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Synthesis of Novel C_{60}-containing Polymers Based on Poly(vinyl phenol) and Their Photo-transformation Properties

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Summary

Nitroxide-terminated poly(*p*-*tert*-butoxystyrene), poly(*p*-acetoxystyrene), and poly(*p*-*tert*-butoxycarbonyloxystyrene) were synthesized by a 'living' radical polymerization technique. C_{60}-bearing polymers were obtained by the reaction of C_{60} with nitroxide-terminated polymers. Transformation of the precursor polymers into C_{60}-bearing poly(vinyl phenol) was carried out by UV (254 nm) irradiation of the films of the C_{60}-bearing precursor polymers in the presence of a photoacid generator and followed by post-exposure baking. The transformation was confirmed by the appearance of O-H stretching in IR spectra. C_{60}-bearing poly(vinyl phenol) showed the some solubility in solvents as observed for poly(vinyl phenol).

Introduction

Much attention has been paid to C_{60}, one of fullerene family, because of its potential applicability to advanced materials [1,2]. To apply C_{60} to new functional materials, polymer-bound C_{60} derivatives are the potential candidates in terms of solubility, tractability, and processibility [3,4]. However, there are a few reports concerned as photoreactive C_{60} polymer derivatives [5-8].

Photoreactive C_{60} derivatives have two categories in brief. Firstly, C_{60} works as a photoreactive site itself. Optical limiting property [5,6] and photoconductivity [7] were reported. Another type is that C_{60} derivatives have other photoreactive sites in addition to a C_{60} moiety. In this case, a C_{60}-porphyrin dyad [9] and photosensitized properties of C_{60} for polymers bearing furan moiety [10] are included. In the former one, C_{60} works as an electron accepter and porphyrin works as an electron donor during photoirradiation. In the latter, oxidation of furan moiety proceeded by singlet oxygen generated by sensitization by a C_{60} moiety [11]. Our research concerns the photo-transformation of polymers bearing C_{60}. The development of photosensitive polymer systems is one of the most interesting topics in the field of photolithography. Photolithography technique enables us to produce micron-order devices using C_{60}. When we use C_{60} derivatives as functional devices, it is preferable to choose positive type images to prevent the damage of a C_{60} moiety by UV irradiation.

Our research topic in this paper is the synthesis of photo-transformable polymers having a C_{60} moiety with well-defined structure. In this work, we prepared C_{60}-bearing poly(*p-tert*-butoxystyrene) (C_{60}-PBOS), poly(*p*-acetoxystyrene) (C_{60}-PAOS) and poly(*p-tert*-butoxycarbonyloxystyrene) (C_{60}-PBCOS), which are precursors of C_{60}-bearing poly(vinyl phenol) (C_{60}-PVP). Addition of two polymer chains to a C_{60} molecule can be easily achieved by the reaction of nitroxide-terminated polymers [12,13] prepared by a living radical polymerization technique. This technique is useful to prepare the polymers with accurate control over molecular weight distribution, chain ends, and polymer architecture [14,15]. The possibility for the photo-transformation of the C_{60}-bearing precursor polymers to C_{60}-PVP was investigated. The effect of a C_{60} moiety on the photo-transformation was also discussed.

Experimental

Measurements

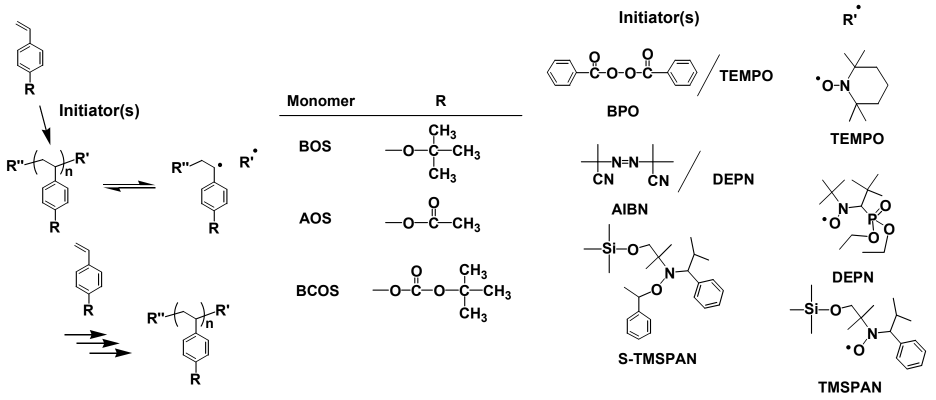
^{1}H NMR spectra were observed at 400 MHz using a JEOL LA-400 or at 270 MHz using a JEOL GX-270 spectrometer. UV-vis spectra were obtained with a Shimadzu UV-2400 PC. FT-IR measurements were carried out using a JASCO IR-410. Glass Transition temperature was investigated with a Rigaku TAS 100 differential scanning calorimeter (DSC) under nitrogen flow. Heating rate was 10 ^{o}C/min. Size exclusion chromatography (SEC) was carried out in tetrahydrofuran (THF) on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex GMNHR-$_H$ + GMNHR-$_N$; 8.0 mm i.d. x 30 cm each) and a differential refractometer JASCO RI1530. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated on the basis of a polystyrene calibration.

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. *o*-Dichlorobenzene (Wako Chemicals), *p*-acetoxystyrene (AOS; Aldrich), and *p-tert*-butoxystyrene (BOS; Wako Chemicals, Japan) were distilled from CaH_2. Benzoyl peroxide (BPO; Nacalai Tesque, Japan) and 2,2'-azobisisobutyronitrile (AIBN; Nacalai Tesque, Japan) were purified by recrystallization from ethanol. 2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO) (Aldrich) and triphenylsulfonium triflate (TPST; Midori Kagaku, Japan) were used as received. *p-tert*-Butoxycarbonyloxystyrene [16] (BCOS), *N-tert*-butyl *N*-(1-diethylphosphono-2,2-dimethyl)propyl nitroxyl (DEPN) [17,18], and 1-trimethylsiloxy-2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (S-TMSTPAN) [18] were prepared according to the literature method.

Polymerization (Scheme 1)

Polymerization of BOS, AOS and BOCS was carried out as described previously [19,20]. Polymerization conditions and characteristics of the polymers are summarized in Table 1. In brief, a mixture of BOS (5.5 g, 31 mmol), BPO (72 mg, 0.30 mmol), and TEMPO (48 mg, 0.31 mmol) was 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 9 h to yield a polymer. The polymer was recovered by pouring the reaction mixture into a large excess of methanol. The polymer was purified by reprecipitation with a chloroform/methanol system, and thoroughly dried (conversion: 28%). The obtained polymer had a number-average molecular weight M_n of 8800 and M_w/M_n ratio of 1.10.



Scheme 1. Polymerization of BOS, AOS and BCOS

C_{60}-polymer derivatives (Scheme 2)

The radical addition of nitroxide-terminated polymers to C_{60} was carried as described in the previous papers [12,13]. Reaction conditions are summarized in Table 2. For example, synthesis of C_{60}-PBOS was as follows. Nitroxide-terminated PBOS (M_n = 8800, 308 mg, 0.035 mmol) and C_{60} (100 mg, 0.139 mmol) were dissolved in *o*-dichlorobenzene (4 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 to yield products. The crude products mainly contain C_{60}-PBOS, unreacted PBOS and C_{60}. In determining yield and molecular weight distribution, the reaction mixture was dissolved in THF and insoluble C_{60} was precipitated. The THF solution was concentrated and a four-fold volume of methanol was added dropwise to the solution. Then, C_{60}-PBOS was gradually precipitated. The precipitate was carefully collected by centrifugation, and dried. The supernatant obtained by centrifugation contained only PBOS derivatives.

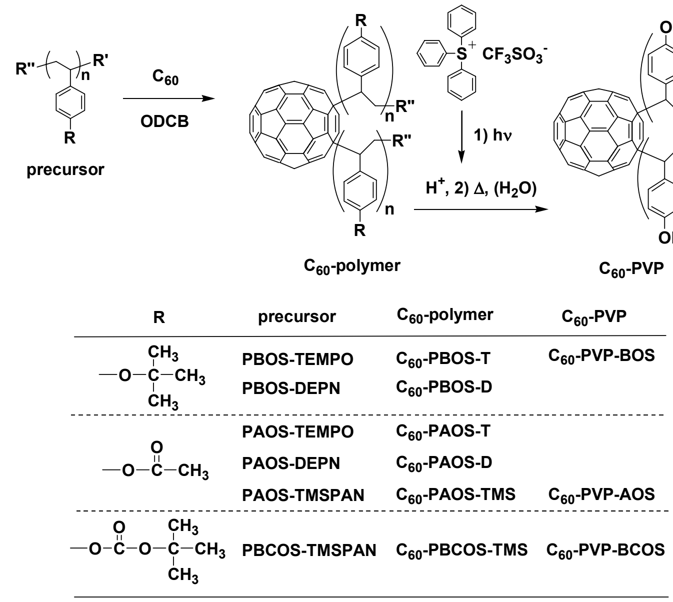
Photoirradiation

All sample films were prepared on silicon wafers by spin-casting from solutions of 2-butanone containing sample polymer and TPST. The sample films were dried on a hot plate at 90 °C for 2 min. The thickness of films was about 0.5 μm except for the sample films for the FT-IR measurements (1.0 μm). Irradiation was performed at 254 nm in air or under nitrogen atmosphere using a low-pressure mercury lamp (Ushio ULO-6DQ, 6 W) without a filter for the sample containing PBOS and PBCOS. The sample containing PAOS was irradiated by using medium-pressure mercury lamp (Ushio UM-102, 100 W) without a filter. The intensity of the light was measured with an Orc Light Measure UV-M02. Post-exposure-bake (PEB) treatments were carried out at 120 °C for 1 min on a conventional hot plate. Insoluble fraction was determined by comparing the film thickness before and after developments in methanol or THF

Table 1. Polymerization conditions and characteristics of polymers

polymer	monomer $\times10^2$ (mol)	nitroxide derivative $\times10^4$ (mol)	AIBN $\times10^4$ (mol)	BPO $\times10^4$ (mol)	toluene (mL)	polym. temp. (°C)	polym. time (h)	conv. (%)	$M_n \times10^{-3}$ [a]	M_w/M_n [a]
PBOS-TEMPO	3.1[b]	3.1[e]		3.0		125	9	28	8.8	1.10
PBOS-DEPN	1.6[b]	3.4[f]	1.4			125	2	13	6.0	1.13
PBOS	1.7[b]		1.8		1.7	60	5	27	75.4	1.81
PAOS-TEMPO	3.9[c]	3.1[e]		3.0		125	3	17	4.0	1.19
PAOS-DEPN	1.4[c]	2.3[f]	1.0			125	2	38	9.0	1.22
PAOS-TMSPAN	1.3[c]	2.3[g]				125	1	71	6.9	1.32
PAOS	2.7[c]		2.7		4.9	55	6	30	87.6	1.65
PBCOS-TMSPAN	0.6[d]	1.5[g]				100	1	29	12.5	1.23

[a] Determined by SEC; [b] BOS; [c] AOS; [d] BCOS; [e] TEMPO; [f] DEPN; [g] S-TMSTPAN



R	precursor	C_{60}-polymer	C_{60}-PVP
$-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_3}$	PBOS-TEMPO PBOS-DEPN	C_{60}-PBOS-T C_{60}-PBOS-D	C_{60}-PVP-BOS
$-\mathrm{O}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{CH_3}$	PAOS-TEMPO PAOS-DEPN PAOS-TMSPAN	C_{60}-PAOS-T C_{60}-PAOS-D C_{60}-PAOS-TMS	C_{60}-PVP-AOS
$-\mathrm{O}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_3}$	PBCOS-TMSPAN	C_{60}-PBCOS-TMS	C_{60}-PVP-BCOS

Scheme 2. Preparation and transformation of C_{60}-polymer derivatives

Table 2. Reaction of nitroxide-terminated polymers with C_{60}[a]

code	precursor					product			
	molar ratio for C_{60}	reaction time (h)	reaction temp. (°C)	M_n[b] × 10^{-3}	M_w/M_n[b]	M_n[b] × 10^{-3}	M_w/M_n[b]	M_n× 10^{-3} by UV[c]	yield (%)[d]
PBOS-TEMPO	4.0	24	145	8.8	1.10	12.7	1.22	14.3	54
PBOS-DEPN	1.0	16	90	6.0	1.13	10.0[e]	1.36	11.8	33
PAOS-TEMPO	4.0	6	145	4.0	1.19	6.8	1.24	7.2	14
PAOS-DEPN	1.0	5	90	9.0	1.22	14.0[e]	1.28	18.2	38
PAOS-TMSPAN	1.0	6	145	6.9	1.32	11.3	1.39	11.1	25
PBCOS-TMSPAN	4.0	6	100	12.5	1.23	16.9	1.30	19.6	35

[a] In o-dichlorobenzene, $[C_{60}] = 3.5 \times 10^{-4}$ mol/L in all cases; [b] Determined by SEC calibrated by standard PSs; [c] Calculated based on the molar absorption coefficirent of C_{60}-$(BS)_2$ [12] of 5.01×10^3 $mol^{-1}\cdot L \cdot cm^{-1}$ at 440 nm; [d] 100 x (wt of polymer in C_{60}-polymer)/(wt of polymer); [e] Bimodal

for 5-10 min. Thickness of films was measured by interferometry (Nanometrics Nanospec M3000).

Results and discussion

Synthesis and characterization of nitroxide-terminated PBOS, PAOS, and PBCOS

PVP is a useful polymer in photolithography, especially for KrF resist because of film-forming ability, high etch resistance, and high solubility for aqueous alkali. C_{60}-containing PVP is considered be a potential candidate for the functional materials containing a C_{60} moiety. C_{60}-bisadduct was easily prepared by the radical addition of nitroxide-terminated polymer to C_{60}. We investigated the synthesis of nitroxide-terminated PBOS, PAOS, and PBOCS. These polymers can be transformed into PVP by the hydrolysis or thermal treatment. As nitroxide derivatives, we used DEPN [17,18] and 1-trimethylsiloxy-2,2,5-trimethyl-4-phenyl-3-azahexane 3-nitroxide (TMSPAN) [18] in addition to TEMPO. It was reported that the polymerization of styrene derivatives and acrylate monomer could be achieved with controlled molecular weight by using DEPN as a nitroxide [17]. Living radical polymerization of styrene, acrylate, acrylamide, and butadiene can be performed by using TMSPAN as a nitroxide [18].

The polymerization was carried out as described in Experimental section. S-TMSPAN was used as a unimolecular initiator. TEMPO/BPO system or DEPN/AIBN system were used as a two-component initiating system. In terms of the properties of the film, the molecular weight of the polymer was preferable to be ca. 20000. However, the content of a C_{60} moiety in C_{60}-polymer derivatives decreases with the increase of the molecular weight of precursor polymers. Thus, the molecular weight of precursor polymer was controlled to be 5000~10000. The conversion of the precursor polymer was less than ca. 50 % to prevent the decomposition of the terminal chain end. The polymerization conditions and characteristics of polymers are summarized in Table 1. The polymerization of BOS and AOS using nitroxide derivatives gave good results. For comparison, PBOS and PAOS were prepared by the conventional radical polymerization using AIBN as an initiator. In case of the polymerization of BCOS, the polymerization at 125 ^{o}C did not proceed well in using TEMPO and DEPN as nitroxide derivatives. The obtained samples were not soluble in $CHCl_3$, and FT-IR measurements of the samples revealed the broad peak at 3400 cm^{-1} due to phenolic O-H stretching. The result suggested the decomposition of *tert*-butoxycarbonyl group in PBCOS. In using S-TMSPAN as an initiator, polymerization of BCOS at 100 ^{o}C gave good results. The resultant polymer showed no decomposition of *tert*-butoxycarbonyl group, which were confirmed by ^{1}H NMR and FT-IR measurements.

Synthesis and characterization of C_{60}-bearing PBOS, PAOS, and PBCOS

The addition reaction of nitroxide-mediated polymers to C_{60} was carried out as previously reported [12]. The results are summarized in Table 2. The abbreviations of C_{60}-polymer derivatives are shown in Scheme 2. The yield and characteristics of C_{60}-polymer showed strong dependence on a starting material. In general, the yields in this work were lower than that for the reaction of PS-TEMPO with C_{60} (60-80%) [12]. This may be due to the steric hindrance of bulky functional groups in the side chain of the polymers. The addition reaction of DEPN-terminated PBOS and PAOS with C_{60} proceeded to generate C_{60}-PBOS-D or C_{60}-PAOS-D, however, the SEC traces of the products showed bimodal. The product was the mixture of the monoadduct and bisadduct as estimated by the value of peak top. It suggests that the radical addition of DEPN-terminated polystyrene derivatives to C_{60} did not proceed quantitatively. The produced polymer radical from DEPN-terminated polymer was the same as that from TEMPO-terminated polymer. As an intermediate, DEPN-C_{60}-polymer derivatives may be more stable than TEMPO-C_{60}-polymer derivatives. The results were not consistent with the stability of polymer-DEPN and polymer-TEMPO. On the other hand, PBOS-TEMPO, PAOS-TMSPAN, and PBCOS-TMSPAN gave good results. The values of M_n by SEC and those by UV [12] were in good agreement, and both values were close to those calculated for the bisaddcut structure. Figure 1 shows SEC traces of C_{60}-PBOS-T, C_{60}-PAOS-TMS and C_{60}-PBCOS-TMS recorded by different detectors, respectively. For comparison, precursor polymers, PBOS-TEMPO, PAOS-TMSPAN, and PBCOS-TMSPAN were also shown. The polymer is detectable by RI, but not by UV-440 nm, while the C_{60}-bearing polymer is detectable by both UV-440 nm and RI. The two SEC curves of C_{60}-polymer 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 about twice larger than that of the precursor polymers. This indicates that the reaction of PAOS-TMSPAN and PBCOS-TMSPAN with C_{60} leads predominantly to a bisadduct, as observed in the case of PS-TEMPO [12]. M_n value of C_{60}-PBOS-T is slightly lower than twice of that of PBOS-TEMPO. This may be due to the existence of monoadduct. UV-vis spectroscopy of C_{60}-PBOS-T and C_{60}-PBCOS-TMS indicated the formation of 1,4-disubstituted dihydrofullerene derivatives [12]. Therefore, the photo-transformation of C_{60}-polymer to C_{60}-PVP was carried out using C_{60}-PBOS-T, C_{60}-PAOS-TMS, and C_{60}-PBCOS-TMS.

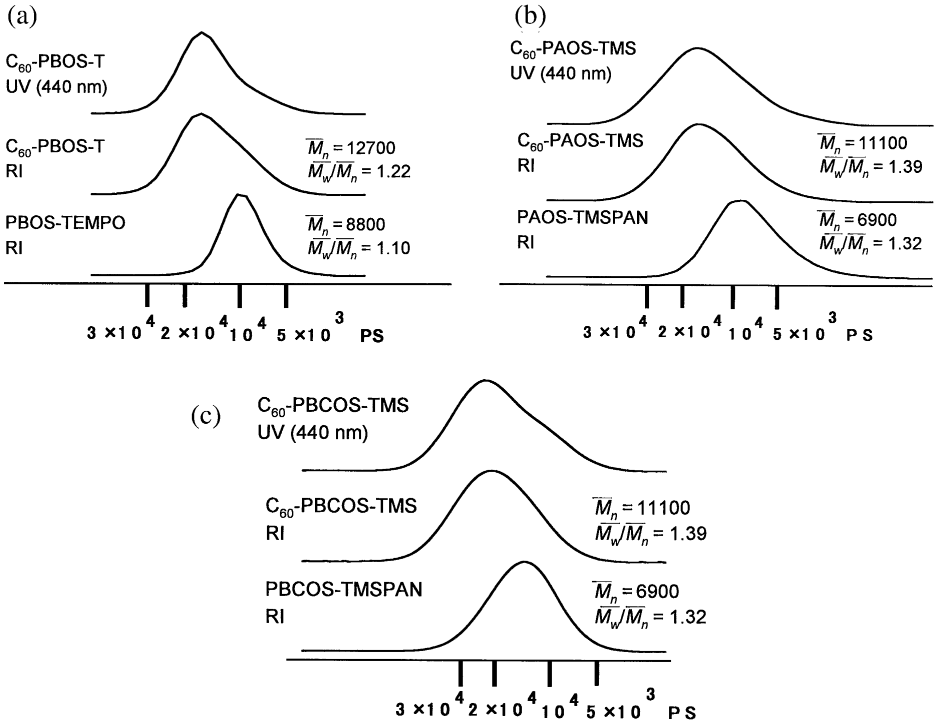


Figure 1. SEC curves of C_{60}-polymer measured by UV (440nm) and RI detector, and compared with the curve for nitroxide-terminated polymer by RI. For the reference, M_n and M_w/M_n values of the polymers calculated by RI detector are shown; (a) C_{60}-PBOS-T and PBOS-TEMPO, (b) C_{60}-PAOS-TMS and PAOS-TMSPAN, and (c) C_{60}-PBCOS-TMS and PBCOS-TMSPAN

Photo-transformation of C_{60}-bearing polymers into C_{60}-PVP

PBCOS/TPST system is used as KrF (248 nm) photoresist. PBCOS was transformed into PVP by the photoirradiation and the following post-exposure-baking (PEB) treatment in this system. PBOS and PAOS are also the precursor of PVP. The photo-transformation of C_{60}-polymer was carried out. The effect of C_{60} on photo-transformation properties of these polymers was investigated. Irradiation was performed at 254 nm in air or under nitrogen atmosphere using a low-pressure mercury lamp without a filter. The irradiated sample films were prepared as follows. For example, C_{60}-PBOS-T and TPST (5 wt% for C_{60}-PBOS-T) were dissolved in 2-butanone, and spin-casting on a silicon wafer or a quarts plate. The film thickness was prepared to ca. 0.5 μm. The absorbance of the film at 254 nm was 0.212, which was about four times as large as that for PBOS (A = 0.053). PEB treatments were carried out at 120 °C for 1 min. Figure 2(a) shows the FT-IR spectra of C_{60}-PBOS-T after irradiation and PEB treatment. With increase of the irradiation dose, the peak ascribed to phenolic hydroxyl group (3400 cm^{-1}) became larger, and the decrease of the peak due to C-H stretching (3000 cm^{-1}) was observed. In this figure, we can see that the reaction almost completed by irradiation at 10 mJ/cm^{-1} and followed by PEB treatment. The spectral changes of C_{60}-PBOS-T were essentially identical with those for PBOS. The photosensitivity curves of C_{60}-PBOS-T and PBOS-TEMPO for methanol as a developer with different atmosphere are shown in Figure 3. Little effect of atmosphere during irradiation was observed for the photo-transformation of C_{60}-PBOS-T into C_{60}-PVP-BOS.

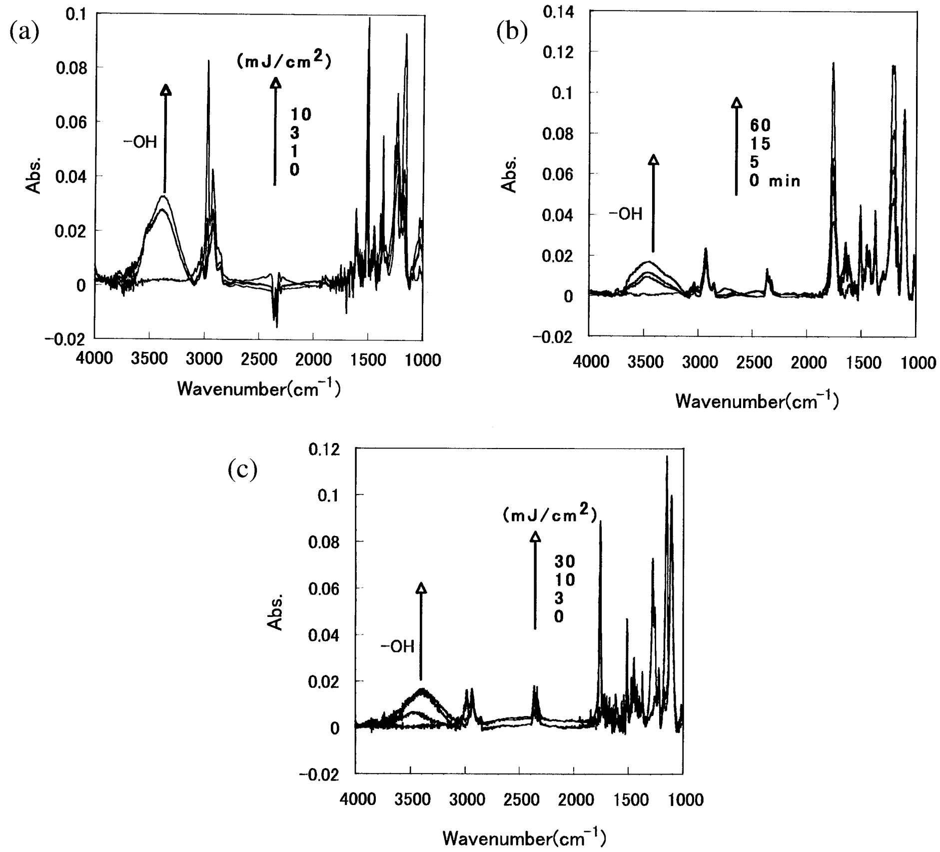


Figure 2. IR spectral changes of (a) C_{60}-PBOS-T, (b) C_{60}-PAOS-TMS, and (c) C_{60}-PBCOS-TMS films containing 5 wt% of TPST irradiated under N_2, and followed by PEB treatment at 120 °C for 1 min; Irradiation: (a),(c) 254 nm; (b) medium-pressure mercury lamp (3.3mW/cm^2 at 254 nm) without filter

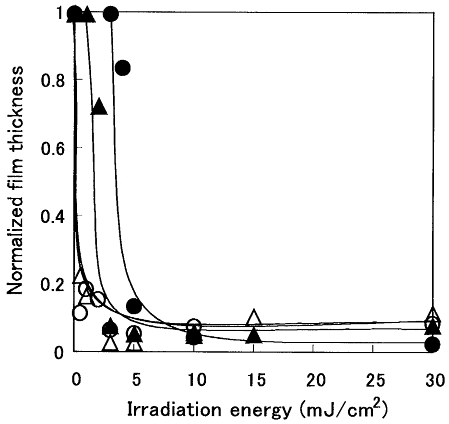


Figure 3. Dissolution properties of sample films containing 5 wt% of TPST, (○) PBOS-TEMPO in air, (△) PBOS-TEMPO under N_2, (●) C_{60}-PBOS-T in air, and (▲) C_{60}-PBOS-T under N_2 on irradiation at 254 nm; PEB: 120 °C for 1 min; Development: methanol for 5 min

On the other hand, the behavior of the photo-transformation of C_{60}-PAOS-TMS was quite different from that for C_{60}-PBOS-T. The photo-transformation of C_{60}-PAOS-TMS by the irradiation at 254 nm did not proceed because of the low reactivity. Thus, a medium-pressure lamp without a filter was used as light source. The light intensity at 254 nm was 3.3 mW/cm^2. Figure 2(b) shows the FT-IR spectra of C_{60}-PAOS-TMS after irradiation and followed by PEB treatment. The spectral changes were observed after irradiation for 1 min, which corresponds to 100 mJ/cm^2 at 254 nm and finished after irradiation for 120 min. With increase of the irradiation dose, the peak ascribed to phenolic hydroxyl group (3400 cm^{-1}) became larger, and the decrease of the carbonyl C=O stretching (1730 cm^{-1}) was observed. However, the C=O stretching did not completely disappear. The normalized peak intensity of C=O stretching was plotted against irradiation time in Figure 4(a). This figure indicates that the reaction properties of the decrease of C=O stretching for C_{60}-PAOS-TMS is similar to that for PAOS-TMSPAN, and there is no influence with the atmosphere during irradiation. Nevertheless, the solubility properties were largely affected by atmosphere. Photosensitivity curves of C_{60}-PAOS-TMS and PAOS-TMSPAN under N_2 or in air are shown in Figure 4(b). In this figure, we observe that C_{60}-PAOS-TMS became soluble in methanol on irradiation in air. C_{60}-PAOS-TMS and PAOS-TMSPAN films irradiated under N_2 for 60 min became insoluble in THF. The phenomenon may be due to the crosslinking reaction of PAOS by Fries rearrangement of acetoxy group in PAOS. Irradiated C_{60} moiety in the presence of O_2 may suppress the reaction. Precise reaction mechanism is under investigation. Photo-transformation of C_{60}-PAOS-TMS into C_{60}-PVP-AOS was difficult under N_2.

Figure 2(c) shows the FT-IR spectra of C_{60}-PCBOS-TMS after irradiation and PEB treatment. With increase of the irradiation dose, the peak ascribed to phenolic hydroxyl group (3400 cm^{-1}) became larger, and the decrease of the peak for C=O stretching (1750 cm^{-1}) was observed. The carbonyl peak disappeared completely with a dose of 10 mJ/cm^2. The normalized peak intensity of C=O stretching was plotted for the irradiation dose in Figure 5(a). Interestingly, the decrease of the peak intensity in C_{60}-PBCOS-TMS was about twice faster than that for PBCOS-TMSPAN. The photosensitivity curves of C_{60}-PBCOS-TMS and PBCOS-TMSPAN for methanol as developer under different atmosphere are shown in Figure 5(b). The decrease of the film thickness almost corresponds to the increase of the decomposition degree of C=O group shown in Figure 5(a). The photo-transformation of C_{60}-PBCOS-TMS into C_{60}-PVP-BCOS was achieved much faster than that for PBCOS regardless of atmospheric conditions during irradiation. The high sensitivity in C_{60}-PBCOS-TMS may be due to the photosensitization of TPST from a C_{60} moiety. A detailed study is now in progress.

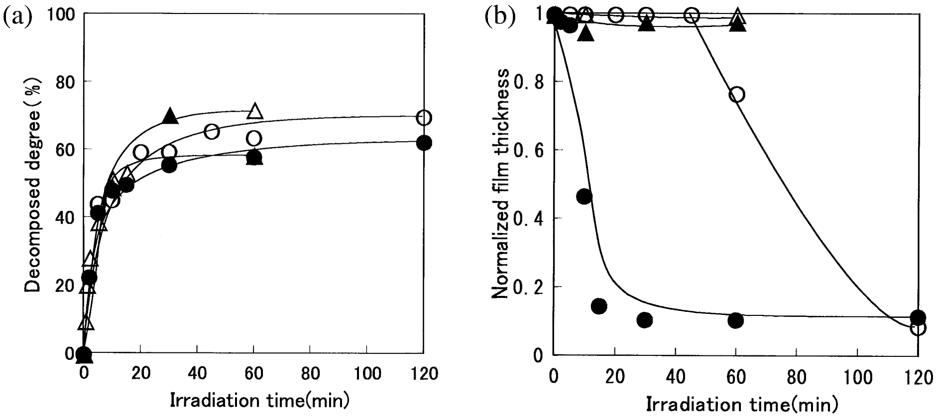


Figure 4. (a) Relationship between irradiation time and decomposed degree of the peak due to C=O in sample films and (b) dissolution properties of sample films containing 5 wt% of TPST, (○) PAOS-TMSPAN in air, (△) PAOS-TMSPAN under N_2, (●) C_{60}-PAOS-TMS in air, and (▲) C_{60}-PAOS-TMS under N_2 on irradiation with medium-pressure mercury lamp (3.3 mW/cm^2 at 254 nm); PEB: 120 °C for 1 min; Development: methanol for 5 min

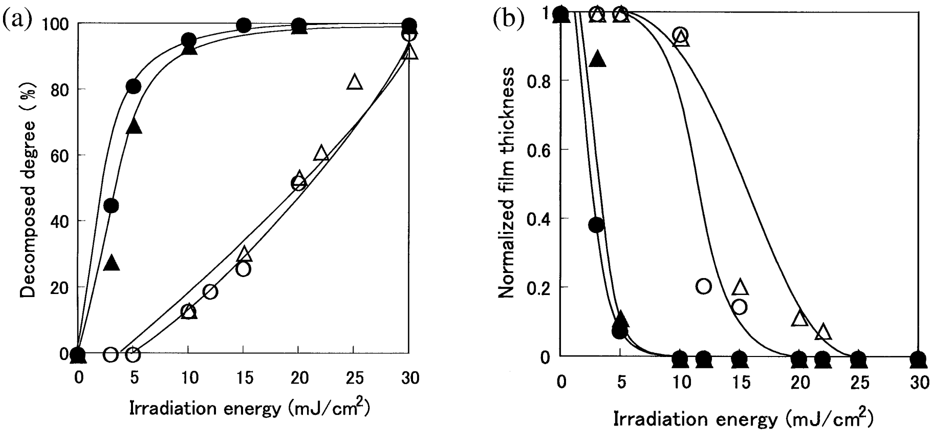


Figure 5. (a) Relationship between irradiation energy and decomposed degree of the peak due to C=O in sample films and (b) dissolution properties of sample films containing 5 wt% of TPST, (○) PBCOS-TMSPAN in air, (△) PBCOS-TMSPAN under N_2, (●) C_{60}-PBCOS-TMS in air, and (▲) C_{60}-PBCOS-TMS under N_2 on irradiation at 254 nm; PEB: 120 °C for 1 min; Development: methanol for 10 min

Conclusions

Three kinds of C_{60}-bearing styrene polymers having *tert*-butyl, acetoxy, and *tert*-butoxycarbonyl groups were prepared and their photo-transformation properties were studied. TMSPAN was effective to synthesize C_{60}-PAOS and C_{60}-PBCOS. Photo-transformation of C_{60}-PBOS and C_{60}-PBCOS was achieved with low irradiation dose at 254 nm and PEB treatment in the presence of 5 wt% TPST. The photo-transformation of C_{60}-PAOS was affected by atmospheric conditions during irradiation.

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