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Crosslinking reaction of glycidyl methacrylate copolymers containing oxime-urethane groups using photogenerated pendant amines

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Summary

Copolymers containing epoxy and oxime-urethane groups were prepared by copolymerization of glycidyl methacrylate (GMA) and benzophenone oxime allylurethane (BAU). The physical properties of these copolymers were characterized by GPC, NMR and DSC analyses. Photo-crosslinking reaction of the copolymers were studied by measuring the insoluble fraction of copolymer films under various reaction conditions. The degree of cross-linking reaction increased with irradiation time, heating temperature and the amount of BAU units in the copolymer. UV and IR absorption spectral studies indicate that thermal cross-linking reaction of the copolymer was catalyzed by the pendant photogenerated amines.

Introduction

Photoinduced acid formation has been utilized to develop several new and commercially important technologies. Similarly, photoinduced base formation has also gained importance in such fields as microlithography (1), photoresists (2,3) UV curing (4,5) and imidation catalysts (6). However, only a few studies on the photoinduced base formation have been reported.

Willson et. al. (7) studied the formation of ammonia by the photolysis of cobalt-amine complex. Cameron and Fréchet (8,9) reported on the photogeneration of amine by the photolysis of o-nitrobenzyl carbamates and urethanes. Tsunooka et. al. (10) investigated the formation of amine by the photolysis of oxime-ester derivatives after treatment with water. Nishikubo et. al. (4,5) reported on the photogeneration of free amine by the pholysis of blocked amine.

Amines are very important reagents for thermal cross-linking reactions of epoxy resins in adhesives, paints, and coatings industry. However, a mixture of epoxy resins with aliphatic amines is very unstable due to the high reactivity of aliphatic amines. Therefore, light induced amine formation from blocked amine groups is a very useful technique for the formulations of epoxy resins which can lead to a new industrial technology.

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It was previously reported that the photolysis of oxime-urethane derivatives results in the formation of amines which induce cross-linking reaction of epoxy resins upon heating (11). In this paper, we report that glycidyl methacrylate (GMA) copolymers containing oxime-urethane groups were anionically photo-crosslinked by photogenerated pendant amines produced from the photolysis of oxime-urethane groups.

Experimental

Materials

GMA was obtained from Fluka Chemical Company and used after vacuum distillation. Allylisocyanate was purchased from Aldrich Chemical Company and used as received. Benzophenone oxime was prepared by the reported procedure (12).

Synthesis of benzophenone oxime allylurethane (BAU)

Allylisocyanate (0.5 ml, 5.6 mmol) was added dropwise to a stirred solution of benzophenone oxime (1 g, 5.1 mmol) and triethylamine (0.1 ml, 0.7 mmol) in 14 ml of chloroform at room temperature. Stirring was continued for 4 hours with reflux. The reaction mixture after partial concentration in vaccum was kept for 3 hours in the refrigerator. The resulting solid mixture was filtered and recrystallized in methanol. The yield and melting point were 73 % (1.04 g) and 116-117 °C, respectively.

IR (KBr pellet, cm^{-1}); 3265 (-NH), 1716 (C=O), 1529 (-NH), 1496 (C=C, aromatic), 1238 (C-N), 937 (allyl), 700 (aromatic C-H). ^{1}H-NMR ($CDCl_3$, δ, ppm); 7.5-7.36 (10 H, m, phenyl), 6.5 (1H, s, NH), 5.9 (1H, m, =CH-), 5.1-5.3 (2H, m, =CH2), 3.9-4.1 (2H, m, -CH2-).

Polymerization procedure

A solution of 1.32 ml (10 mmol) of GMA, corresponding amount of BAU as shown in Table 1, and AIBN (1 wt% of the solute) in 3 ml of THF were bubbled with nitrogen for 20 min. The mixture was heated at 60 °C for 24 hours in a sealed

Table 1. Physical Properties of the Copolymers

Copolymer	Mole % of BAU		Conversion of BAU (%)	Yield (%)	Intrinsic Viscosity	Tg [c] (°C)	Molecular weight		
	in feed	in copolymer					Mn	Mw	Dispersity
I	9.1	0.7	8.1	55	0.32	87	138,000	166,000	1.20
II	16.7	1.2	7.3	60	0.26	90	129,000	162,000	1.26
III	33.3	3.1	9.4	59	0.23	85	124,000	162,000	1.31

[a] Polymerization was carried out with 1 wt% of AIBN in 3 ml of THF at 60 °C for 24 hours.

[b] The content of BAU units in the copolymer was determined from 300 MHz NMR spectra.

[c] Obtained from DSC thermogram under N_2 atmosphere with scan speed of 10 °C/min.

tube. THF (10 ml) was added to the reaction mixture to dilute the viscous solution, and the resulting polymer was purified by double precipitation in methanol, then dried under reduced pressure at 60 ºC for 12 hours. Yields are shown in Table 1.

Irradiation experiments

Cross-linking of copolymer: 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 (3x7 cm). It was spread evenly by pushing the capillary tube manually. The plate was dried in vacuum at room temperature for 7 hours. The thickness of the films measured by optical microscope was 13-16 µm. The coated plates were irradiated first with 254 nm UV light under atmospheric conditions, heated, then 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:

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

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.

UV and IR absorption spectral changes: Copolymer I was dissolved in THF and the absorbance at 254 nm was adjusted to 1.8. UV absorption spectra were obtained with irradiation times of 0, 2, 4, 6, 8, 10, 12, 15, 20 min.

A transparent KBr pellet containing copolymer II was irradiated with 254 nm UV light for 50 min. The difference IR spectrum was obtained between before and after irradiation.

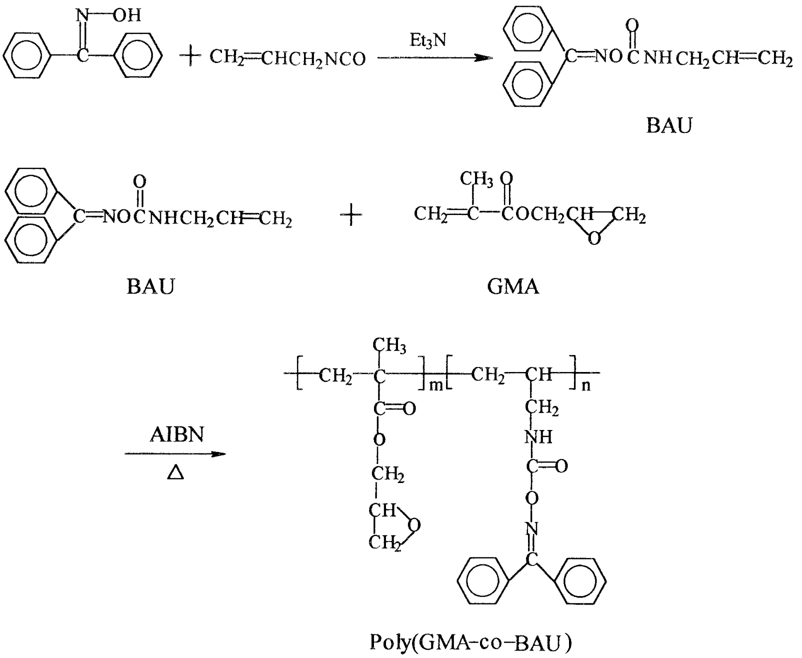
Results and discussion

Copolymer synthesis and properties

A synthetic route for the preparation of copolymers is shown in Scheme 1. BAU, a monomer containing oxime-urethane groups was prepared from benzophenone oxime with allyl isocyanate in the presence of triethylamine. White rod-like crystals were obtained after recrystallization in methanol. The structure of BAU was characterized by instrumental analyses. The melting point of this compound is 116-117 ºC and the onset of decomposition temperature was observed at 196 ºC by DSC analysis, which indicate relative thermal stability of this compound. The exothermic peak due to thermal unblocking reaction of oxime-ester to isocyanate groups (13) was not observed by DSC analysis.

Copolymers containing epoxy and oxime-urethane groups were prepared by copolymerization of GMA and BAU in THF with 1 wt% of AIBN. The resulting copolymer was purified by double precipitation in methanol. The polymer was fairly soluble in THF and DMF, but insoluble in methanol, acetone, and ether. IR absorption spectra of these copolymers show that the absorption band of urethane N-H groups appears at 3377 cm^{-1} and that of ester and urethane carbonyl groups appears at 1720 cm^{-1}. The IR spectral patterns were similar to those of poly(glycidyl methacrylate) (PGMA) indicating that a small amount of BAU units

Scheme 1. Synthetic route for the preparation of poly(GMA-co-BAU)



were incorporated into the copolymer. The absorption band of -NH groups increased with the amount of BAU units in the copolymer. The NMR spectral patterns of the copolymers were similar to those of PGMA.

Physical properties of the copolymers are summarized in Table 1. The copolymers were prepared by varying the molar ratio of BAU units from 9 to 33 % and the polymer composition was determined by 300 MHz NMR spectra. Conversion and content of BAU units in the copolymer were in the range of 7-10 % and 0.7-3.0 %, respectively. The reason for the small amount of BAU unit incorporation into the copolymer may be due to the low reactivity of allyl groups as well as steric hindrance from phenyl groups on BAU.

Intrinsic viscosity of the copolymers appears in the range of 0.23-0.32 and the number average molecular weight ranged between 124,000-138,000. Polydispersity ranged between 1.20-1.31 indicating relatively uniform molecular weight distribution. Molecular weight and intrinsic viscosity decreased with the amount of BAU units in the copolymer. Tg of these copolymers ranged between 85-90 °C and Tm ranged between 280-283 °C. There is no appreciable difference in thermal properties of these copolymers since they contain similar amounts of BAU units.

Cross-linking reaction

Previously, we reported that irradiation of the compounds containing oxime-urethane groups produce photogenerated amines which in turn induce thermal cross-linking reaction of epoxy resins (11). Photo-crosslinking reaction of the copolymers containing epoxy and oxime-urethane groups was studied by

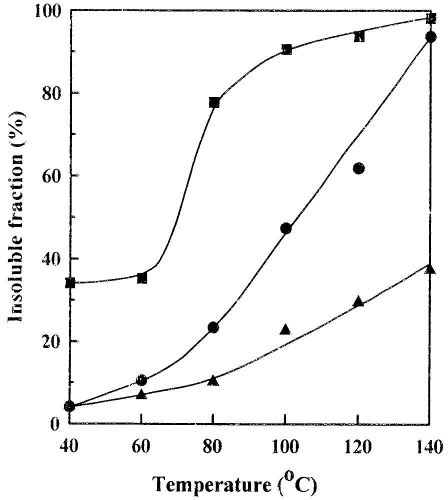


Figure 1. Effect of heating temperature on the insoluble fraction of PGMA (▲) and copolymer I film in THF before (●) and after (■) irradiation for 40 min with heating time of 40 min.

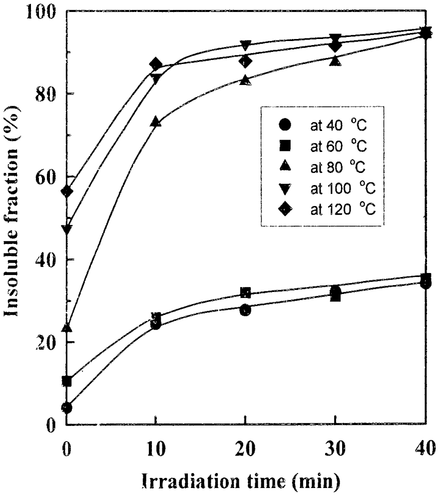


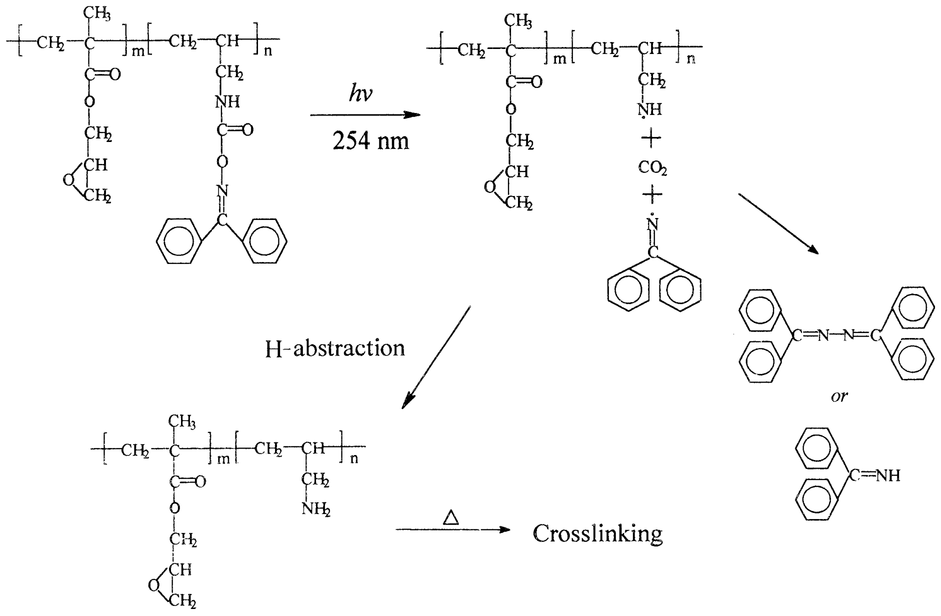
Figure 2. Insoluble fraction of copolymer I film in THF as a function of irradiation time at different heating temperatures and heating time of 40 min.

measuring the insoluble fraction of copolymer films under various reaction conditions.

Figure 1 shows the effect of heating temperature on the insoluble fraction of PGMA and copolymer I films in THF, before and after irradiation with UV light of 254 nm for 40 min. The PGMA films thermally cross-linked up to 37 % at 140 °C with heating time of 40 min. The insoluble fraction of non-irradiated copolymer I film containing 0.7 % of BAU units increased about twice that of PGMA. This may be due to the thermal transformation of oxime-urethane to isocyanate groups, which then reacted with epoxy groups of the copolymer resulting in cross-links (13). Insoluble fraction of copolymer I films after irradiation for 40 min was 25-30 % higher than that of non-irradiated copolymer I films at 40-60 °C. However, the difference of insoluble fraction between irradiated and non-irradiated copolymer films increased up to 55 % at 80 °C. Thus, the higher insoluble fraction observed for the irradiated copolymer films can be attributed to the thermal cross-linking reaction of the copolymer catalyzed by the amines produced from the photolysed oxime-urethane groups, as shown in Scheme 2.

Figure 2 shows the insoluble fraction of copolymer I films in THF as a function of irradiation time at different heating temperatures. The insoluble fraction increased with irradiation time and heating temperature. The maximum insoluble fraction of copolymer I film was 35 % below 60 °C, but it increased up to 95 % above 80 °C at the irradiation time of 40 min. Thus, there was a large difference in the insoluble fraction of copolymer films between 60-80 °C. This can be explained by the mobility difference of photogenerated amino groups in the polymer chain at temperatures below and above Tg; since Tg of these copolymers are 85-90 °C, the reaction between amino and epoxy groups was restricted by the low mobility of polymer chain at temperatures below Tg. However, the mobility of polymer chain increased at temperatures above Tg, which increases the possibility of reaction between amino and epoxy groups.

Scheme 2. Photo-crosslinking Mechanism of Poly(GMA-co-BAU)



The insoluble fraction of three copolymer films as a function of irradiation time was studied when heating temperature and heating time were 90 °C and 40 min, respectively. The insoluble fraction of these copolymer films was 30 % before irradiation, but it increased with irradiation time and the content of BAU units in the copolymer. The maximum insoluble fraction was about 95 % after irradiation time of 40 min. This result also indicates that the photogenerated pendant amines produced by the photodecomposition of oxime-urethane groups in the polymer chain can effectively induce thermal cross-linking of these copolymers.

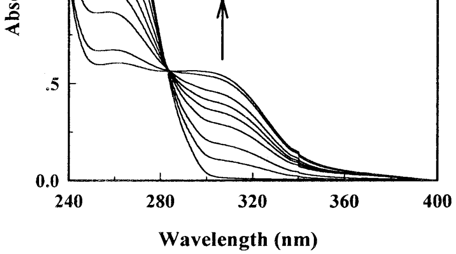


Figure 3. UV absorption spectral changes of copolymer I in THF with irradiation time of 0, 2, 4, 6, 8, 12, 15, 20 min in the direction of arrows, respectively.

Photochemical reaction

UV and IR absorption spectral changes with irradiation were observed in order to study the photochemical reaction of copolymers. Figure 3 shows UV absorption spectral changes of copolymer I in THF upon irradiation with UV light of 254 nm for various irradiation time. An isosbestic point appears at 283 nm. The absorption band at shorter wavelength than the isosbestic

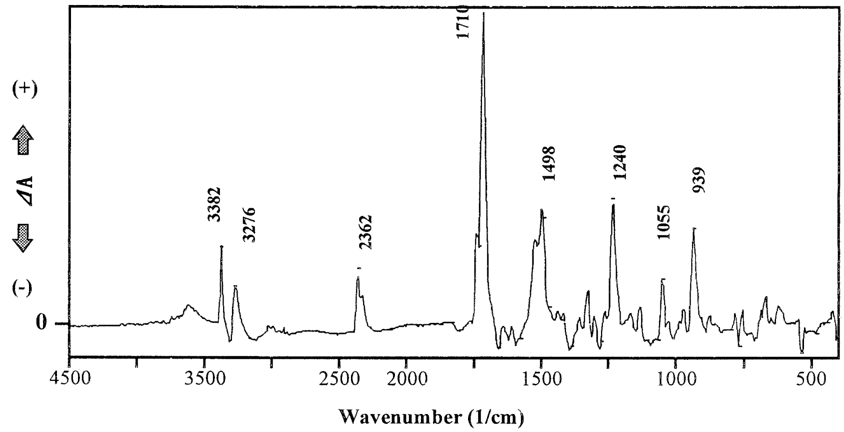
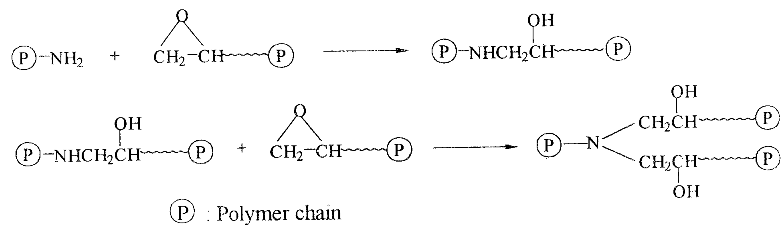


Figure 4. Difference FT-IR spectrum of copolymer II between before and after irradiation with 254 nm UV light for 50 min (KBr pellet): (+), absorbance increase; (-), absorbance decrease.

point decreased while that at longer wavelength than the isosbestic point increased. The decrease in absorbance at shorter wavelength than 283 nm is due to the photodecomposition of oxime-urethane groups and the increase at longer wavelength than 283 nm is due to the formation of azine type compounds (14).

Photochemical reaction of the copolymer was also studied by observing the IR absorption spectral changes between before and after irradiation. Figure 4 shows difference FT-IR spectrum of copolymer II after photolysis with UV light of 254 nm for 20 min. The increase of absorption band at 3382 and 3276 cm^{-1} indicates formation of amino groups and that at 3600 and 1055 cm^{-1} indicates formation of hydroxyl groups. The increase of absorption band at 1710 cm^{-1} results from photooxidation of the copolymer. This result shows that the ring opening reaction of the epoxy groups on glycidyl methacrylate unit occurred to form hydroxyl groups, and the cross-linking reaction was catalyzed by the pendant photogenerated amine as shown in Scheme 3.

Scheme 3.



In conclusion, both the content and conversion of BAU units in the poly(GMA-co-BAU) was quite low due to their steric hindrance and low reactivity. Cross-linking reaction of the copolymer films increased with irradiation time, heating temperature, and BAU units in the copolymer. The cross-linking reaction of these copolymers was restricted due to the low mobility of polymer chains at temperatures below T_g, but at temperatures above T_g, the insoluble fraction of the copolymer films increased greatly, up to 95 %. UV and IR absorption spectral studies indicate that oxime-urethane groups in the polymer chain photodecomposed to form pendant amines, and those photogenerated pendant amines effectively catalyzed the thermal cross-linking reaction of epoxy groups in the copolymer chain.

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