree of Swelling of C_{60}-PEG Gel

Dried C_{60}-PEG gels used for the measurement of degree of swelling were prepared by following conditions: C_{60}, 5.0×10^{-2} g (6.9×10^{-5} mol); (Azo-PEG)*n*, 1.7 g (4.1×10^{-4} mol); toluene, 20 mL; 70 °C; 24 h. Each dried C_{60}-PEG gels were placed into five sampling bottles. Ion-exchange water, methanol, THF, *n*-hexane were poured into the each five bottles, respectively. The C_{60}-PEG gels were swelled at ambient temperature, under normal pressure for 24 h. The degree of swelling of C_{60}-PEG gels was calculated by the following equation:

$$\text{Degree of swelling} = (C - D)/D$$

where C is swelled C_{60}-PEG gel (g), D is dried C_{60}-PEG gel (g).

Mechanical Strength of C_{60}-PEG Gel

Dried C_{60}-PEG gel was swelled in ion-exchange water at ambient temperature, under normal pressure for 24 h. The swelled C_{60}-PEG gel was used as the sample. Mechanical strength of the swelled gel was evaluated from compression test. The mechanical strength of C_{60}-PEG gel was measured with a digital push-pull gauge (Aikoh Engineering Co., Ltd. Model-RX).

Measurements

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

RESULTS AND DISCUSSION

Effects of Reaction Conditions on the Formation of C_{60}-PEG Gel

The reaction of C_{60} fullerene with (Azo-PEG)$_n$ under various conditions was investigated. Figure 1 shows the effect of feed molar ratio of PEG unit of (Azo-PEG)$_n$ to C_{60} fullerene on gel fraction of C_{60}-PEG gel. The molar ratio of PEG unit to C_{60} fullerene (PEG/C_{60}) was changed from 1 to 10. As shown in Figure 1, PEG-grafted C_{60} was formed but the gelation does not proceed under the condition that the feed ratio (PEG/C_{60}) was less than 3. PEG-grafted C_{60} was soluble in good solvents of PEG such as THF, water, and methanol. According to the observation using UV-vis spectra, size exclusion chromatograph, it was expected that the structure of PEG-grafted C_{60} was *bis*-adduct, C_{60}-$(PEG)_2$.[10]

When the feed ratio (PEG/C_{60}) exceeded 4, the gelation of PEG successfully proceeded (the gel fraction was about 80%). It was confirmed that the gel contains no undecomposed azo groups by DSC.

On the contrary, the gel fraction gradually decreased with an increase in the feed ratio. It was found that soluble part of the reaction product contains ungrafted PEG and PEG-grafted C_{60} fullerene (*tetrakis*-adduct and unknown adducts). These results indicate that when the feed ratio (PEG/C_{60}) increased, the gelation was inhibited by the acceleration of the grafting of PEG onto C_{60} fullerene and coupling reaction of PEG radicals.

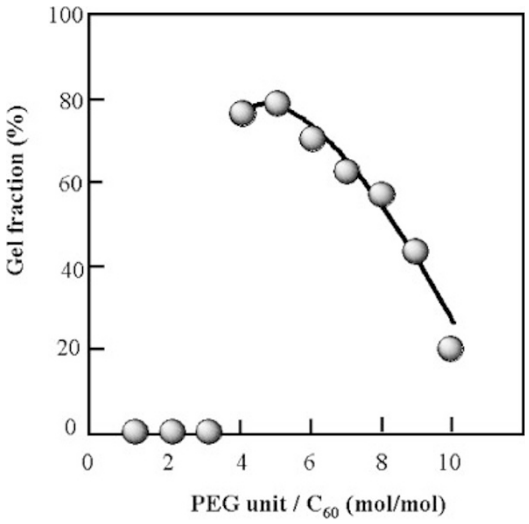


Figure 1. Effect of molar ratio of PEG unit of (Azo-PEG)$_n$ to C_{60} on gel fraction of C_{60}-PEG gel. C_{60}, 5.0×10^{-2} g (6.9×10^{-5} mol); (Azo-PEG)$_n$, 0.28 g (6.9×10^{-5} mol)–2.8 g (6.9×10^{-4} mol); toluene, 20 mL; 70 °C; 24 h.

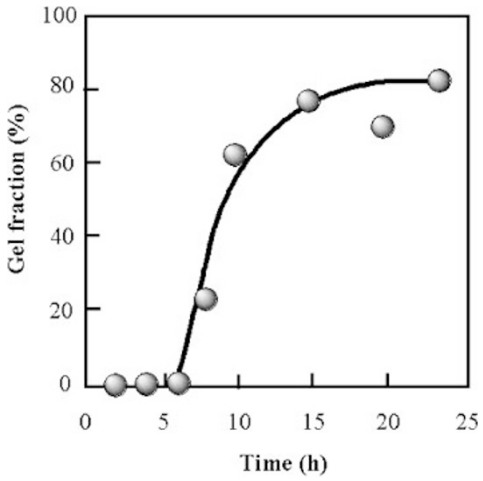


Figure 2. Relationship between reaction time and gel fraction of C_{60}-PEG gel. (Azo-PEG)$_n$/C_{60} = 3.5×10^{-4}/7.0×10^{-5}, 5 (mol/mol); toluene, 20 mL; 70 °C.

Figure 2 shows the relationship between reaction time and gel fraction of C_{60}-PEG gel. The gel fraction increased after 6 h and reached to 80% after 24 h. On the contrary, the grafting of PEG onto C_{60} was proceeded before 6 h.

Figure 3 shows the relationship between reaction temperature and gel fraction of C_{60}-PEG gel. When C_{60} fullerene was reacted with (Azo-PEG)$_n$ below 60 °C, no gelation was observed. The gel fraction increased with increasing reaction temperature and reached to 80% at 80 °C but decreased to 65% at 90 °C.

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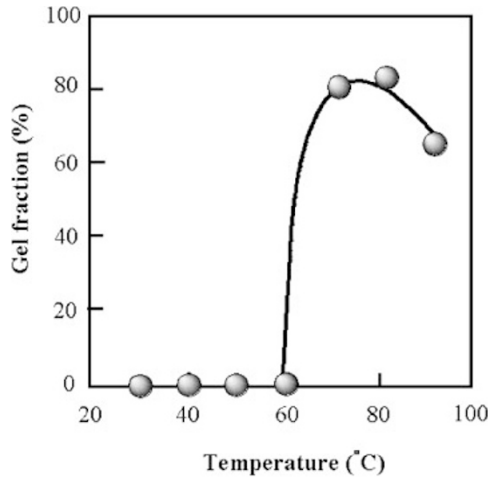


Figure 3. Relationship between reaction temperature and gel fraction of C_{60}-PEG gel. $(Azo\text{-}PEG)_n/C_{60} = 3.5 \times 10^{-4}/7.0 \times 10^{-5}$ (mol/mol); toluene, 20 mL; 24 h.

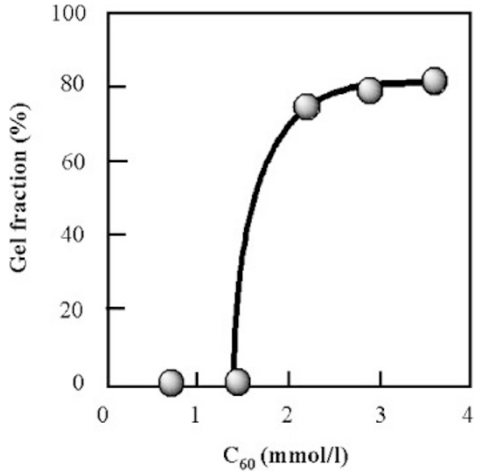


Figure 4. Effect of concentration on gel fraction of C_{60}-PEG gel. $(Azo\text{-}PEG)_n/C_{60} = 5$ (mol/mol); toluene, 20 mL; 70 °C, 24 h.

In addition, the color change of the reaction solution was carefully observed. Purple color of C_{60} fullerene solution below 40 °C and dark brown color of C_{60}-PEG solution below 60 °C were observed. We have reported that no grafting of $(Azo\text{-}PEG)_n$ onto carbon black proceeded below 40 °C, but above 60 °C, because the decomposition of $(Azo\text{-}PEG)_n$ hardly proceeded.[9] Therefore, the results show that the reaction of $(Azo\text{-}PEG)_n$ with C_{60} was scarcely proceeded below 40 °C, because of no formation of PEG radicals. Only the grafting of PEG onto C_{60} produced between 40 °C and 60 °C.

Although a rate of generation of PEG radicals was more increased above 80 °C, the cross-linking reaction was inhibited by the acceleration of the grafting of PEG onto C_{60} fullerene and coupling reaction of PEG radicals: the soluble part of the reaction product also contains ungrafted PEG and PEG-grafted C_{60} fullerene (*tetrakis*-adduct and unknown adducts).

Figure 4 shows the effect of concentration of reactants on gel fraction of C_{60}-PEG gel. The feed concentration of reactants was changed with keeping constant molar ratio of $(Azo\text{-}PEG)_n/C_{60} = 5$ (mol/mol). As shown in Figure 4, the formation of gel was observed above the molar ratio 1.4 mmol/L of C_{60} and reached to 80% at 3.5 mmol/L. When the molar ratio was less than 1.4 mmol/L, the reaction product contains ungrafted PEG and unreacted C_{60} fullerene, and the formation of PEG-grafted C_{60} fullerene was scarcely observed. Therefore, it is concluded that when the concentration of C_{60} was less than 1.4 mmol/L, most of PEG biradicals were deactivated before trapping by C_{60} fullerene.

Based on the above results, it is concluded that the formation of C_{60}-PEG gel to give highest gel fraction is summarized as follows: the feed molar ratio (PEG/C_{60}), 5 (mol/mol); concentration of C_{60}, 3.5 mmol/L; reaction temperature, 70 °C; reaction time, 24 h.

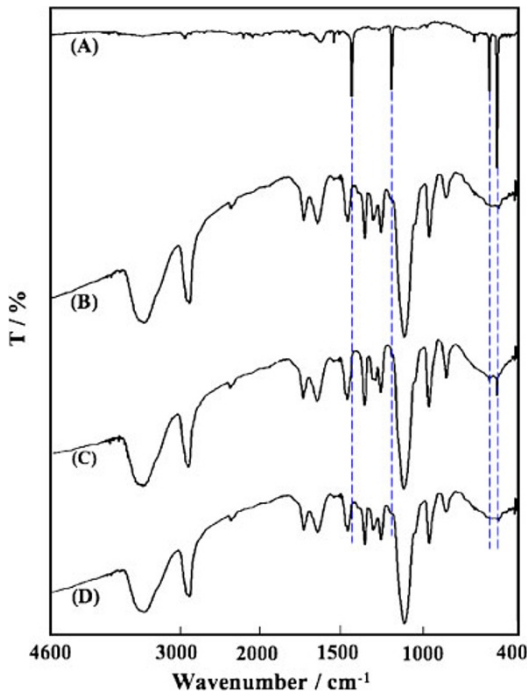
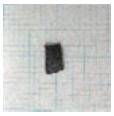


Figure 5. FT/IR spectra of (A) untreated C_{60} fullerene, (B) $(Azo\text{-}PEG)_n$, (C) mixture of C_{60} fullerene and $(Azo\text{-}PEG)_n$, and (D) dry C_{60}-PEG gel.

Characterization of C_{60}-PEG Gel

Figure 5 shows FT/IR spectra of (A) untreated C_{60} fullerene, (B) $(Azo\text{-}PEG)_n$, (C) mixture of C_{60} fullerene and $(Azo\text{-}PEG)_n$, and (D) dry C_{60}-PEG gel. The spectrum of (D) dry C_{60}-PEG gel showed characteristic absorptions of PEG at 2925 and 1110 cm^{-1}, which is characteristic of $-CH_2-$ and -O-, respectively. Although the spectrum of (A) untreated C_{60} fullerene showed four characteristic absorptions at 528, 577, 1183 and 1429 cm^{-1}, these signals disappeared completely after the reaction with $(Azo\text{-}PEG)_n$. The spectrum of (D) dry C_{60}-PEG gel was almost the same as that of (B) $(Azo\text{-}PEG)_n$. On the contrary, the spectra of (C) the mixture of C_{60} fullerene (10 wt %) and $(Azo\text{-}PEG)_n$ showed characteristic absorptions of PEG and C_{60} fullerene.

Table I. Photographs of C_{60}-PEG gels and degree of swelling

Solvents	Dry gels	Swelled gels	Degree of swelling
Water			5.7
Methanol			4.1
THF			4.2
n-Hexane			0

Preparation condition of the dry C_{60}-PEG gel: C_{60}, 5.0×10^{-2} g (6.9×10^{-5} mol); $(Azo\text{-}PEG)_n$, 2.50 g (5.6×10^{-4} mol); toluene, 20 mL; 70 °C; 24 h.

Chen and his co-workers reported that FT/IR spectra of poly(bromostyrene)-grafted[11] and polystyrene-grafted[12] C_{60} fullerene were in agreement with those of poly(bromostyrene) and polystyrene, respectively.

Based on the results, it is concluded that PEG biradicals were trapped by C_{60} fullerene to give C_{60}-PEG gel having C_{60} fullerene at cross-linked point.

Swelling of C_{60}-PEG Gel

The photographs of swelled C_{60}-PEG gel with various solvents and degree of swelling of C_{60}-PEG gels were summarized in Table I. C_{60}-PEG gel was swelled in good solvents, such as water, methanol, and THF and degree of swelling of the gels was about 5.1 to 7.8%. In contrast, the gel was not swelled in poor solvent, *n*-hexane. Theses results indicate that C_{60} fullerene trapped PEG biradicals and incorporated into PEG network to give C_{60}-PEG gel.

Compression Property of C_{60}-PEG Gel

Figure 6 shows relationship between feed molar ratio (PEG/C_{60}) and breaking strength (solid line) and degree of swelling of C_{60}-PEG gels (broken line). Breaking strength decreased with increasing feed molar ratio. On the other hand, the degree of swelling increased with increasing the feed ratio. These results suggest that cross-linked density of C_{60}-PEG gel decreased with increasing the feed molar ratio.

Thermal Stability of C_{60}-PEG

Figure 7 shows TGA curves of (A) $(Azo\text{-}PEG)_n$ and (B) dry C_{60}-PEG gel. Thermal stability was compared by the temperature at 10 wt % weight loss measured by TGA. The temperatures of dry C_{60}-PEG gel and PEG were determined to be 359 °C and 220 °C, respectively. It was found that the thermal stability of dry C_{60}-PEG gel was dramatically increased in comparison with that of PEG.

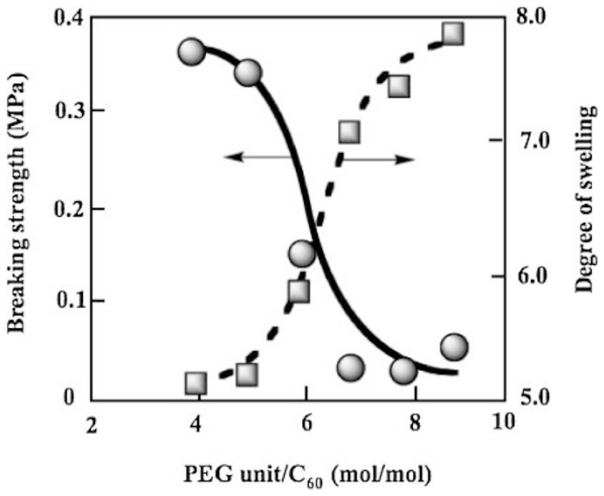


Figure 6. Dependence of feed molar ratio (PEG unit/C_{60}) on breaking strength (solid line) and degree of swelling of C_{60}-PEG gels (broken line). Swelling conditions: in ion-exchange water for 24 h at ambient temperature under normal pressure.

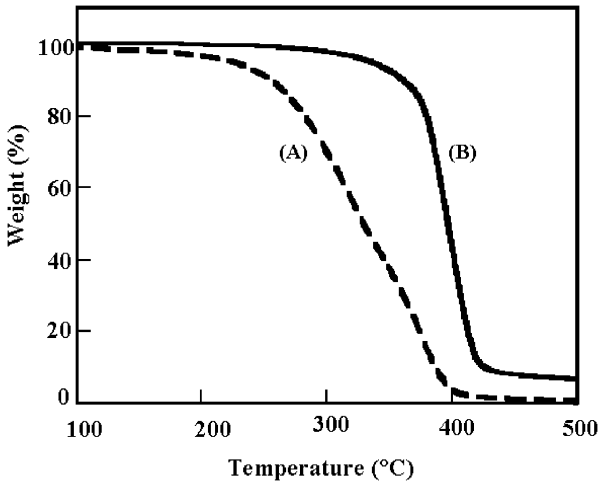


Figure 7. TGA curves of (A) $(Azo\text{-}PEG)_n$ and (B) dry C_{60}-PEG gel. C_{60}-PEG gel: C_{60}, 5.0×10^{-2} g (6.9×10^{-5} mol); $(Azo\text{-}PEG)_n$, 1.4 g (3.5×10^{-4} mol); toluene, 20 mL; 70 °C; 24 h.

It is well known that C_{60} fullerene retard and inhibit the thermal decomposition of poly(methyl methacrylate),[13] polystyrene,[14] acrylic polymers,[15] and poly(*N*-vinylcarbazole).[16] We have also reported that C_{60} fullerene retard and inhibit the thermal decomposition of PEG.[10] As mentioned in our previous paper, it is assumed that this is due to the ability of C_{60} fullerene to trap active small radical species formed by initial thermal decomposition of PEG.

The effect of molecular weight of PEG unit in $(Azo\text{-}PEG)_n$ on the gelation reaction and properties of C_{60}-PEG gel is now under investigation.

CONCLUSIONS

1. PEG biradicals formed by thermal decomposition of $(Azo\text{-}PEG)_n$ were successfully trapped by C_{60} to give C_{60}-PEG gel having C_{60} fullerene at cross-linked point.

2. When the feed ratio (PEG/C_{60}) was less than 3, PEG-grafted C_{60} fullerene was formed, but the gelation does not proceed. On the contrary, when the feed ratio exceeded 4, the gelation of PEG successfully proceeded.
3. It is concluded that the formation of C_{60}-PEG gel to give highest gel fraction is summarized as follows: the feed molar ratio, 5 (mol/mol); concentration of C_{60}, 3.5 mmol/L; 70 °C; 24 h.
4. C_{60}-PEG gel was swelled in good solvents, such as water, methanol, and THF, but the gel was not swelled in poor solvent, *n*-hexane.
5. Breaking strength of C_{60}-PEG gel was decreased with increasing the feed ratio (PEG/C_{60}).
6. The thermal stability of C_{60}-PEG gel was dramatically increased in comparison with that of $(\text{Azo-PEG})_n$.

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