

Synthesis of Fluorine-containing Poly(acetal)s by the Polyaddition of Bisphenol AF with Divinyl Ether Compounds and Their Photoinduced Depolymerization

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ABSTRACT: Fluorine-containing poly(acetal)s were synthesized by the polyaddition of bisphenol AF (BPAF) with divinyl ether compounds. It was found that the poly(acetal) (PA-1) with a number average molecular weights of 4400 was obtained in 71% yield by the polyaddition of BPAF with ethylene glycol divinyl ether (EGDVE) using 1 mol % of pyridinium *p*-toluene sulfonate (PTS) as a catalyst in THF at room temperature for 24 h. Furthermore, the polyaddition of BPAF with other divinyl ether compounds were also carried out to give corresponding poly(acetal)s (PA-2–PA-3) in appropriate reaction conditions. It was also found that the photoinduced depolymerization of the resulting poly(acetal)s proceeded using photo-acid generator (PAG) by the photo-irradiation in the film state. It was found that transmittance of PA-1 was 39% at 157 nm for 0.1 μm thickness. [DOI 10.1295/polymj.36.531]

KEY WORDS Fluorine-containing Poly(acetal) / Divinyl Ether Compound / Polyaddition / Photoinduced Depolymerization / Photoresist /

Semiconductor device manufacture has been supported with the photolithography technology. Development of photolithography technology has made possible the high resolution and high performance of a semiconductor device. Therefore, the new photolithography technology requires the development of new photoresist materials.

Recently, the vacuum ultraviolet (VUV) lithography using F_2 excimer laser with a wavelength of 157 nm is expected as the next generation lithography technology. Photoresist materials for VUV lithography must be high transparent at 157 nm. Fluorinated polymers and silsesquioxane polymers are fairly transparent in the VUV regions. Recently, many research groups investigated on developing 157 nm photoresists based on fluorinated polymers.^{1–6} Willson *et al.*⁷ described that the approach to the design of the resist materials requires identification of four modules: backbone, etch barrier, acidic group, and acid labile protecting group. These modules must be high transparent at 157 nm. Ober *et al.*² focused on acetal groups as transparent protecting groups of acidic module. Because, it is useful as protecting groups for 157 nm resist that acetal groups have high reactivity to the photo-produced acids in the chemically amplification system. Meanwhile, Zhang and Ruckenstein⁸ reported recently the synthesis of poly(acetal)s by the polyaddition of bisphenol A with divinyl ether compounds using pyridinium *p*-toluene sulfonate (PTS) as a cata-

lyst. These polymers have been expected as recyclable polymers. Ueda and co-workers⁵ reported an interesting polymer, poly(methyl vinyl sulfonate), which showed excellent transparency at 157 nm as suggested by the theoretical calculation.

We previously reported the polyaddition of fluorine-containing bis(epoxide)s⁹ or bis(oxetane)s¹⁰ with fluorine-containing diols to produce corresponding fluorine-containing poly(ether)s with pendant hydroxyl groups. These polymers were highly transparent at 157 nm. On the above results, it was also found that fluorine-containing diols such as bisphenol AF (BPAF) exhibited highly transparent at 157 nm and excellent thermal properties.

In this article, we examined the synthesis of fluorine-containing poly(acetal)s by the polyaddition of BPAF with divinyl ether compounds. Furthermore, we investigated on the photoinduced depolymerization of resulting fluorine-containing poly(acetal)s.

EXPERIMENTAL

Materials

Solvents were dried using P_2O_5 , CaH_2 , or Na metal wire, and purified in the usual way before use. Tetrabutylammonium bromide (TBAB) was recrystallized twice from ethyl acetate. Reagent grades of pyridinium *p*-toluenesulfonate (PTS), potassium hydroxide (KOH), potassium *tert*-butoxide (*t*-BuOK) were used

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without further purification. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (BPAF) was purified by sublimation. Ethylene glycol divinyl ether (EGDVE), 1,4-cyclohexane dimethanol divinyl ether (HMDVE) and 1,2-dibromoethane was used without further purification. Photo-acid generator such as bis-[4-(diphenylsulfonio)phenyl]sulfide bis(hexafluorophosphate) (DPSP; Degussa) was also used without further purification.

Measurements

Infrared (IR) spectra were measured on a Jasco Model IR-420 spectrometer. The ^1H NMR spectra were recorded on JEOL Model JNM α -500 (500 MHz for ^1H NMR, 125 MHz for ^{13}C NMR, 470 MHz for ^{19}F NMR) instruments in CDCl_3 or $\text{DMSO-}d_6$ using Me_4Si (TMS) for ^1H NMR and C_6F_6 for ^{19}F NMR as an internal standard. The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers were estimated by gel permeation chromatography (GPC) with the use of a Tosoh model HLC-8120 GPC equipped with refractive index and ultraviolet detectors using TSK gel columns (eluent THF, calibrated with narrow molecular weight polystyrene standards). The T_g s of the polymers were measured on a Seiko Instruments differential scanning calorimeter (DSC) Model EXSTAR6000/DSC6200 at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. The thermal analysis was performed on a Seiko Instruments thermogravimetric analysis (TGA) Model EXSTAR6000/TG/DTA6200 at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. Vacuum ultraviolet (VUV) spectra were recorded on a Jasco Model VU-201.

Synthesis of 2,2-Bis[4-(2-Bromoethoxy)phenyl]hexafluoropropane (BPAFBE)

An NMP (30 mL) solution of BPAF (10.1 g, 30 mmol), KOH (10.1 g, 120 mmol) as a base, and TBAB (97 mg, 5.0 mol%) was stirred at room temperature for 2 h. Then, 1,2-dibromoethane (112.8 g, 600 mmol) was added to the solution, and the mixture was stirred for 48 h at the same temperature. The reaction mixture was diluted with ethyl acetate, washed three times with water, and dried with anhydrous MgSO_4 . Solvent was evaporated, and then crude product was purified by silica gel column chromatography with ethyl acetate/*n*-hexane (1/2) as an eluent. The yield of BPAFBE was 11.8 g (67%).

IR (neat, cm^{-1}): 2934, 2865 ($\nu\text{C-H}$), 1612, 1515 ($\nu\text{C=C}$, aromatic), 1254, 1173 ($\nu\text{C-F}$), 1130 ($\nu\text{C-O-C}$, ether), 573 ($\nu\text{C-Br}$). ^1H NMR (200 MHz, CDCl_3 , TMS): δ 3.65 (t, $J = 6.0$ Hz, 4.0H, $\text{CH}_2\text{CH}_2\text{-Br}$), 4.31 (t, $J = 6.0$ Hz, 4.0H, $\text{CH}_2\text{CH}_2\text{-Br}$), 6.89–7.31 (m, 8.0H, aromatic H).

Synthesis of 2,2-Bis(4-vinyloxyphenyl)hexafluoropropane (BPAFVE)

The mixture of BPAFBE (11.0 g, 20 mmol) and *t*-BuOK (5.4 g, 48 mmol) in NMP (20 mL) was stirred at 80°C for 2 h. The reaction mixture was diluted in ethyl acetate, washed three times with water, and dried with anhydrous MgSO_4 . Solvent was evaporated, and then crude product was purified by alumina column chromatography with ethyl acetate/*n*-hexane (1/20) as an eluent. The yield of BPAFVE was 3.8 g (48%).

IR (neat, cm^{-1}): 3069, 3053 ($\nu\text{C-H}$), 1647 ($\nu\text{C=C}$, vinyl), 1607, 1512 ($\nu\text{C=C}$, aromatic), 1251, 1175 ($\nu\text{C-F}$), 1130 ($\nu\text{C-O-C}$, ether). ^1H NMR (500 MHz, CDCl_3 , TMS): δ 4.53 (dd, $J = 1.5, 13.7$ Hz, 2.0H, CH_2 in vinyl), 4.86 (dd, $J = 1.5, 5.9$ Hz, 2.0H, CH_2 in vinyl), 6.66 (dd, $J = 5.9, 13.7$ Hz, 2.0H, CH in vinyl), 6.99 (d, $J = 9.0$ Hz, 4.0H, aromatic H), 7.34 (d, $J = 9.0$ Hz, 4.0H, aromatic H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, TMS): δ 63.7 (C), 96.7 ($\text{CH}_2=$), 124.2 (q, $J = 285.9$ Hz, CF_3), 147.1 ($=\text{CH-}$), 116.3, 127.7, 131.7, 157.1 (aromatic C). ^{19}F NMR (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -66.8 (s, CF_3).

Typical Procedure for the Synthesis of PA-1 by the Polyaddition of BPAF with EGDVE

A typical procedure for polyaddition of BPAF with EGDVE was as follows: BPAF (168.1 mg, 0.5 mmol), EGDVE (57.1 mg, 0.5 mmol), PTS (2.5 mg, 1.0 mol%) as a catalyst, and THF (0.5 mL, 1 mol/L) as a solvent were charged into a flask. The reaction was performed at room temperature for 24 h under stirring. The reaction mixture was diluted in ethyl acetate, washed three times with aq. 1 N NaOH, and once with water, and dried with anhydrous MgSO_4 . The solvent was evaporated, and then the resulting polymer was reprecipitated from THF into *n*-hexane, and dried *in vacuo*. The yield of resulting polymer (PA-1) was 132.6 mg (59%). The number-average molecular weight (M_n) of the polymer determined by GPC was 3500 ($M_w/M_n = 2.19$). IR (film, cm^{-1}): 3328 ($\nu\text{O-H}$), 2990, 2939, 2879 ($\nu\text{C-H}$), 1612, 1514 ($\nu\text{C=C}$, aromatic), 1249, 1172 ($\nu\text{C-F}$), 1206, 1132, 1078 ($\nu\text{C-O-C}$, acetal). ^1H NMR (500 MHz, $\text{DMSO-}d_6$, TMS): δ 1.46 (d, $J = 6.0$ Hz, 6.0H, CH_3), 3.61–3.79 (m, 4.0H, CH_2), 5.41–5.48 (m, 2.0H, CH), 6.77–6.93 (m, 4.0H, aromatic H), 7.24–7.28 (m, 4.0H, aromatic H). ^{19}F NMR (470 MHz, $\text{DMSO-}d_6$, C_6F_6): δ -62.9 to -63.0 (m, CF_3).

Synthesis of PA-2 by the Polyaddition of BPAF with HMDVE

The reaction was carried out with BPAF (168.1 mg, 0.5 mmol) and HMDVE (98.1 mg, 0.5 mmol) using PTS (2.5 mg, 1.0 mol%) as a catalyst in THF

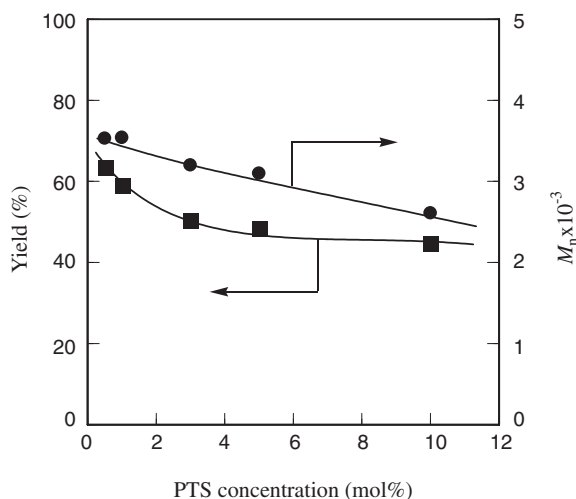


Figure 1. Effect of PTS concentration on the polyaddition of BPAF (0.5 mmol) with EGDVE (0.5 mmol) using PTS in THF (1 mol/L) at room temperature for 24 h: (●) M_n ; (■) yield.

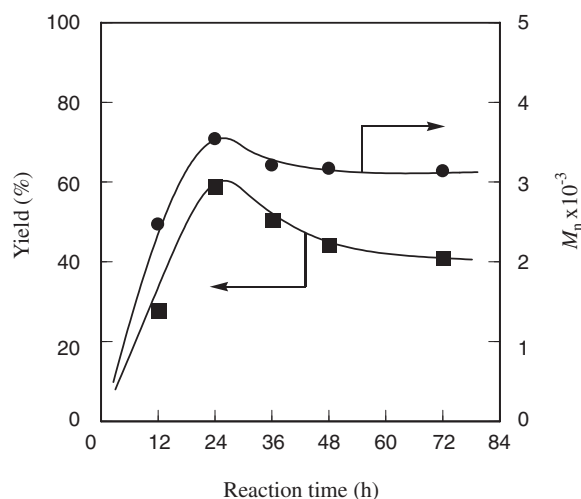


Figure 2. Effect of reaction time on the polyaddition of BPAF (0.5 mmol) with EGDVE (0.5 mmol) using PTS (1 mol %) in THF at room temperature: (●) M_n ; (■) yield.

yields and M_n 's of the resulting polymer decreased after 24 h. It seems that the decomposition of the polymer occurred as a side reaction during long reaction time, although the polyaddition proceeded smoothly until at 24 h.

The effect of the reaction temperature on the polyaddition was also examined using 1 mol % of PTS in THF for 24 h. As shown in Table I, the yield and the M_n 's of the resulting polymer increased with reaction temperature, and the polymer with $M_n = 4000$ was obtained in 70% yield, when the polyaddition was performed at 50 °C.

Table I. Effect of reaction temperature on the polyaddition of BPAF with EGDE^a

No.	Temp./°C	Yield ^b /%	$M_n \times 10^{-3c}$	M_w/W_n^c
1	r.t.	59	3.54	2.19
2	50	70	4.04	1.99

^aThe reaction was carried out with BPAF (0.5 mmol) and EGDE (0.5 mmol) using PTS (1 mol %) in THF (1 mol/L) for 24 h. ^bInsoluble parts in *n*-hexane. ^cEstimated by GPC (THF) based on polystyrene standards.

Furthermore, the polyaddition of BPAF with certain divinyl ether compounds using 1 mol % of PTS in THF was examined, and the results are summarized in Table II. PA-2 with $M_n = 8400$ was obtained in 60% yield by the polyaddition of BPAF with HMDVE at room temperature for 24 h. Although the reaction of BAPFVE with BPAF did not proceed at room temperature, PA-3 was obtained when the polyaddition was carried out from 50 °C to 100. PA-3 with $M_n = 8100$ was synthesized in 65% yield when the reaction of BPAF with BPAFVE carried out at 80 °C for 24 h (Scheme 2). This result means that polymerization proceeded smoothly by heating because the electron density of vinyl group of BPAFVE is lower than that of EGDVE and HMDVE. The structures of all resulting polymers were confirmed by IR, ¹H NMR, and ¹⁹F NMR spectra.

T_g 's of the resulting polymers were measured by DSC. The T_g 's of PA-1, PA-2, and PA-3 were 39, 47, and 87 °C, respectively. This shows that poly(acetal)s (PA-3) with rigid structures in the main chain had relatively higher T_g 's than poly(acetal)s (PA-1, PA-2) with flexible alkyl groups in the main chain.

Table II. Synthesis of certain poly(acetal)s by the polyaddition of BPAF with divinyl ether compounds^a

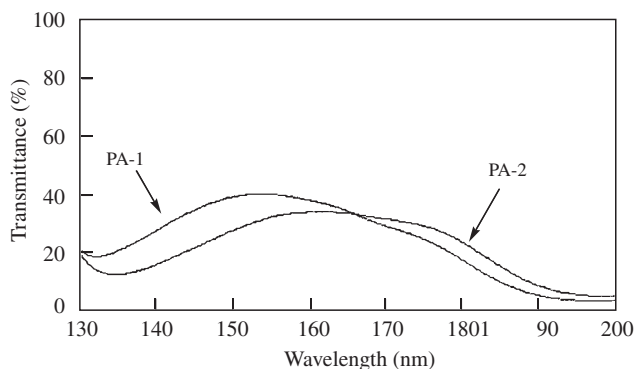
Poly(acetal)s	Divinyl ethers	Temp./°C	Yield ^b /%	$M_n \times 10^{-3c}$	M_w/W_n^c
PA-1	EGDVE	r.t.	59	3.54	2.19
PA-2	HMDVE	r.t.	60	8.38	1.45
PA-3	BPAFVE	r.t.	0	—	—
PA-3	BPAFVE	50	76	4.61	1.66
PA-3	BPAFVE	80	65	8.09	1.32
PA-3	BPAFVE	100	63	6.37	1.36

^aThe reaction was carried out with BPAF (0.5 mmol) with divinyl ether compounds (0.5 mmol) using PTS (1 mol %) in THF (1.0 mol/L) for 24 h. ^bInsoluble parts in *n*-hexane. ^cEstimated by GPC (THF) based on polystyrene standards.

Table III. Characteristics of poly(acetal)s

poly(acetal)s	$T_g/^\circ\text{C}^a$	$T_d/^\circ\text{C}^b$	T at 157 nm/% ^c
PA-1	39	247	39
PA-2	47	237	33
PA-3	87	267	

^aDetermined by DSC at a heating rate of 10 °C/min in nitrogen. ^bDetermined by TG/DTA at a heating rate of 10 °C/min in nitrogen. ^cFilm thickness: 1000 Å.


Figure 3. VUV spectra of poly(acetal)s (film thickness: 1000 Å).

The transmittances of resulting polymers were measured by VUV spectra. Transmittance at 157 nm and VUV spectra of resulting polymers are shown in Table III and Figure 3. It was found that these poly(acetal)s are transparent at 157 nm for 0.1 μm thickness, and transmittance of PA-1 and 2 were 39 and 33%, respectively.

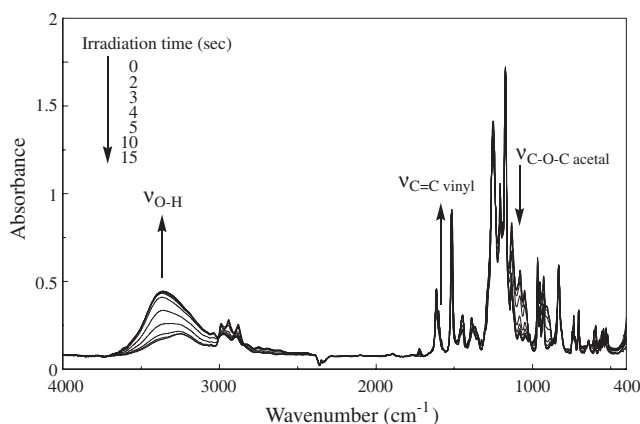
The solubility of the resulting polymers was summarized in Table IV. All of the obtained polymers were soluble in all solvents excepting *n*-hexane. It seems that the obtained fluoropolymers had good solubility.

The photoinduced depolymerization of poly(acetal)s was examined using DPSP as PAG (5 wt %) on photo-irradiation with a 250-W high-pressure mercury lamp in the film state (Scheme 4). As shown in Figure 4, the conversion of depolymerization in PA-1 was estimated from the decreases of the absorption

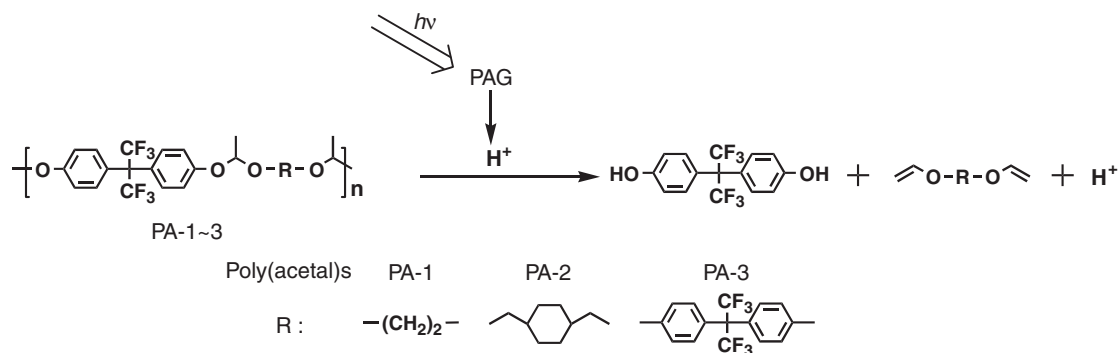
Table IV. Solubility of fluorine-containing poly(acetal)s^a

Solvent	PA-1	PA-2	PA-3
<i>n</i> -Hexane	–	–	–
Methanol	+-	+-	–
Acetonitrile	++	–	–
Acetone	++	++	++
Ethyl acetate	++	++	++
Chloroform	++	++	++
Toluene	++	++	++
Anisole	++	++	++
<i>o</i> -Dichlorobenzene	++	++	++
THF	++	++	++
DMF	++	++	++
NMP	++	++	++
DMSO	++	+	–

^a ++: soluble at room temperature, +: soluble by heating, +-: partially soluble or swelling, -: insoluble.


Figure 4. Change of IR spectra on the photoinduced depolymerization of PA-1 in the presence of DPSP (5 wt %) under UV irradiation (15 mW/cm² at 365 nm).

peaks due to the C–O–C stretching at 1115 cm⁻¹ in the IR spectra. As shown in Figure 5, depolymerization of PA-1 and PA-2 with 5 mol % of DPSP proceeded only by the photo-irradiation in the film state. On the other hand, the depolymerization of PA-3 with 5 wt % of DPSP did not occur only by the photo-irradiation in the film state. However, when the reaction


Scheme 3.

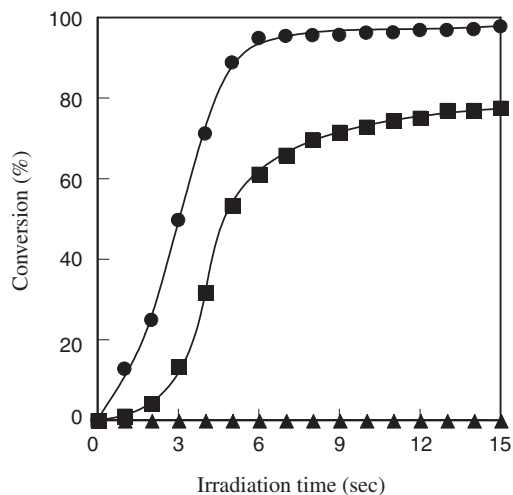


Figure 5. Effect of irradiation time on the photoinduced depolymerization of poly(acetal)s film in the presence of DPSP (5 wt %) under UV irradiation (15 mW/cm² at 365 nm): (■) PA-1; (●) PA-2; (▲) PA-3.

of PA-3 was carried out with 5 wt % of DPSP on photo-irradiation followed by heating for 1 h at certain temperature such as 50, 100, and 150 °C, it was found that depolymerization at each temperature occurred smoothly. As the result, absorption peaks resulting from C–O–C stretching at 1115 cm⁻¹ in the IR spectra decreased, and absorption peaks resulting O–H stretching at around 3500 cm⁻¹ increased. As shown in Figure 6, the conversion of depolymerization increased with heating temperature, the conversion reached about 60% by heating at 150 °C. This result is explained by the following two reasons. An important reason is T_g of polymers. It seems that depolymerization occurred smoothly by heating at high temperature, because the diffusion of generated acid in the PA-3 film with high T_g than PA-1 and PA-2 would be not effective at room temperature. Another one is stability of acetal bond. It is considered that the reaction did not enough proceed because acetal bond of PA-3 is more stable than that of PA-1 and PA-2. This result suggests that electron density of acetal groups of PA-3 is low as well as vinyl group of BPAFVE.

CONCLUSIONS

The polyaddition of BPAF with divinyl ether compounds proceeds using PTS as a catalyst to produce the corresponding fluoropolymers with acetal bond in the main chains. The transmittance of fluorine-containing poly(acetal)s, PA-1 and PA-2 were 39 and 33%, respectively, which are good transparent at 157 nm. Furthermore, the photoinduced depolymerization of poly(acetal)s was examined using PAG on photo-irradiation. It was found that the depolymeriza-

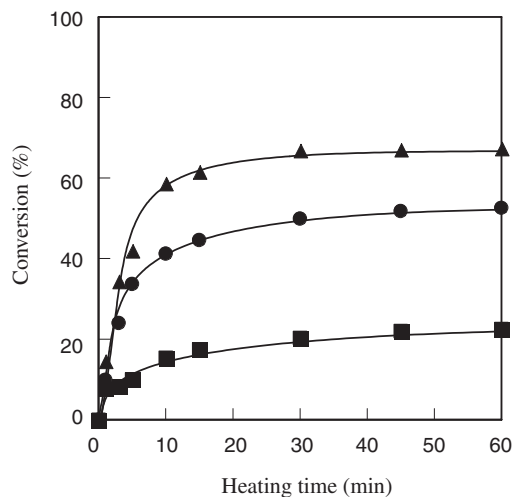


Figure 6. Effect of heating time on the photoinduced depolymerization of PA-3 film in the presence of DPSP (5 wt %) under UV irradiation (15 mW/cm² at 365 nm) for 5 min: (■) 50 °C; (●) 100 °C; (▲) 150 °C.

tion of PA-1 and PA-2 proceeded only by the photo-irradiation. On the other hand, PA-3 was depolymerized by the photo-irradiation followed by heating.

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