Photocrosslinking and Thermal Degradation of Epoxy-containing Polymers Using Photobase Generators

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A new system consisting of a photobase generator and an oligomer bearing both epoxy and tertiary ester units was prepared as a photocrosslinkable and thermally de-crosslinkable polymer system. The sample film became insoluble on UV-irradiation and followed by baking at 100–160 °C. The crosslinked film became soluble in methanol when baked at 180–200 °C.

Photocrosslinkable polymers have been used in many fields such as photoresist, inks, coatings, and adhesives, because of their excellent mechanical and thermal properties. These properties are, however, disadvantageous when the photocrosslinked polymers are required to be removed from substrates without damaging underlayer. Recently, some systems consisting of crosslinkable and thermally cleavable units were proposed.[1–6] We have reported that polymers having both crosslinkable epoxy and tertiary ester units are photocrosslinked on UV-irradiation and themally de-crosslinked in the presence of photoacid generators.[7,8] In this case, the de-crosslinking reaction occurred at 90–160 °C, which is not high enough for practical uses. In this communication, we report a photocrosslinkable polymer system that contains a photobase generator (PBG) and is thermally degradable at above 180 °C.

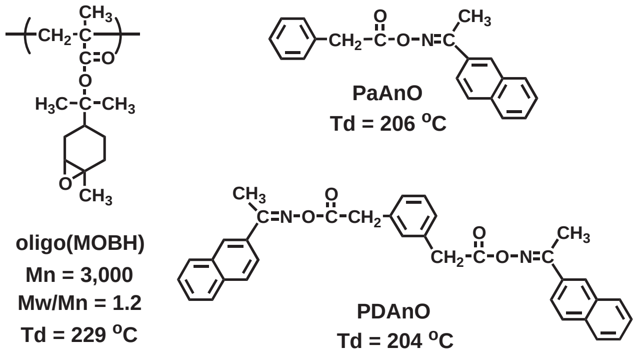
1-Methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl methacrylate (MOBH)[7] was oligomerized in DMF using 2,2′-azobisisobutyronitrile and 1-dodecanethiol at 55 °C. The resulting oligomer was purified by reprecipitation from hexane after dissolving in chloroform. The molecular weight of oligo(MOBH) was measured by size exclusion chromatography at 40 °C using THF as an eluent and polystyrene as standard. The decomposed temperature (T_d) was determined by thermogravimetry at a heating rate of 10 K/min under N_2.

2-Acetonaphthone *O*-phenylacetyloxime (PaAnO)[9] and 2-acetonaphthone *O*,*O*′-1,3-phenylenediacetyldioxime (PDAnO)[10] were used as PBG. Scheme 1 shows the structures and physical properties of oligo(MOBH), PaAnO, and PDAnO.

Oligo(MOBH) films (ca. 0.5 μm) were obtained by casting cyclohexanone solution of oligo(MOBH) and PaAnO or PDAnO on silicon wafers, and baked at 80 °C for 3 min on a hot plate. UV-irradiation was performed using an Ushio ULO-6DQ low pressure mercury lamp (6 W) in air. Light intensity was 1.0 mW/cm^2 at 254 nm. The irradiated films were baked at a given temperature for 10 min on the hot plate. Insoluble fraction of the films was obtained from ratio of thickness before and after soaking the films in methanol for 10 min.

PaAnO and PDAnO are reported to generate benzylamine and *m*-xylylenediamine, respectively, on UV-irradiation.[9,10]

Figure 1 shows solubility changes of oligo(MOBH) films containing PaAnO or PDAnO in methanol on irradiation and baking. The films became insoluble in methanol on irradiation followed by baking at 100–160 °C because of network formation due to addition reaction of epoxy groups and amines generated from PBG as shown in Scheme 2. The insolubilization of oligo(MOBH) film containing di-functional PDAnO was enhanced in comparison with that containing mono-functional PaAnO.[10]



Scheme 1. Structures and properties of oligo(MOBH) and photobase generators.

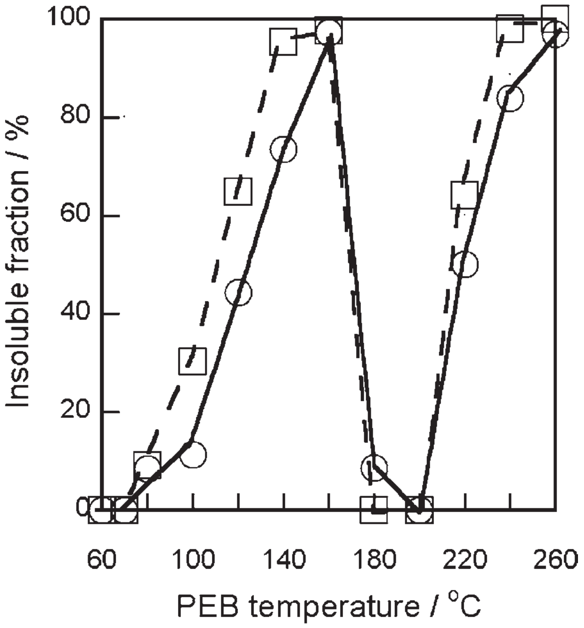
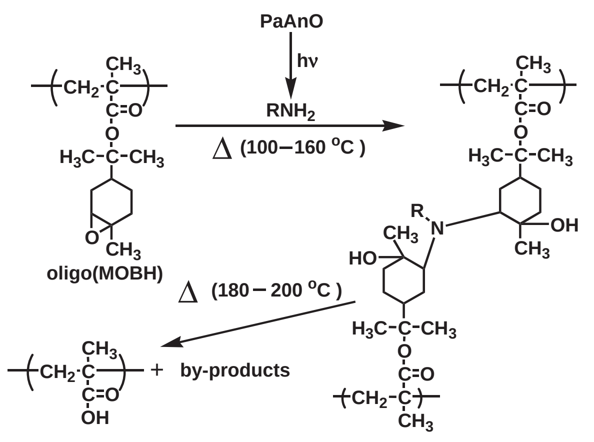


Figure 1. Effect of post-exposure bake (PEB) temperature on dissolution of oligo(MOBH) films containing PaAnO (—○—) or PDAnO (– – □ – –). Irradiation dose: 2000 mJ/cm2. Development: methanol for 10 min. [MOBH unit]:[PaAnO] = 100:10 (mol/mol). [MOBH unit]:[PDAnO] = 100:5 (mol/mol).

When baked at 180–200 °C, the films containing PBGs became soluble in methanol. This was due to thermal transfor-



Scheme 2. Photocrosslinking and thermal decomposition of oligo(MOBH) containing PaAnO.

mation of the tertiary ester units into carboxylic acid groups, which was confirmed by IR spectral changes as shown in Figure 2a. On baking at 180 °C for 10 min, the peak at 1722 cm^{-1} assigned to carboxylic acid ester shifted to 1704 cm^{-1} along with the decrease in the peak at 1125 cm^{-1} assigned to C–O–C. Redissolution of the crosslinked oligo(MOBH) film containing PDAnO started at almost the same temperature as observed for the film crosslinked by PaAnO. At this temperature, amidation between resulting carboxylic acid units and amines did not proceed. A complete re-dissolution was not observed if poly(MOBH) ($M_n = 150{,}000$) film containing PaAnO or PDAnO was used.

The films became insoluble in methanol on baking above 220 °C. When the films were baked at 240 °C for 10 min, peaks assigned to carboxylic acid anhydride appeared at 1803, 1758, and 1018 cm^{-1} as shown in Figure 2b. The formation of acid anhydride linkage induced the insolubilization once again.

In conclusion, photocrosslinking and de-crosslinking of oligo(MOBH) using PBG were demonstrated. Onset temperature for the thermal degradation of the crosslinked oligo(MOBH) increased up to 180 °C using PBG.

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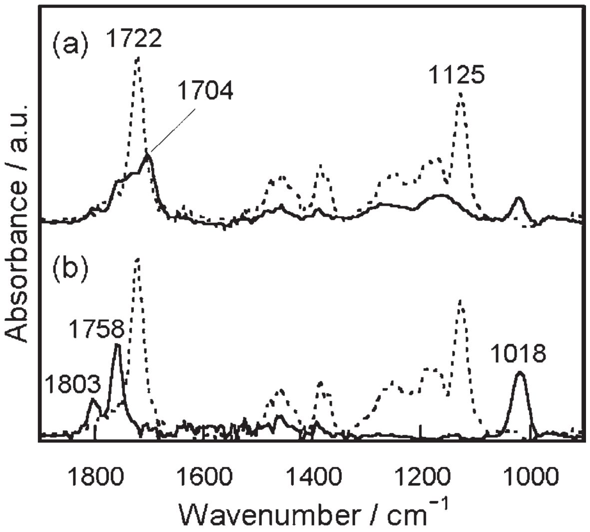

Figure 2. IR spectra of irradiated oligo(MOBH) films containing PaAnO before (- - -) and after (—) baking at (a) 180 °C and (b) 240 °C. Irradiation dose: 2000 mJ/cm^2.

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