Photoinduced Depolymerization of Poly(olefin sulfone)s Possessing Photobase Generator Side-Chains: Effect of Spacer-Chain Length

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Received 21 March 2013; accepted 14 May 2013; published online 11 June 2013
DOI: 10.1002/pola.26787

ABSTRACT: Photoinduced depolymerization of poly(olefin sulfone)s possessing photobase generators in the side-chain was investigated. Irradiation with UV light generated base on the side-chains and induced depolymerization based on proton abstraction on the main-chain. The effect of the length of the spacer chain, which connects the photobase-generating moiety to the polymer main chain on the photoinduced depolymerization, also was investigated. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 3873–3880

KEYWORDS: degradation; lithography; photobase generator; photoinduced depolymerization; photoresists; poly(olefin sulfone)s

INTRODUCTION The photoinduced depolymerization reaction of poly(olefin sulfone)s possessing a photobase generator (PBG) has been investigated.[1–3] The poly(olefin sulfone) is a 1:1 alternating copolymer of an olefin monomer and sulfur dioxide.[4,5] The protons on the carbon adjacent to the sulfonyl group are easily abstracted by bases.[6] When this occurs, a poly(olefin sulfone) that possesses a photobase-generating chromophore undergoes a photoinduced unzipping reaction and the main chain of the poly(olefin sulfone) is depolymerized back to the olefin monomer and sulfur dioxide (Fig. 1). This type of polymer is suitable for a wide variety of applications such as removable adhesives, stereolithography, and printable micro-circuit fabrication.

A series of compounds that generates amino groups after UV irradiation was used as a PBG. These polymers underwent photoinduced depolymerization. In this study, the effect of the length of the spacer chain, which connects the PBG chromophore to the polymer main chain, on photoinduced depolymerization of poly(olefin sulfone)s was investigated. The mobility of the PBG chromophore in the side chain was dependent on the length of the spacer chain. Depolymerization of poly(olefin sulfone) is caused by proton abstraction from the polymer main chain by the photogenerated base. Thus, the mobility of the PBG is expected to affect depolymerization. The polymer film was irradiated with 254-nm UV light, causing decomposition of the poly(olefin sulfone) polymer. Decomposition and depolymerization behaviors were compared in the polymers.

EXPERIMENTAL

Samples

The molecular structures of the polymers used in this study are shown in Figure 2. Polymers that possess an [(*o*-nitrobenzyl) oxy]carbonyl group as a photobase-generating group in the side-chain were synthesized. The [(*o*-nitrobenzyl)oxy]carbonyl group degrades upon exposure to UV light to produce an amino group.[7–9] The base generation mechanism is shown in Scheme 1. The photobase-generating group was designed to produce a secondary amino group because a secondary amino group can induce effective depolymerization of poly(olefin sulfone)s.[1] The polymers were synthesized according to Scheme 2.

Synthesis of Olefin Monomer (PNC2-8 Monomer)

2-Nitrobenzyl p-Nitrophenyl Carbonate (Step 1)

2-Nitrobenzyl alcohol (30.64 g, 0.200 mol) and pyridine (15.93 g, 0.200 mol) were dissolved in 300 mL of dry THF and cooled to 0 °C. 4-Nitrophenyl chloroformate (51.12 g, 0.254 mol) dissolved in 150 mL of dry THF was added dropwise to the solution while maintaining the temperature at 0 °C. Then the solution was refluxed for 8 h. After the solution was cooled to room temperature, 1000 mL of water was added and the product was extracted with 1000 mL of chloroform. The chloroform solution was washed with 1000 mL of water and dried over sodium sulfonate. The solvent was evaporated to yield a yellow-green powder. The product was recrystallized from 1:1 toluene:ethanol. Yellow crystals (56.38 g) were obtained in 88% yield.

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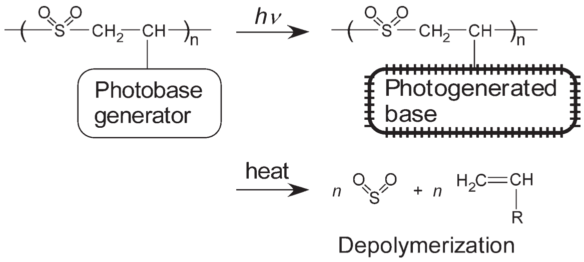
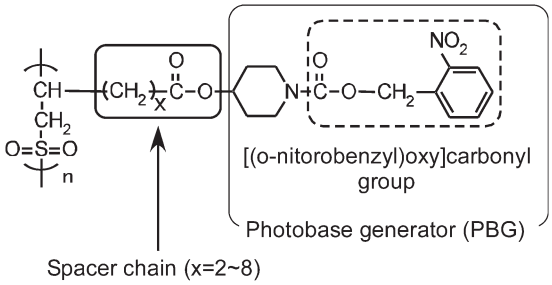


FIGURE 1 Photoinduced depolymerization of poly(olefin sulfone)s possessing a photobase generator in the side-chain.



PNC2-x

FIGURE 2 Structure of poly(olefin sulfone)s PNC2-*x* (*x* = 2–8).

Anal. Calcd. for $C_{14}H_{10}N_2O_7$: C, 52.84%; H, 3.17%; N, 8.80%. Found: C, 52.08%; H, 3.12%; N, 8.67%.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.75 (s, 2H, Ar—CH_2—O—), 7.42 (d, 2H, Ar—H), 7.58 (m, 1H, Ar—H), 7.74 (t, 2H, Ar—H), 8.20 (d, 1H, Ar—H), 8.30 (d, 2H, Ar—H).

IR (KBr) 1244 (s, asymm C—O str), 1341 (s, symm N—O str), 1522 (s, asymm N—O str), 1764 (s, C=O str).

4-Hydroxy-N-[[(o-nitrobenzyl)oxy]carbonyl]pyridine (Step 2)

2-Nitrobenzyl *p*-nitrophenyl carbonate (69.95 g, 0.220 mol), 4-hydroxypyridine (22.96 g, 0.227 mol), and 1-hydroxybenzotriazole (HOBt, 14.94 g, 0.111 mol) were dissolved in 450 mL dry THF. The solution was refluxed for 6 h. The solvent was removed by evaporation and the residue (yellow solid) dissolved in chloroform (1000 mL) and washed with saturated aq. sodium hydrocarbonate (1000 mL) and water (1000 mL). The solution was dried over sodium sulfonate. After the solvent was removed, the product was recrystallized from 1:1 mixture ethyl acetate:-hexane. A slightly yellow solid (50.69 g) was obtained in 82% yield.

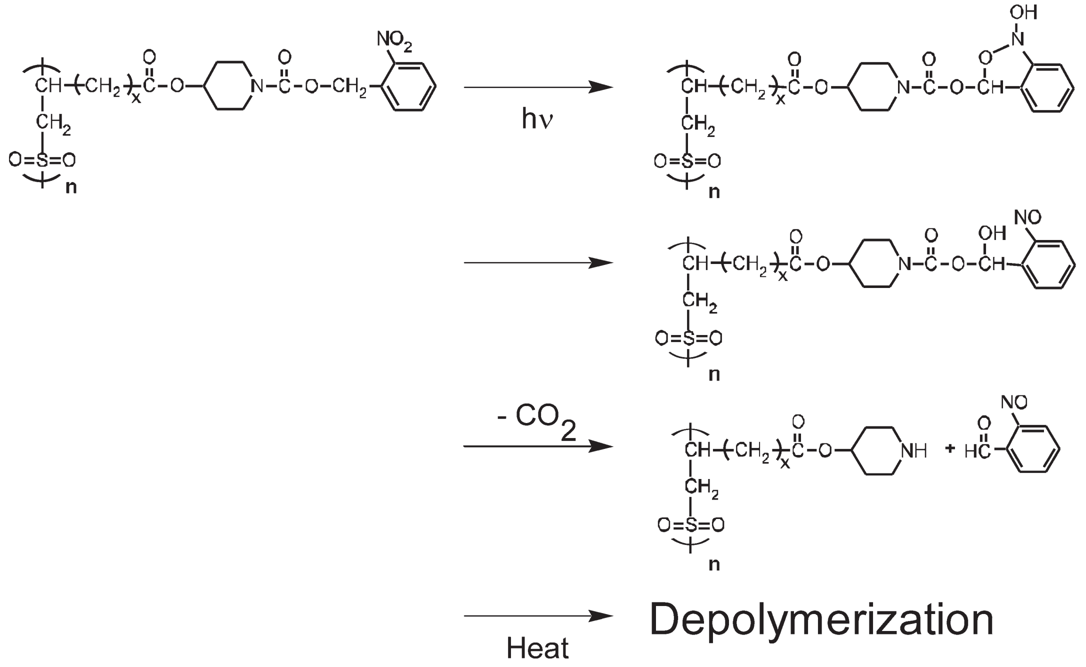
Anal. Calcd. for $C_{13}H_{16}N_2O_5$: C, 55.71%; H, 5.75%; N, 9.99%. Found: C, 56.34%; H, 5.80%; N, 10.13%.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.48–1.57 (m, 2H, Cy—H), 1.87–1.92 (m, 2H, Cy—H), 3.17–3.22 (s, 2H, Cy—H), 3.87–3.94 (m, 3H, Cy—H), 5.52 (s, 2H, Ar—CH_2—O—), 7.47 (t, 1H, Ar—H), 7.55 (d, 1H, Ar—H), 7.63 (t, 1H, Ar—H), 8.05 (d, 1H, Ar—H).

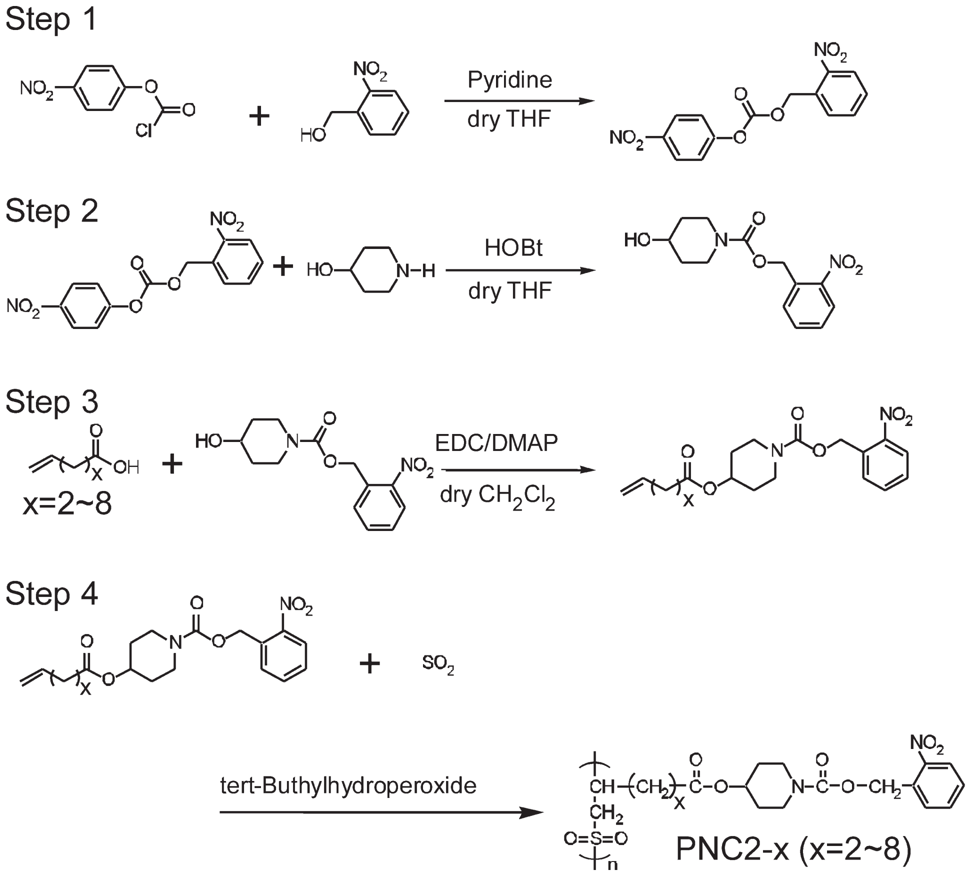
IR (KBr) 1341 (s, symm N—O str), 1524 (s, asymm N—O str), 1764 (s, C=O str), 3484 (s, O—H str).

4-[9-Decenylcarbonyl]oxy-N-[[(o-nitrobenzyl)oxy]carbonyl]piperidine (PNC2-8 Monomer, Step 3)

10-Undecenoic acid (2.00 g, 0.010 mol), 4-hydroxy-*N*-[[(*o*-nitrobenzyl)oxy]carbonyl]pyridine (3.16 g, 0.011 mol),



SCHEME 1 Degradation mechanism of the photobase generator.



SCHEME 2 Synthetic route for PNC2-*x*.

1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 3.02 g, 0.016 mol), and 4-dimethylaminopyridine (DMAP, 3.04 g, 0.025 mol) were dissolved in dry chloroform (120 mL). The solution was stirred for 40 h at room temperature. A 3 N solution of hydrochloride (250 mL) was added and the resulting solution stirred for 30 min at room temperature. The chloroform solution was washed with 3 N hydrochloride (1000 mL) and saturated aq. of sodium chloride (1000 mL). After the chloroform solution was dried over sodium sulfonate, the solvent was removed by evaporation. The yellow oil obtained was purified by silica gel column chromatography (eluent: 1:1 ethyl acetate:chloroform). The product was obtained as white crystals (4.30 g, yield: 89%).

Anal. Calcd. for $C_{13}H_{16}N_2O_5$: C, 64.55%; H, 7.67%; N, 6.27%. Found: C, 64.66%; H, 7.65%; N, 6.23%.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.44 (m, 6H, —CH_2—), 1.62–1.68 (m, 6H, —CH_2—, Cy—H), 1.85–1.90 (m, 2H, Cy—H), 2.040 (q, 4H, —CH_2—), 2.33 (t, 2H, —CH_2—), 3.37 (s, 2H, Cy—H), 3.75 (m, 2H, Cy—H), 4.88 (m, 1H, Cy—H), 4.98 (d, 2H, CH_2=CH—), 5.05 (d, 2H, CH_2=CH—), 5.52 (s, 2H, Ar—CH_2—O—), 5.80 (m, 1H, CH_2=CH—), 7.48 (t, 1H, Ar—H), 7.55 (d, 1H, Ar—H), 7.63 (t, 1H, Ar—H), 8.06 (d, 1H, Ar—H).

^{13}C NMR (DMSO, 500MHz) δ 24.4 (—CH_2—CH_2—CO—O—), 28.2–28.6 (CH_2=CH—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—, —CH_2—CH_2—N— of Cy), 33.1 (CH_2=CH—CH_2—), 33.7 (—CH_2—CO—O—), 40.8 (—CH_2—N— of Cy), 63.2 (—O—CH_2—Ar), 68.7 (—O—CH— $(CH_2)_2$—), 114.5 (CH_2=CH—), 124.6 (—CH— (Ar)), 129.1 (—CH— of Ar), 132.0 (—C— (Ar)), 133.9 (—CH— of Ar), 138.7 (CH_2=CH—), 147.4 (—CH— (Ar)), 153.8 (N—CO—O—), 172.2 (—CH_2—CO—O—)

IR (KBr) 1237 (s, asymm CO—O str), 1333 (s, symm N—O str), 1528 (s, asymm N—O str), 1697 (s, C=O str), 2922 (s, C—H str).

Polymerization (Step 4)

The olefin monomers were dissolved in liquefied SO_2 and polymerized with *tert*-butylperoxide (*t*BuOOH) as an initiator. *t*BuOOH acted as a redox initiator with SO_2, producing a *tert*-butyloxy radical. The initiator (1.56×10^{-2} mol), olefin monomer (1.0 g, 7.1×10^{-3} mol–1.8×10^{-2} mol), and SO_2 (10 g, 1.6×10^{-1} mol) were added to a pressurized glass tube at −196 °C. When the temperature of the tube was raised above −70 °C, the frozen solution fused and polymerization occurred. The tube was maintained at −13 °C for 1 h. After polymerization, the polymer was purified by precipitation from methanol, then washed several times with methanol, and dried under vacuum at room temperature. The presence of SO_2 in the polymer was confirmed by FT-IR (1311 and 1130 cm^{-1}) and ^{1}H NMR. Molecular weights and

TABLE 1 Physical Properties of the Polymers

Polysulfone	M_{w}[a]	$M_{\mathrm{w}}/M_{\mathrm{n}}$	X_{w}[b]	T_{g} (°C)[c]	T_{d} (°C)[d]
PNC2-2	39,000	2.96	91	74.8	186.7
	41,000	2.98	96	79.7	194.3
	46,000	2.62	108	76.4	210.9
	87,000	2.07	204	77.0	219.5
	95,000	1.85	223	76.7	221.0
	137,000	2.48	321	79.2	222.3
PNC2-3	69,000	2.06	157	63.6	205.7
PNC2-4	18,000	2.33	40	49.7	181.3
	44,000	2.79	97	53.2	210.4
	56,000	3.56	123	52.4	191.3
	98,000	2.27	216	42.4	179.5
PNC2-5	90,000	2.58	192	45.5	243.8
PNC2-6	96,000	3.01	199	35.5	188.9
	102,000	3.98	211	39.0	222.6
	105,000	2.46	218	40.2	176.4
	119,000	2.80	247	32.2	203.6
PNC2-7	80,000	2.35	161	34.2	213.9
PNC2-8	19,000	2.34	37	24.7	187.8
	25,000	2.43	47	29.2	188.3
	41,000	2.85	80	22.3	189.2
	80,000	2.67	157	24.1	190.5
	95,000	2.79	186	27.6	223.5

[a] Molecular weights of polymers were determined by GPC with polystyrene standards.

[b] Degree of polymerization calculated from weight-average molecular weight.

[c] Glass transition temperature T_g was obtained by DSC using a heating rate of 10 °C/min under N_2.

[d] Degradation temperature measured by thermogravimetric analysis (TGA); temperature at 10 wt % loss.

thermal properties of the polymers obtained are listed in Table 1. The polymers were soluble in chloroform, tetrahydrofuran, *N,N*-dimethylformamide, dimethyl acetamide, and dimethyl sulfoxide.

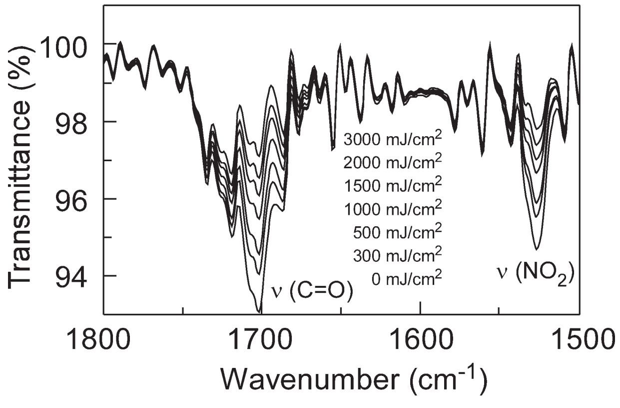


FIGURE 3 IR absorption spectra of the PNC2-4 (M_w = 56,000) film spin-coated on a KBr plate. Film thickness was 2 μm. Sample film was irradiated at 254 nm.

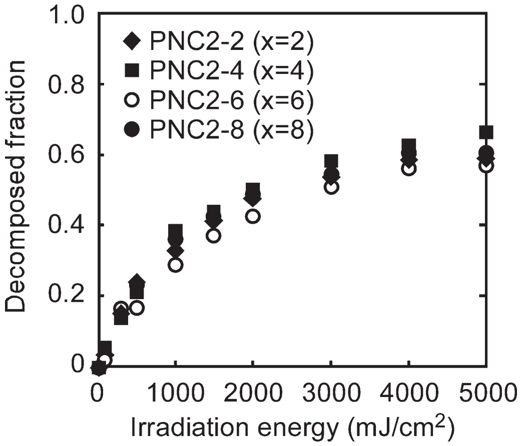


FIGURE 4 Dependence of the photochemical reaction of the photobase generator in PNC2-*x* film on irradiation energy. UV Light (254 nm) from a super-high-pressure mercury lamp was used to irradiate the film. Molecular weights (Mw) of the polymers were 87,000 for PNC2-2, 56,000 for PNC2-4, 96,000 for PNC2-6, and 80,000 for PNC2-8.

Measurements

Infrared spectra were obtained with a Jeol JIR-5500 FT-IR spectrophotometer. The weight-average molecular weight (M_w) of the polymers was determined by gel permeation

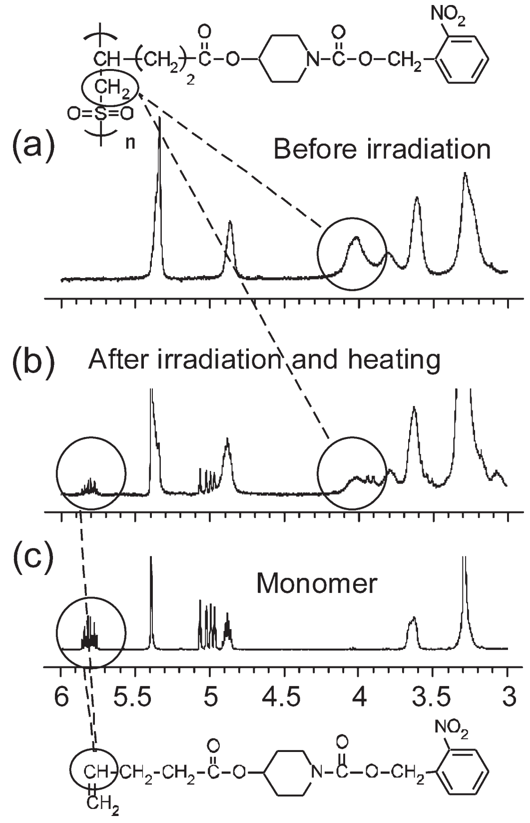


FIGURE 5 ^{1}H NMR spectra of DMSO-d_6 solutions of (a) PNC2-2 and (b) PNC2-2 after irradiation at 254 nm (1.5 J/cm^2) followed by heating at 140 °C for 15 min; and (c) PNC2-2 monomer.

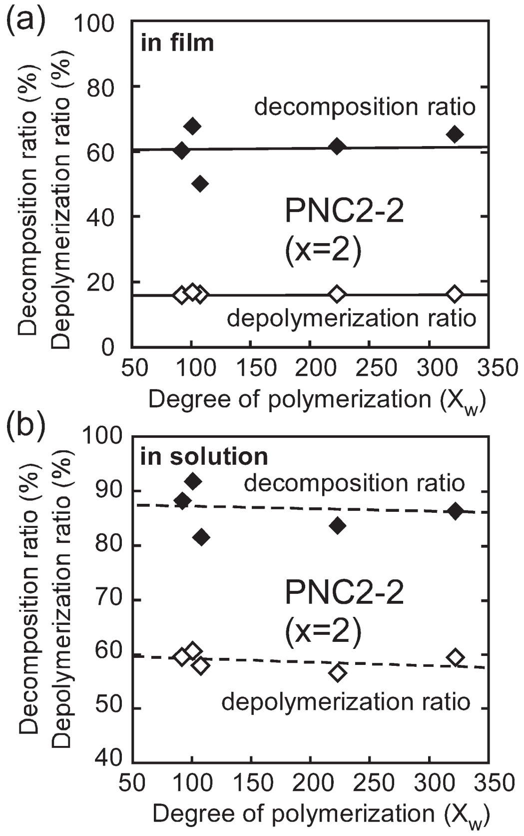


FIGURE 6 Decomposition ratio and depolymerization ratio of PNC2-2 plotted as a function of degree of polymerization (X_w). (a) Heated as a film. Polymer films were irradiated at 254 nm (1.5 J/cm^2), followed by heating at 120 °C for 30 min. (b) Heated in DMSO-d$_6$ solution. Polymer films were irradiated at 254 nm (1.5 J/cm^2) and dissolved in DMSO-d$_6$, followed by heating at 120 °C for 30 min and NMR analysis.

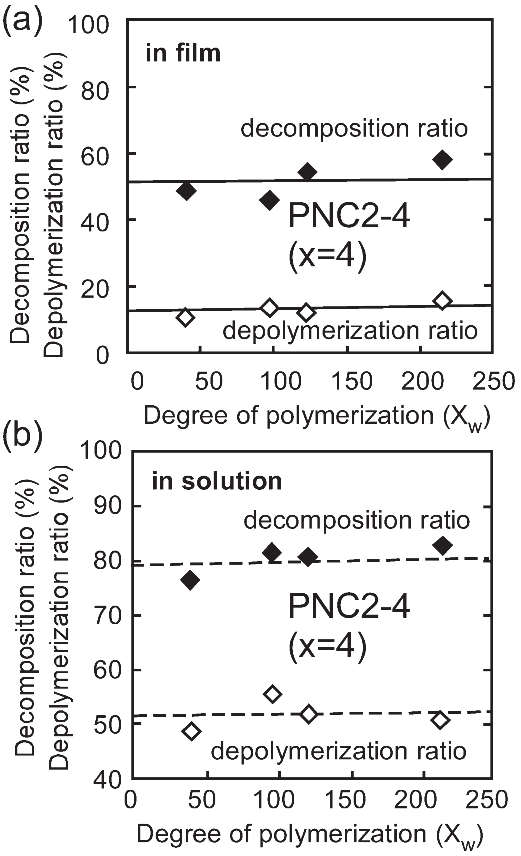


FIGURE 7 Decomposition ratio and depolymerization ratio of PNC2-4 plotted as a function of degree of polymerization (X_w). (a) Heated as a film. Polymer films were irradiated at 254 nm (1.5 J/cm^2), followed by heating at 120 °C for 30 min. (b) Heated in DMSO-d$_6$ solution. Polymer films were irradiated at 254 nm (1.5 J/cm^2) and dissolved in DMSO-d$_6$, followed by heating at 120 °C for 30 min and NMR analysis.

chromatography (GPC; Tosoh HLC-8220 with Super Multipore HZ-M column, tetrahydrofuran eluent), and glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC; Mettler, DSC822e). The decomposition temperature was confirmed by thermogravimetric analysis (TGA, TA instruments, Hi-Res TGA2950). ^{1}H NMR spectra were measured using a Jeol EX-400 spectrometer (500 MHz). The polymer film was irradiated using a 250 W super high-pressure mercury lamp (Ushio, SX-UI250HQ). The intensity of the UV light was maintained at 23 mW/cm^2 (at 254 nm). A color filter (Toshiba, UVD-36C) and an interference filter were used to obtain monochromatic light. Thicknesses of the films were measured by atomic force microscopy (AFM; Keyence, VN-8000).

RESULTS AND DISCUSSION

Photochemical Reaction of PBG in the Polymer Film

Base generation of the photobase generator (PBG) moieties in the poly(olefin sulfone)s was investigated. As shown in Scheme 1, the PBG underwent decarboxylation upon UV light irradiation to yield a secondary amine. When the polymer film was exposed to UV light, the nitro group of the PBG was converted to a nitroso group and carbon dioxide was released. The photochemical reaction was followed by monitoring the IR absorption of the carbonyl group (1700 cm^{-1}) and the nitro group (1530 cm^{-1}). Films were irradiated with UV light (254 nm) and the photochemical reaction of the PBG was examined. Figure 3 shows the IR absorption spectra of a PNC2-4 film coated on a KBr plate. The absorptions at 1700 and 1530 cm^{-1} decreased as irradiation time increased. Decomposed fractions of PBG in the polymer films PNC2-2, PNC2-4, PNC2-6, and PNC2-8 are plotted as a function of irradiation energy in Figure 4. The decomposition fraction increased with irradiation energy. Decomposition of the PBG moiety in the side-chain was not affected by spacer length.

Effect of Degree of Polymerization on Photoinduced Depolymerization

The films of PNC2-*x* (2-μm thick) were transparent and colorless. When a PNC2-*x* film was heated without

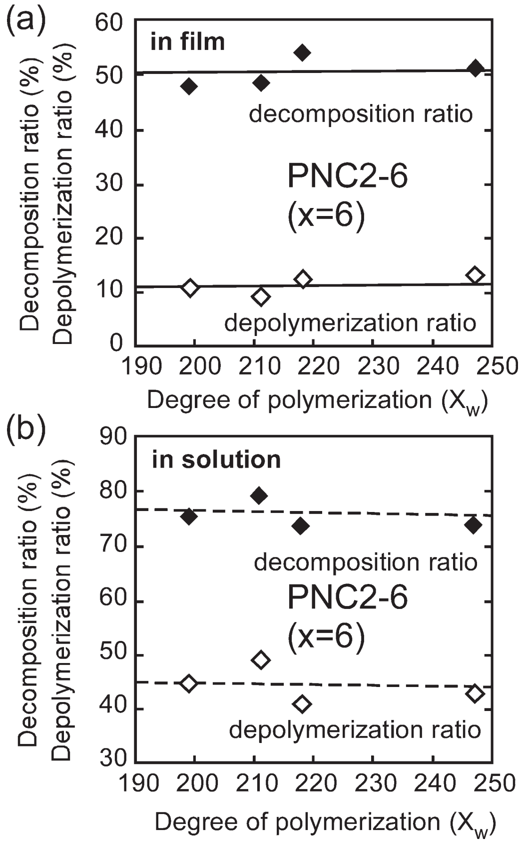


FIGURE 8 Decomposition ratio and depolymerization ratio of PNC2-6 plotted as a function of degree of polymerization (X_w). (a) Heated as a film. Polymer films were irradiated at 254 nm (1.5 J/cm^2), followed by heating at 120 °C for 30 min. (b) Heated in DMSO-d$_6$ solution. Polymer films were irradiated at 254 nm (1.5 J/cm^2) and dissolved in DMSO-d$_6$, followed by heating at 120 °C for 30 min and NMR analysis.

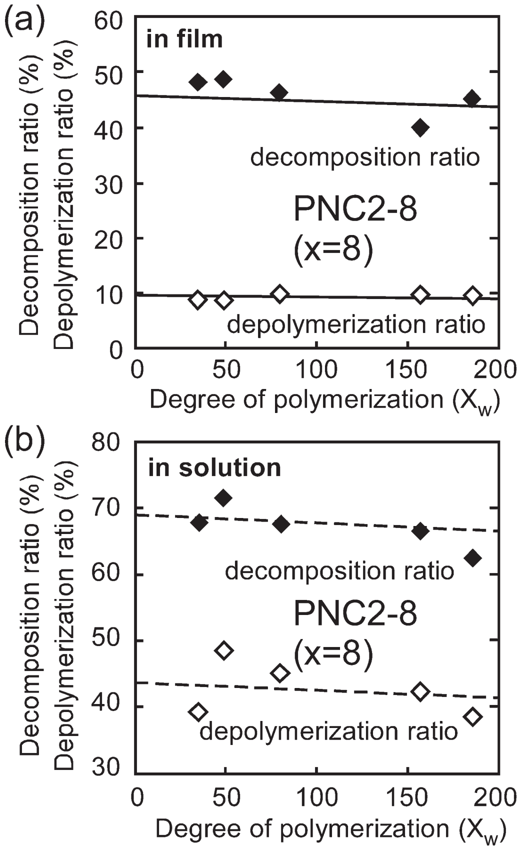


FIGURE 9 Decomposition ratio and depolymerization ratio of PNC2-8 plotted as a function of degree of polymerization (X_w). (a) Heated as a film. Polymer films were irradiated at 254 nm (1.5 J/cm^2), followed by heating at 120 °C for 30 min. (b) Heated in DMSO-d$_6$ solution. Polymer films were irradiated at 254 nm (1.5 J/cm^2) and dissolved in DMSO-d$_6$, followed by heating at 120 °C for 30 min and NMR analysis.

photoirradiation at 140 °C for 15 min, no change was observed. In contrast, when a PNC2-*x* film was irradiated with 254-nm UV light, the film became slightly yellow due to absorption of 2-nitrosobenzaldehyde produced by photoreaction of the PBG. At this stage, no change was observed on the surface of the film except for color. After the PNC2-*x* film was irradiated and then heated at 140 °C for 15 min, the film became soluble in methanol.

Figure 5 shows the NMR spectra of PNC2-2 without light irradiation and after 254 nm light irradiation of 1.5 J/cm^2 and heating at 140 °C for 15 min, and PNC2-2 monomer. After photoirradiation and heating, proton signals of the olefin group appeared. The decomposition ratio was estimated from the decrease in signal of the methylene protons on the polymer main chain (4 ppm), and the depolymerization ratio was obtained from the increase in the signal of the olefin protons (5.8 ppm). After 254 nm irradiation of 1.5 J/cm^2 and post-exposure heating (120 °C, 30 min), the film was dissolved in deuterated dimethylsulfoxide (DMSO-d$_6$) and ^{1}H-NMR spectra were obtained. The decomposition and depolymerization ratios in DMSO solution as well as those in polymer films were measured. Polymer films were irradiated with 254 nm UV light (1.5 J/cm^2) and dissolved in DMSO-d$_6$. The solution in the NMR tube then was immersed in an oil bath at 120 °C for 30 min.

The effect of degree of polymerization on the photoinduced depolymerization of PNC2-*x* was investigated. The degree of polymerization (X_w) is defined as:

$$X_w = \frac{\text{Weight}-\text{average molecular weight}\,(M_w)\,\text{measured by GPC}}{\text{Molecular weight of the olefin monomer and sulfur dioxide}}$$

Degree of polymerization of the polymers used in this study is listed in Table 1. The decomposition and depolymerization ratios in PNC2-*x* as a function of the degree of polymerization are shown in Figures 6–9. Both the decomposition ratio and depolymerization ratio were higher in solution than in films and were nearly independent of the degree of polymerization regardless of the condition of the polymer (in film or in solution).

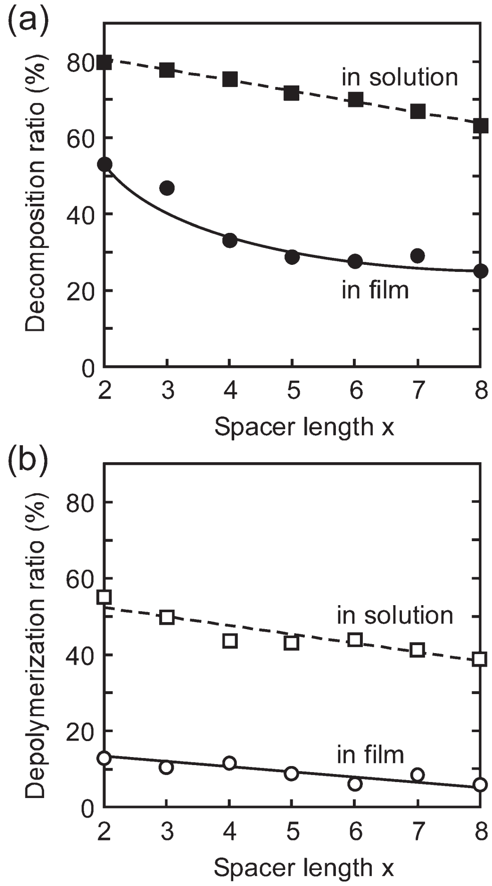


FIGURE 10 (a) Decomposition ratio of PNC2-*x* as a function of spacer length x (x = 2–8). Polymer films were irradiated at 254 nm (1.5 J/cm^2), followed by heating at 120 °C for 30 min (■) in DMSO-d$_6$ solution or (•) as a film. (b) Depolymerization ratio of PNC2-*x* as a function of spacer length x (x = 2–8). Polymer films were irradiated at 254 nm (1.5 J/cm^2), followed by heating at 120 °C for 30 min in (□) DMSO-d$_6$ solution or (○) as a film.

Effect of Spacer-Chain Length on Photoinduced Depolymerization of Poly(olefin sulfone) films

The decomposition ratios and depolymerization ratios of PNC2-*x* films after UV irradiation and heating are plotted as a function of spacer length (the number of the methylene units in the spacer chain) in Figure 10(a). Approximately 30–50% of the polymer decomposed during the post-exposure heating. With an increase in spacer chain length from x = 2 to x=4, the decomposition ratio decreased and reached to a constant value of 30%. Although flexible spacer chain length increased, decomposition was depressed. There seemed no evidence of the affection of the mobility of the base moiety. The decrease in the decomposition ratio was considered to be attributed to an increase in steric hindrance around the polymer main chain. As the length of the spacer chain increased, proton abstraction was inhibited. The depolymerization ratio decreased slightly with spacer chain length [Fig. 10(b)]. Approximately 32% of the decomposed polymer was converted to monomers in film.

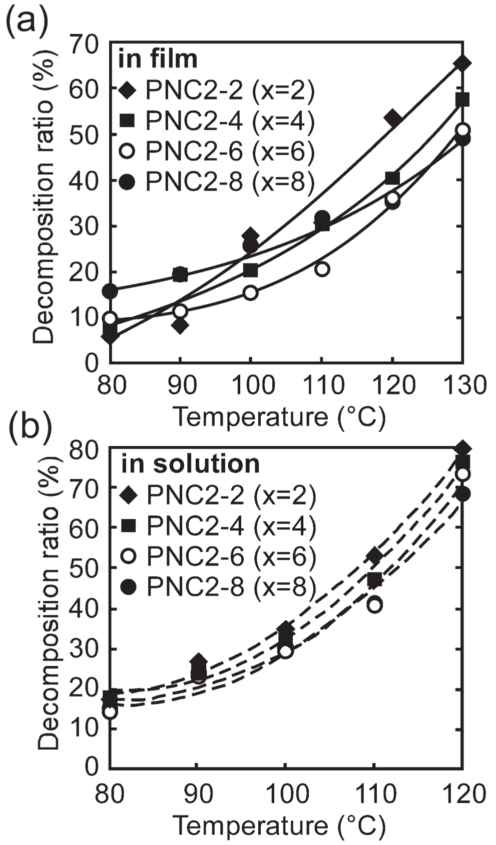


FIGURE 11 (a) Decomposition ratio of PNC2-*x* heated after UV irradiation (254 nm and 1.5 J/cm^2) as a film as a function of post-exposure heating temperature. (b) Depolymerization ratio of PNC2-*x* film [after irradiation at 254 nm (1.5 J/cm^2), dissolution of the film in DMSO-d$_6$, and heating] as a function of post-exposure heating temperature. Molecular weights (M_w) of the polymers were 87,000 for PNC2-2, 56,000 for PNC2-4, 96,000 in PNC2-6, and 80,000 in PNC2-8.

The decomposition and depolymerization ratios of the polymers in solution and in the film state also were measured. Both decomposition and depolymerization ratios were greater in polymers heated in solution compared to those heated as films. The decomposition and depolymerization ratios of the polymers heated in solution decreased with increasing spacer chain length. Dependences of decomposition and depolymerization ratios on spacer length were similar in solution and as film. Although mobility of the photogenerated amine moieties was higher in solution, the decomposition reaction did not depend on the spacer length. The effect of steric hindrance of the spacer chain on proton abstraction on the polymer main chain may be large enough to cancel out the increase in mobility of the amine moieties.

The decomposition ratios of PNC2-*x* are plotted as a function of post-exposure heating temperature in Figure 11. The decomposition ratio increased with baking temperature. No effect of chain length on the temperature dependence of the decomposition ratio was observed either in films or in

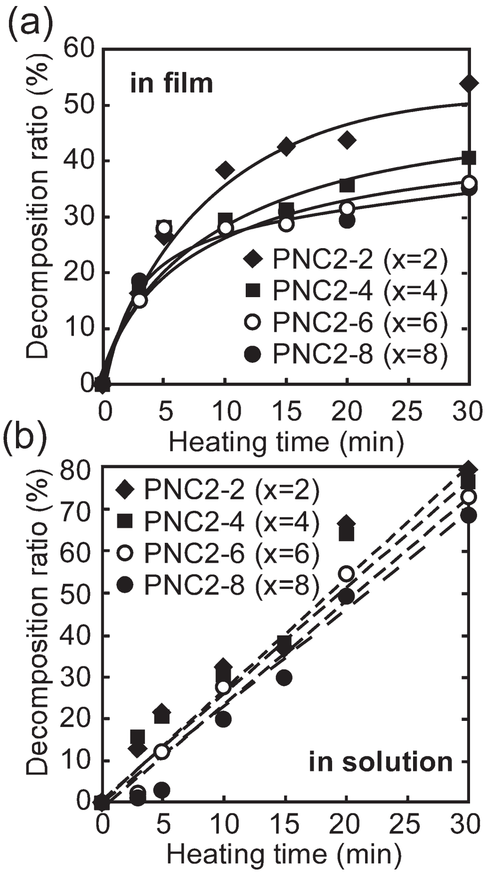


FIGURE 12 (a) Decomposition ratio of PNC2-*x* heated after UV irradiation (254 nm UV light of 1.5 J/cm^2) in film as a function of post-exposure heating time. The temperature was maintained at 120 °C. (b) Depolymerization ratio of PNC2-*x* film [after irradiation at 254 nm (1.5 J/cm^2), dissolution of the film in DMSO-d_6, and heating] as a function of post-exposure heating time. The temperature was maintained at 120 °C. Molecular weights (Mw) of the polymers were 87,000 in PNC2-2, 56,000 in PNC2-4, 96,000 in PNC2-6, and 80,000 in PNC2-8.

solution. Figure 12 shows the dependence of decomposition ratio of PNC2-*x* on post-exposure heating time. Although the decomposition ratio of PNC2-2 was slightly greater than those of PNC-*x* with longer side-chains, almost no difference was observed in PNC2-*x* polymers.

CONCLUSIONS

Photoinduced depolymerization of poly(olefin sulfone)s that possess photobase generators in a side-chain was investigated. The effect of the length of the alkyl side chain connecting PBG and the polymer main chain on photoinduced depolymerization was examined. Polymers with different spacer-lengths and different degrees of polymerization were prepared subjected to photoinduced degradation. The length of the spacer of the photodegradable side-chain of the poly(olefin sulfone)s did not significantly affect degradation behavior. This may be due to cancellation of the increase in the freedom of motion of the reactive chromophore photobase generator in the side-chain by the increase in steric hindrance of the connecting spacer unit between the photobase-generating moiety and the polymer main chain.

ACKNOWLEDGMENT

This work was supported by the Suzuki Foundation.

REFERENCES AND NOTES

1 H. Yaguchi, T. Sasaki, *Macromolecules* **2007**, *40*, 9332–9338.

2 T. Sasaki, H. Yaguchi, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 602–613.

3 T. Sasaki, T. Kondo, M. Noro, K. Saida, H. Yaguchi, Y. Naka, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 1462–1468.

4 M. Matsuda, *Yuuki Gousei Kagaku* **1967**, *25*, 1151–1161.

5 E. R. Cais, H. J. O'Donnell, A. F. Bovey, *Macromolecules* **1977**, *10*, 254–260.

6 T. Shinoda, T. Nishiwaki, H. Inoue, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 2760–2766.

7 J. E. Urankar, J. M. J. Fréchet, *Chem. Mater.* **1997**, *9*, 2861–2868.

8 J. E. Urankar, I. Brehm, J. Q. Niu, J. M. J. Fréchet, *Macromolecules* **1997**, *30*, 1304–1310.

9 R. B. Harkness, K. Takeuchi, M. Tachikawa, *Polym. Adv. Technol.* **1999**, *10*, 669–677.