GENERATION OF POLYMER BASES BY THE USE OF PHOTOCHEMICAL REACTION OF POLYMERS BEARING ACYLOXYIMINO GROUPS AND ITS APPLICATION TO UV CURING SYSTEMS

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Photo-initiated crosslinking of epoxides is very promising from the view point of application to photocurable coating and photoresist.[1] Although amines are known to be useful as crosslinkers for epoxides, only a few studies on the photo-initiated formation of amines are reported. We reported that in the photolysis of copolymers of O-acryloyl acetophenone oxime (AAPO) with styrene, pendant acyloxyimino (AOI) groups led to pendant amino groups in a good yield [2] and that the pendant amino groups were effective in crosslinking of the pendant epoxy groups in the same polymer.[3] Willson et al. reported that photolysis of a cobalt-ammine complex led to the formation of ammonia which induced the crosslinking of a glycidyl methacrylate - ethyl acrylate copolymer upon heating.[4] Fréchet et al. reported that photolysis of α,α -dimethyl-3,5-dimethoxybenzyl carbamates [5] and o-nitrobenzyl carbamates [6] led to the formation of amines and that resulting amines could be utilized as crosslinkers. Nishikubo et al. utilized amines generated by photolysis of blocked amines as crosslinkers of epoxy resin or polyurethane.[7]

In previous papers [8,9], we have reported that monoamines or diamines are formed efficiently by the photolysis of O-acyloximes in a polystyrene film and the diamines were more efficient crosslinkers for poly(glycidyl methacrylate) (PGMA) films. However, these amines were not efficient crosslinkers for epoxy resins. In this paper we report thermal crosslinking of epoxy resin by polymer amines formed by the photolysis of AAPO copolymers.

AAPO copolymers were prepared by radical copolymerization of AAPO with ethyl acrylate (EA) or styrene (St) in benzene using 2,2'-azoisobutyro-nitrile as initiator under vacuum at 60 °C.[2] Commercial epoxy resin, EPOLIGHT 100MF

(trimethylol propane triglycidyl ether, TMPGE, epoxy equivalent: 140) was provided by Kyoeisha Yusi Kagaku Kogyo Co. Ltd. The structures of copolymers and epoxy resin are shown in Fig. 1.

Fig. 1. Structures of AAPO copolymers and epoxy resin.

Thin films (ca. 0.15 μm thick) of the copolymers with 10 wt% TMPGE and 10 wt% benzophenone (BP) as sensitizer were prepared by casting a tetrahydrofuran (THF) solution of the copolymer and additives on a quartz plate (1 $\times$ 4cm). The films were irradiated on the quartz plate with a high-pressure mercury lamp (Sen Tokusyu Kogen Co. Ltd., HL-100, 100 W) at a distance of 7 cm at room temperature under air for a given time. After irradiation the films were heated at a given temperature for a given time. Then the films were immersed in THF for 10 min at room temperature. The insoluble fraction was determined from the thickness of the films before and after the immersion measured using an interference microscope (Nikon OPTIPHOT).

Scheme 1. Photoreaction mechanism of copolymers bearing AOI groups

In the photolysis of AAPO-St copolymers in films pendant AOI groups leads to pendant amino groups as shown in Scheme 1. The yields of amino groups of AAPO(26.3)-St copolymer were ca. 70% under air and N_2 . [2] Therefore, it is expected that the pendant amino groups of AAPO copolymers react with epoxy groups of epoxy resins, which results in crosslinking.

Figure 2 shows the change on the UV spectra of AAPO(34)-St films containing 10 wt% TMPGE and 10 wt% BP upon UV irradiation under air. The peak at 248 nm due to

AOI groups of the copolymer decreased rapidly with irradiation time.

Fig. 2. Change on the UV spectra of AAPO(34)-St film (ca. 0.15 μm thick) with 10 wt% BP and 10 wt% TMPGE upon UV irradiation under air.

Fig. 3. Relationship between heating temperature and insoluble fraction of AAPO copolymers films with 10 wt% BP and 10 wt% TMPGE (ca. 0.15 μm thick): (■) AAPO(28)-EA, (●) AAPO(34)-St. After irradiation for 10 min under air, heated for 10 min.

Figure 3 shows the relationship between heating temperature after irradiation and insoluble fraction of AAPO copolymers. AAPO(34)-St ($\bar{M}_n=85000$, $T_g=93.3$ °C) films could be insolubilized by heating at a temperature above ca. 70 °C, while AAPO(28)-EA ($\bar{M}_n=77000$, $T_g=17.3$ °C) films could be done at a room temperature and the insoluble fraction of the film reached ca. 50%. Since local segment motion of main chains in AAPO(28)-EA copolymer occurs at temperatures higher than the T_g of the copolymer, it is deduced that the reaction of amino groups of the copolymer with epoxy groups of TMPGE occurs efficiently to insolubilize the copolymer at the room temperature. This result suggests that the lowering of T_g of copolymer plays a important role on the curing.

Figure 4 shows the effect of heating temperature on photocrosslinking of AAPO(34)-St films (a) and AAPO(28)-EA films (b). In the case of heating at 150 °C after irradiation, both films were insolubilized rapidly at the same rate. The insoluble rate of AAPO(34)-St films fell significantly with lowering of heating temperature, while that of AAPO(28)-EA films did only slightly.

Figure 5 shows the Arrhenius plot of photocrosslinking of AAPO(34)-St and AAPO(28)-EA films. The photocrosslinking rates were determined as the reciprocal of time required for insolubilization of 50% of the copolymer films in Fig. 3. The apparent activation energies (E_{act}) of insolubilization for AAPO(34)-St and AAPO(28)-EA films which were calculated from the plot were 64.3 kJ/mol and 21.3 kJ/mol, respectively. One of causes of lower E_{act} of AAPO(28)-EA copolymer is thought to be that the energy required for the segment motion of AAPO(28)-EA copolymer is lower than that of AAPO(34)-St copolymer from the T_g s of both copolymers. Further details are now under investigation.

Fig. 4. Effect of heating temperature on photocrosslinking of AAPO(34)-St films (a) and AAPO(28)-EA films (b) with 10 wt% BP and 10 wt% TMPGE (ca. 0.15 μm thick): (■) 60 °C, (□) 80 °C, (●) 100 °C, (○) 150 °C. After irradiation under air, heated for 5 min.

Fig. 5. Arrhenius plot of photocrosslinking of copolymer films (ca. 0.15 μm thick) with 10 wt% BP and 10 wt% TMPGE: (○) AAPO(34)-St, (△) AAPO(28)-EA. κ : Photocrosslinking rate at 50% of insoluble fraction of copolymer films.

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