

Preparation and Properties of Epoxy Copolymers Containing Oxime-urethane Groups as Photobase Generators

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Epoxy copolymers containing oxime urethane groups were prepared by the polymerization of glycidyl methacrylate and *N*-[5-(benzophenoneoximinocarbonylamino)pentanyl]maleimide (BOPM). Their physical properties were characterized by GPC, DSC and TGA analyses. Photochemical changes of the copolymers were studied by UV, IR spectroscopy, and contact angle measurements. A photoinduced cross-linking reaction in copolymer films was observed by measuring the insoluble fraction. Irradiation of the copolymers at 254 nm UV light leads to the formation of pendant amino groups by photodissociation of the oxime-urethane groups. Treatment of the amino groups with HCl resulted in the formation of ammonium salts, which changed the polymer surface to be hydrophilic. An insoluble fraction of the copolymers increased with irradiation time, heating time, and heating temperature. Cross-linking of the epoxy resin effectively catalyzed by the photogenerated pendant amines upon heating.

Introduction

The light induced polymerization process is widely used in industries such as photocurable coatings, UV inks, paints, printing inks and adhesives. Most of the technically applied photochemical processes are based on free radical photo-reactions. However, the ionic photopolymerization process has several advantages over the radical photopolymerization process such as no oxygen inhibition, induction of ring opening polymerization, and no volume contraction during polymerization. It appears that in addition to the free radical process, the ionic photopolymerization process will be increasingly applied in the future.

Amines are very important compounds for thermal cross-linking reactions of epoxy resins in adhesives, paints, and coatings applications. However, the mixture of epoxy resins and amines is very unstable due to the high reactivity of the amines. Therefore, photoinduced amine formation and its application to epoxy resins are a very important new concept in advanced industrial technology.^{1,2} However, only a few have been reported in the thermal curing reaction of epoxy copolymers by the use of photochemically produced amines.

The chemical systems such as cobalt-amine complex,³ ammonium salts,⁴ *o*-nitrobenzoyl carbamates and urethanes,⁵⁻⁷ *o*-acyloximes,⁸ blocked aniline,^{1a} and benzoin carbamate⁹ have been studied to produce free amines photochemically, which initiate anionic polymerization reactions, such as curing reactions of epoxy resins. Kutal and Willson³ reported a thermal crosslinking reaction of poly(glycidyl methacrylate-*co*-ethyl methacrylate) by the photochemically produced ammonia from a cobalt-amine complex. Tsunooka *et al.*¹⁰ reported crosslinking of glycidyl methacrylate copolymer

films containing *o*-acyloxyimino groups by the use of photochemically produced pendant amino groups. Nishikubo *et al.*¹ reported the thermal curing reaction of epoxy resins and polyurethane oligomers using photogenerated polyfunctional amine or thiol.

In previous studies, we reported that the photolysis of oxime-urethane derivatives led to the photochemical formation of amines which induce a cross-linking reaction of epoxy resin upon heating.¹¹⁻¹² The photochemical and photo-physical phenomena of the oxime-urethane derivative was investigated using a laser flash photolysis study.¹³ The copolymer containing oxime-urethane groups, which led to the formation of pendant aromatic amines photochemically, was used for an image recording material via a diazo coupling reaction.¹⁴

The copolymers of glycidyl methacrylate (GMA) and benzophenoneoxime allyl urethane (BAU), a monomer containing oxime-urethane group, effectively cross-linked by the photochemically produced pendant amines.¹² However, no more than 3% of oxime-urethane groups could be incorporated into the polymer chains due to the low polymerization reactivity of allyl groups. In order to understand more about the photoinduced thermal curing reaction of epoxy resin containing oxime-urethane groups, we prepared *N*-[5-(benzophenoneoximinocarbonylamino)pentanyl]maleimide (BOPM), a monomer containing oxime-urethane and maleimide polymerizable group,¹⁵ and studied the thermal curing reaction of the copolymer, poly(GMA-*co*-BOPM), by the use of photochemically produced pendant amines.

Experimental Section

Materials. 6-aminocaproic acid and benzophenone were purchased from Aldrich Chemical Co. Maleic anhydride and sodium azide were obtained from Yakuri and Wako Chemi-

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cal Co., respectively. Thionyl chloride was purified by distillation in the presence of quinoline. GMA was purchased from Fluka Chemical Company and used after vacuum distillation. General solvents such as ethyl acetate, chloroform, methanol, THF were purified by distillation. Benzophenone oxime (BPO) was prepared by the reported procedure.¹⁶

Instruments. ¹H nuclear magnetic spectra were recorded on a Bruker 300 MHz ASX-32 FT-NMR spectrometer. Infrared (IR) spectra were obtained with the use of Shimadzu model FTIR-8300 spectrophotometer. Ultra-violet (UV) spectra were taken on a Jasco model V-530 spectrophotometer. Differential scanning calorimetry (DSC) measurements were carried out with Dupont model 910 thermal analyzer under N₂ atmosphere at a heating rate of 10 °C/min. Thermal stability was examined on a TA instruments model 2100 at a heating rate of 20 °C/min under nitrogen atmosphere. Gel permeation chromatography (GPC) was carried out with a Young-in model 910 solvent delivery module equipped with a Shimadzu UVD-2 detector. Intrinsic viscosity was measured with an Ostwald viscometer (size 25, No. 244 or 414) immersed in a constant temperature bath at 25 °C. Contact angle was measured with an ERMA model G-I contact anglemeter. Irradiations were carried out in a Rayonet photochemical reactor (The Southern New England UV Company model RPR-100 or 208) equipped with 254 nm fluorescent lamps. Light intensity measured by a Vilber Lourmat radiometer model VLX-3W was 2.3 mW/cm² at 254 nm.

Synthesis of Monomer.

***N*-(5-Carboxypentanyl)maleamic acid (CPMA):** A solution of 6-aminocaproic acid (2.62 g, 20 mmol) in 10 mL of water was added dropwise to a solution of maleic anhydride (1.96 g, 20 mmol) in 10 mL of DMF and stirred for 4 hours at room temperature. The reaction mixture was poured into 100 mL of distilled water. The precipitate was filtered and dried. The product was purified by recrystallization from methanol. The yield and melting point were 75% (3.4 g) and 167-169 °C, respectively. IR (KBr pellet, cm⁻¹); 3309 (s; N-H), 3500-2500 (s; COOH), 2946 (w; aliphatic C-H), 1710 (s; acid C=O), 1680 (m; amide II band), 1621 (w; vinyl), 1507 (s; amide III band). ¹H NMR (DMSO-d₆, δ, ppm); 9.15 (NH, 1H), 6.41, 6.37 (doublet, =CH, 1H), 6.25, 6.21 (doublet, =CH, 1H), 3.16 (quartet, -CH₂-NHCO, 2H), 2.22 (triplet, -CH₂-COOH, 2H), 1.52-1.41 (multiplet, -(CH₂)₂-, 4H), 1.31-1.25 (multiplet, -CH₂-, 2H).

***N*-(5-Carboxypentanyl)maleimide (CPMI):** A mixture of CPMA (4.58 g, 20 mmol) and sodium acetate (1.96 g, 24 mmol) in 40 mL of acetic anhydride was stirred for 10 hours at 100 °C under N₂ atmosphere. After the reaction was finished, excess acetic anhydride was removed by vacuum distillation at 80 °C. The remaining small amount of acetic anhydride was further removed by vacuum distillation after addition of 10 mL of toluene. The crude product was isolated by column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) and then recrystallized from methylene chloride / *n*-hexane (1 : 2). The yield and melting point were 30% (1.27 g) and 82-84 °C, respectively. IR (KBr pellet, cm⁻¹); 3300-2500 (s; COOH), 2941, 2869 (m; aliphatic C-H), 1768

(w; imide C=O), 1705 (s; C=O). ¹H NMR (CDCl₃, δ, ppm); 11.16 (broad, -COOH, 1H), 6.69 (singlet, =CH, 2H), 3.52 (triplet, N-CH₂-, 2H), 2.35 (triplet, -CH₂-C=O, 2H), 1.57-1.72 (multiplet, -(CH₂)₂-, 4H), 1.31-1.39 (multiplet, -CH₂-, 2H).

***N*-[5-(Chlorocarbonyl)pentanyl]maleimide (CCPMI):** A mixture of CPMI (0.25 g, 1 mmol) and thionyl chloride (5 mL, 1 mmol) was refluxed for 4 hours at 70 °C under N₂ atmosphere. After the reaction was finished, thionyl chloride was removed by distillation under reduced pressure at 60 °C. The small amount of remaining thionyl chloride was further removed by vacuum distillation after dissolving the reaction mixture in 10 mL of petroleum ether. The residue was used for the next reaction step without further purification. The yield and melting point were 63% (0.17 g) and 76-78 °C, respectively.

***N*-[5-(Azidocarbonyl)pentanyl]maleimide (ACPM):** A solution of sodium azide (0.16 g, 2.4 mmol) in 5 mL of H₂O was added dropwise to a solution of CCPMI (0.5 g, 2 mmol) in 8 mL of methylene chloride at 0 °C and stirred for 4 hours at the same temperature under nitrogen. The reaction mixture was washed with water (40 mL) three times, and dried over anhydrous magnesium sulfate. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (ethyl acetate : *n*-hexane = 1 : 2) and then recrystallization from methylene chloride / *n*-hexane. The yield and melting point were 80% (0.4 g) and 78-80 °C, respectively. IR (KBr pellet, cm⁻¹); 2146 (m, N₃), 1701 (s, azide C=O), 1680, 1550, 1406, 1236, 840, 694. ¹H NMR (CDCl₃, δ, ppm); 6.70 (singlet; =CH, 2H), 3.50-3.55 (triplet, N-CH₂-, 2H), 3.19-3.26 (multiplet, -CH₂CON₃, 2H), 1.63-1.51 (multiplet, -(CH₂)₂-, 4H), 1.35-1.26 (multiplet, -CH₂-, 2H).

***N*-[5-(Benzophenoneoximinocarbonylamino)pentanyl]maleimide (BOPM):** ACPM (0.6 g, 5 mmol) was added to a solution of BPO (1 g, 5 mmol) and dibutyltin dilaurate (DBTDL, 0.15 mL) and the solution was refluxed for 6 hours at 110 °C. After evaporation of solvent, the product was isolated by recrystallization from acetone. The yield and melting point were 69% (0.69 g) and 78 °C, respectively. IR (KBr pellet, cm⁻¹); 3381 (sharp; N-H), 2947 (m; aliphatic C-H), 1743 (s; imide C=O), 1704 (s; urethane C=O), 1512 (s; aromatic), 1242 (m; C-N), 961, 827, 696 (s; aromatic). ¹H NMR (CDCl₃, δ, ppm); 7.31-7.51 (multiplet, aromatic, 10H), 6.66 (singlet, =CH, 2H), 6.39 (N-H, 1H), 3.51-3.67 (triplet, N-CH₂-, 2H), 3.24-3.40 (quartet, NH-CH₂-, 2H), 1.68-1.60 (multiplet, -(CH₂)₂-, 4H), 1.41-1.26 (multiplet, -CH₂-, 2H).

Copolymerization. The typical procedure is as follows. A solution of GMA (1.32 mL, 10 mmol), a corresponding amount of BOPM as shown in Table 1, and AIBN (1 wt%) in THF was charged into a capped tube (10 mL). The mixture was purged with nitrogen for 20 min and the tube was sealed under nitrogen. Polymerization was carried out at 60 °C for 24 hours. The resulting polymer was isolated by precipitation into methanol and purified by reprecipitation from THF (10 mL) into methanol. Yield, 75-80%.

Measurements.

Insoluble fraction: A solution of copolymer (0.2 g) in 4.3 mL of THF was prepared and 4 drops (*ca.* 0.04 mL) of this

solution were placed on the aluminum plate (3 × 7 cm). It was spread evenly by pushing another aluminum plate. The film on the aluminum plate was dried in a vacuum at room temperature and irradiated with 254 nm UV light. The film was heated and immersed in THF for 50 sec.

The weight of the plate (W_3) was measured after drying at reduced pressure. The insoluble fraction of the copolymer film was determined from the following equation:

$$\text{Insoluble fraction (\%)} = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

Where, W_1 : weight of the uncoated plate, W_2 : weight of the coated plate, and W_3 : weight of the coated plate after curing and development.

Contact angle: 8 drops of 5 wt% of copolymer (0.2 g) in THF (4.3 mL) were coated on slide glass (2.5 × 5 cm). The film on the glass plate after drying under reduced pressure was irradiated. The irradiated film on the glass plate was dipped 0.1 N HCl for 1 min, washed 3 times with distilled water, and then dried under reduced pressure. 0.01 mL of distilled water was dropped on the surface of the film and contact angle before and after dipping in HCl was measured after 30 sec. The contact angle was measured at five different sites on each specimen, and the mean value was calculated.

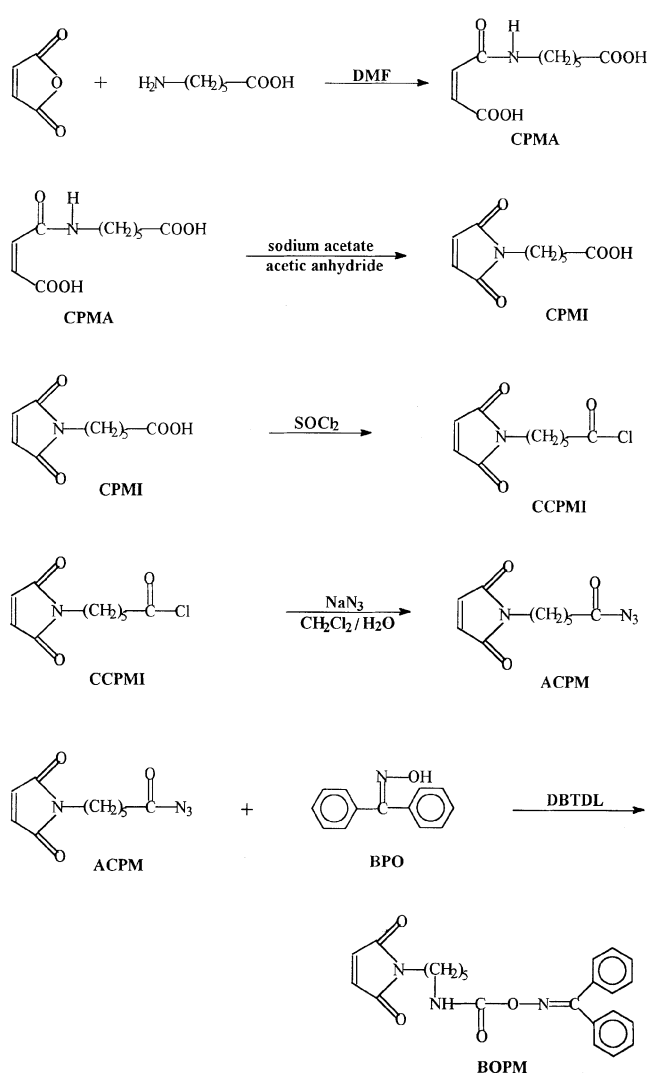
UV and IR absorption spectral changes: A copolymer was dissolved in THF and the absorbance at 254 nm was adjusted to 1.9. UV absorption spectra were obtained with various irradiation times at 254 nm UV light. A transparent KBr pellet containing copolymer II was irradiated with 254 nm and IR absorption spectra were obtained with various irradiation times.

Results and Discussion

Monomer Synthesis and Polymerization. *N*-Substituted maleimides bearing pendant photofunctional group are readily copolymerized with vinyl monomers under the radical polymerization conditions. The resultant polymers are known to exhibit high T_g s due to the rigid imide rings in their backbones. Because of the feasibility of their radical polymerization and the excellent thermal stability of the resultant polymers, many interesting compounds have been attached to them and their polymerization was studied extensively.¹⁵

A synthetic route for the preparation of a monomer containing oxime-urethane groups is shown in Scheme 1. Chemical structure of the compounds was characterized by spectroscopic methods. CPMA was prepared by the reaction of maleic anhydride and 6-aminocaproic acid. The mixture should be cooled to room temperature since some heat was generated during the reaction. CPMA was precipitated in the course of the reaction, and it was purified by recrystallization from methanol.

CPMI was prepared by the dehydration reaction of CPMA with acetic anhydride and sodium acetate. Acetic anhydride can be removed by azeotropic distillation with toluene or xylene. Acetic anhydride should be completely removed since

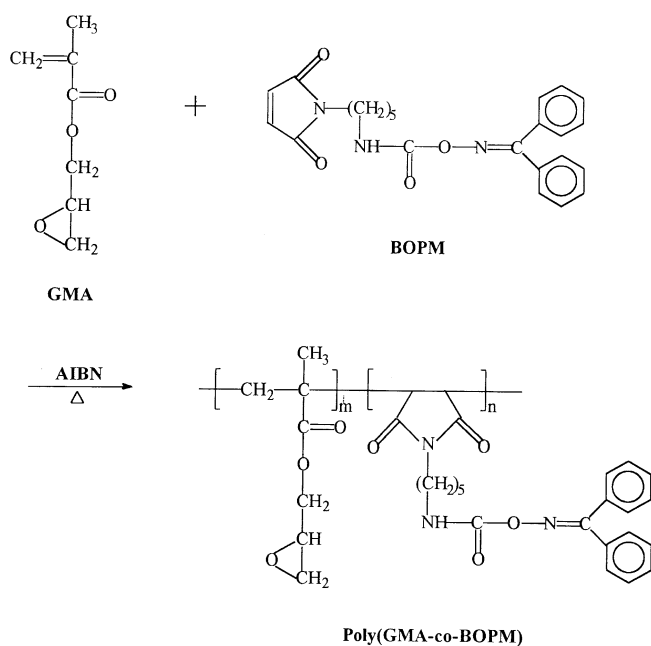


Scheme 1

it incorporated to the product during column chromatography. Aromatic maleimide derivatives can be separated by precipitation from the reaction mixture into water quantitatively, but aliphatic maleimide derivatives cannot be separated by this method.

CCPMI was prepared by a chlorination reaction of CPMI with thionyl chloride. Unreacted thionyl chloride was removed under reduced pressure and the remaining solid was used without further purification since CCPMI is moisture sensitive. ACPM was prepared by the reaction of CCPMI with sodium azide. ACPM in methylene chloride was reacted with sodium azide in water. Reaction temperature should be maintained below 0 °C. Reaction occurred at the interface of an aqueous and an organic layer. ACPM was isolated as a white solid at room temperature, but slowly decomposes above 50 °C.

BOPM, a monomer containing oxime-urethane group, was prepared by a reaction of ACPM with benzophenone oxime in the presence of DBTDL as a catalyst. The product was isolated by column chromatography, and crystallization from acetone yielded white crystals. DSC analysis of BOPM shows



a sharp endotherm ($\Delta H = 42.48$ J/g) at 78 °C due to the melting of this compound.

Copolymerization of BOPM with GMA was carried out with 1 wt% of AIBN in THF (Scheme 2). The polymers are soluble in THF and purified by double precipitation in MeOH. The polymerization conditions and physical properties of the copolymers are summarized in Table 1. Intrinsic viscosity measured in DMF was in the range of 0.39-0.46. The molecular weights and polydispersity measured by GPC in THF ranged between 38000-48000 and 1.9-2.6, respectively. The contents of BOPM units in the copolymer measured by 300 MHz NMR spectroscopy was nearly similar to the amounts of BOPM in feed. Conversion of BOPM ranged 85-95% indicating the high reactivity of BOPM monomer in copolymerization with GMA.

Thermal stability of the copolymer was examined by DSC and TGA. The glass transition temperature of the copolymers was in the range of 70-80 °C. T_m was not observed and all copolymers began to decompose around 205 °C. The amount of maleimide units in the copolymer does not significantly change thermal properties of the copolymers.

Photochemical Changes. Photochemical changes of the copolymers were studied by UV, IR spectroscopy and contact angle measurements. Figure 1 shows UV spectral changes of copolymer III in THF upon irradiation with 254 nm UV light. An isosbestic point was observed at 283 nm. An ab-

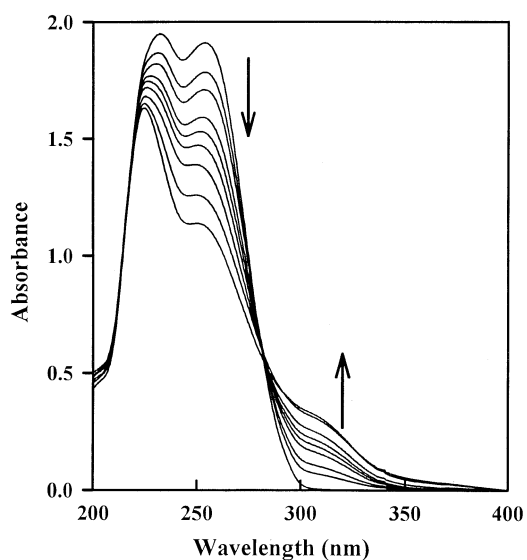


Figure 1. UV absorption spectral changes of copolymer III in THF with irradiation time of 0, 2, 4, 6, 8, 10, 12, 15, 20 min in the direction of the arrows, respectively.

sorption band around 250 nm due to π - π^* transition decreased with irradiation, while that around 320 nm increased. This is due to the formation of azine type of compounds as reported previously.^{11,12} The spectral changes in solution are similar to that of the film state.

A difference IR spectrum of copolymer III film on the KBr pellet between before and after irradiation of 254 nm UV light for 50 min showed that the absorption band at 3417, 1735 cm^{-1} increased, while that of 1257 cm^{-1} decreased. Figure 2 shows the changes in absorbance of copolymer II film as a function of irradiation time in aerobic conditions. An increase in the absorption band at 3417 cm^{-1} indicates the formation of amino groups on irradiation. The absorption band at 1735 cm^{-1} due to carbonyl group and 1492 cm^{-1} due to urethane group increased gradually on UV irradiation. This is due to the photooxidation reaction of the copolymer. Absorption band at 1257 cm^{-1} results from interaction between the N-H bending and C-N stretching¹⁷ decreased on irradiation indicating photocleavage of urethane C-N bond.

Changes of the surface properties of the copolymer film on irradiation were studied by contact angle measurements. Figure 3 shows the contact angle of copolymer III film as a function of irradiation time. The contact angle decreased from 72 to 68 with 40 min of irradiation, indicating that the polymer surface changed to a hydrophilic property. This data shows that the amino groups produced by photodecomposi-

Table 1. Polymerization conditions and physical properties of copolymers

Copolymer	GMA (mL)	BOPM (g)	AIBN (mg)	THF (mL)	BOPM (mole%)		Yield (%)	$[\eta]^c$	\overline{M}_w^b ($\times 10^3$)	$\overline{M}_n/\overline{M}_w$	T_g (°C)	T_d (°C)
					in feed	in copolymer ^a						
I	1.32	0.20	16.2	2.7	4.8	4.5	80	0.46	38.4	1.88	89	208
II	1.32	0.41	18.3	3.2	9.1	7.9	77	0.43	44.8	2.06	75	207
III	1.32	0.81	22.3	3.7	16.7	15.7	75	0.39	48.5	2.55	70	205

^aDetermined from 300 MHz NMR spectra. ^bMeasured by GPC in THF. Calibrated by using polystyrene standards. ^cMeasured in DMF: 0.5 g/dl.

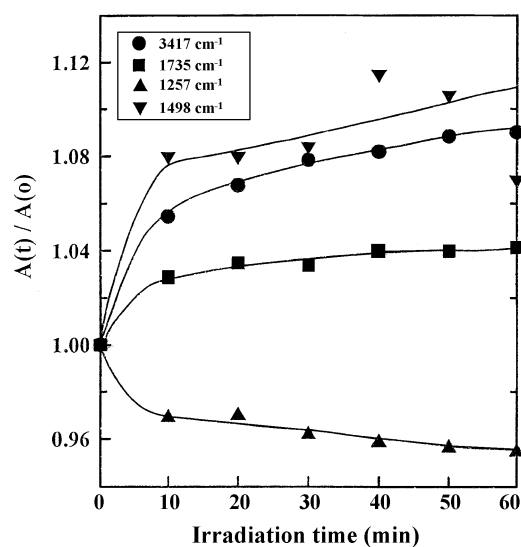


Figure 2. Changes in absorbance of copolymer II as a function of irradiation time in air (KBr pellet).

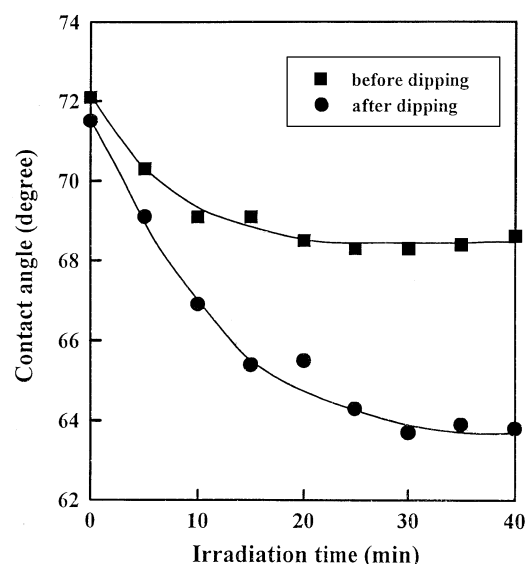


Figure 3. Changes of contact angle of copolymer III film as a function of irradiation time on irradiation with 254 nm UV light; dipping solvent, 0.1 N HCl; dipping time, 1 min.

tion of oxime-urethane groups change the surface of the polymer film to become more hydrophilic. Contact angle of the irradiated polymer film after treatment with 0.1 N HCl decreased from 71.5 to 64 with 40 min of irradiation. Thus, the contact angle of the copolymer film after treatment of HCl decreased more effectively than that before treatment. This is because the polymeric ammonium salts produced by the reaction of amino groups with HCl effectively change the surface property of the polymer making it more hydrophilic.

Cross-linking Reaction. Solubility changes on irradiation of copolymers containing oxime-urethane groups were studied by the measurements of insoluble fractions.

Figure 4 shows the effect of heating temperature on the insoluble fraction of copolymer II film in THF before and

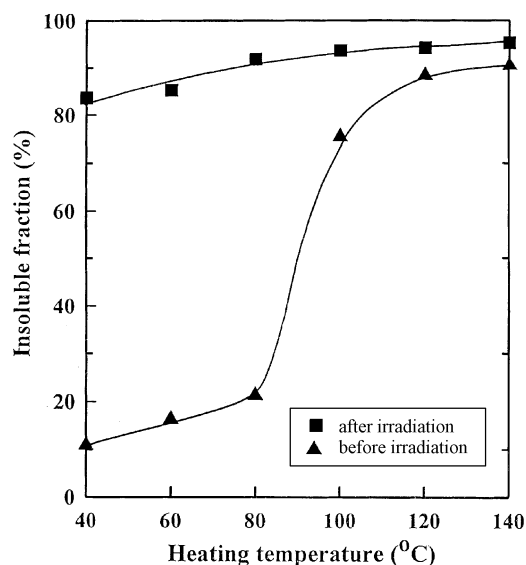


Figure 4. Effect of heating temperature on the insoluble fraction of copolymer II film: irradiation time, 50 min; heating time, 40 min.

after irradiation with 254 nm of UV light for 40 min. Insoluble fraction of the non-irradiated film slightly increased between 40 to 80 °C, while it increases dramatically between 80-100 °C and remains constant above 120 °C. The increase of the insoluble fraction between 80-100 °C is due to the mobility changes of the polymer chain at temperatures below and above T_g .¹² However, the insoluble fraction of the irradiated film was in the range of 85-95% at 40-140 °C. This indicates that a thermal crosslinking reaction of the copolymer was catalyzed by the amines produced from the photolysed pendant oxime-urethane groups.

Insoluble fraction of copolymer III film as a function of heating time at a different irradiation time is shown in Figure 5. An insoluble fraction of the film without irradiation reached

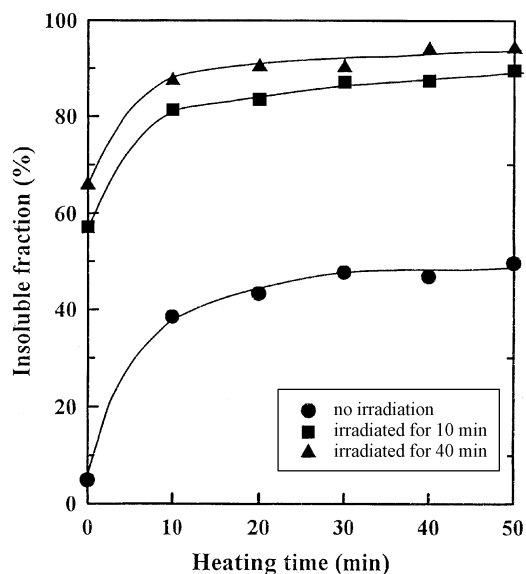


Figure 5. Insoluble fraction of copolymer III film as a function of heating time at various irradiation time: heating temperature, 90 °C.

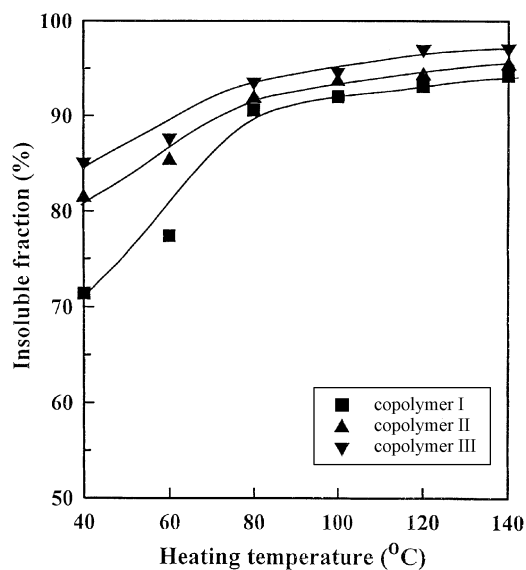


Figure 6. Effect of heating temperature on photo-crosslinking of copolymer films: irradiation time, 50 min; heating time, 45 min.

40-45% above 10 min of heating time at 90 °C. However, it increased with irradiation time and heating time. After 10 min of heating, an appreciable increase in the insoluble fraction, up to 90%, was observed for the film irradiated for 40 min.

Figure 6 shows the effect of heating temperature on the crosslinking of the three copolymer films upon irradiation for 50 min. Insoluble fraction gradually increased with heating temperature. The relative rate of the cross-linking reaction increases in the order: copolymer I < II < III. This shows that the amount of BOPM units in the copolymer increases the rate of the crosslinking reaction, but the difference is not

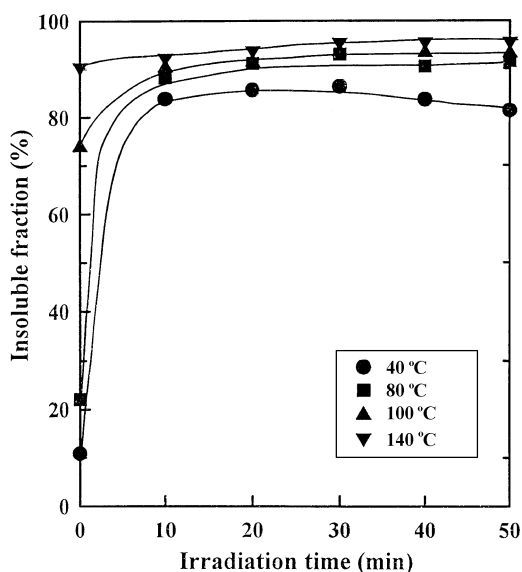
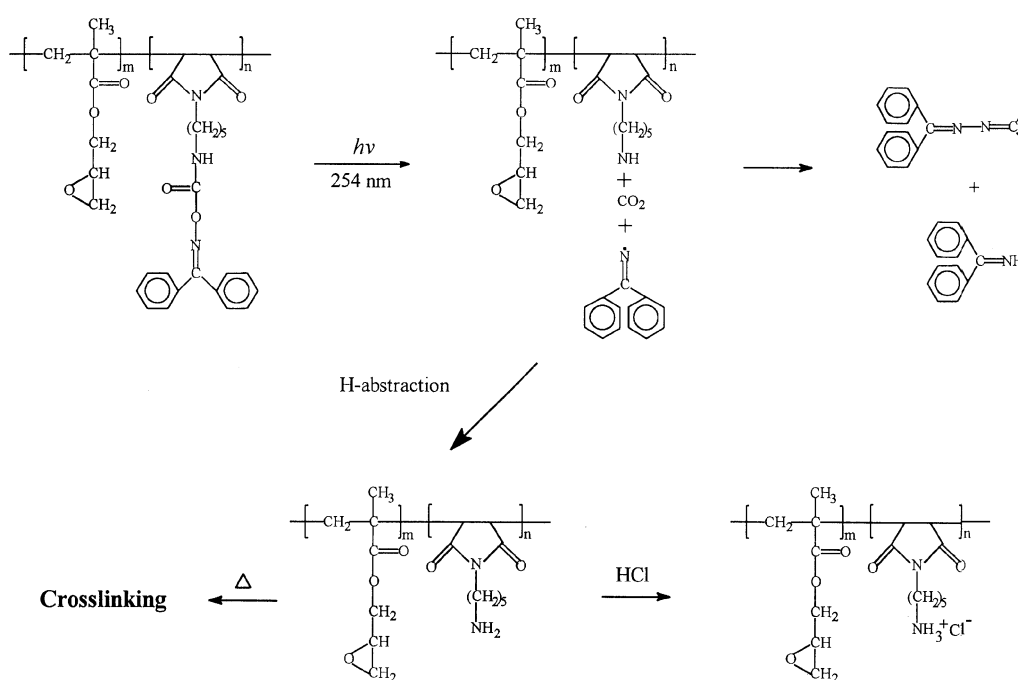


Figure 7. Insoluble fraction of copolymer II film as a function of irradiation time at different heating temperature: heating time, 45 min.

significant at a higher temperature.

Insoluble fraction of copolymer II film as a function of irradiation time at different heating temperatures is shown in Figure 7. The insoluble fraction increases with heating temperature and irradiation time. It increases dramatically between 0-10 min of irradiation time, but remains constant above 10 min. The difference of the insoluble fraction is significant between 80-100 °C for the non-irradiated film, but it becomes similar after irradiation.

Insoluble fractions of the three copolymers upon irradiation were similar each other. This indicates that the larger



amount of BOPM units in the copolymer does not greatly affect cross-linking reactions, because the low degree of cross-linking even decreases the solubility of the polymer effectively.

The photochemical reaction of the copolymer containing oxime-urethane groups is summarized in Scheme 3. Irradiation of 254 nm UV light to the copolymer leads to the homolytic cleavage of the N-O bond, resulting in an iminyl radical and a polymeric aminyl radical pair with generation of CO₂.¹³ The iminyl radical can undergo hydrogen abstraction to form an imine, or dimerization to form an azine. The aminyl radical can undergo hydrogen abstraction to form a pendant amine. Treatment of these amino groups with HCl results in the formation of ammonium salts which change the polymer surface to become more hydrophilic. Those photo-generated pendant amines effectively catalyzed the crosslinking reaction of epoxy groups in the polymer chain upon heating.

Conclusion

Copolymerization of BOPM and GMA results in nearly quantitative amount of BOPM units being incorporated into the copolymer. The amount of BOPM units does not significantly change the thermal properties of the copolymer. Irradiation of the copolymer with 254 nm UV light leads to the formation of pendant amino groups which changes the polymer surface to be more hydrophilic. Treatment of the irradiated copolymer film with HCl results in the formation of ammonium salts which make the polymer surface more hydrophilic than without treatment. The insoluble fraction of the copolymer increased with irradiation time, heating time and temperature. However, the larger amount of BOPM units in the copolymer does not greatly affect photo-induced cross-linking reaction; cross-linking of the epoxy resin effectively catalyzed by low amount of photobase generator, even below 4.5 mole% of BOPM units in the polymer chains.

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