Photo-induced Polymerization and Degradation of Formulations Containing Photolabile Crosslinkers Monitored in a Rheometer

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1. Introduction

Photofunctional molecules are useful for polymerization, degradation, and modification of polymeric materials and have been used in many fields such as UV curing, lithography, and 3D modeling [1]. The use of light is favorable in terms of energy efficiency generally than those use thermal reaction. Photolabile crosslinker is one of promising molecules that are used in polymeric materials [2]. By introducing the photolabile crosslinkers, a drastic change is anticipated in crosslinked polymers which show excellent mechanical and thermal properties. Also, these changes can be controlled spatiotemporally.

Recently, we have proposed two novel photolabile crosslinkers, 1,4-diacetylbenzene 1,4-bis(*O*-methacryloyl)dioxime (DBzM) and 1,3,5-triacetylbenzene 1,3,5-tris(*O*-methacryloyl)-trioxime (TBzM), that contain both a polymerizable methacrylate and degradable *O*-acyloxime moieties in a molecule [3,4]. We prepared pressure-sensitive adhesives (PSAs) composed of the photolabile crosslinkers and succeeded in the reduction of their peel strength on UV irradiation [5].

On the other hand, the evaluations of photofunctional materials using rheometers that can measure viscoelastic parameters with UV irradiation attract much attention. For example, the analysis of photopolymerization and photo-induced gelation [6–8] by using the rheometer were reported in recent years.

We have also attempted to monitor the degradation behavior of the PSAs by using this apparatus and confirmed that 2-isopropylthioxanthene-9-one (ITX) sensitized the degradation of *O*-acyloxime units in the PSAs on irradiation at 365 nm. Furthermore, direct rheological measurement of serial photopolymerization and photodegradation processes of the PSAs were observed in a single measurement [9]. However, we could observe only small decrease in the parameters because the formulation contained a solvent.

In this communication, we report the serial photo-induced polymerization and degradation behavior of formulations without solvent in order to observe more remarkable changes, and compare them to that of formulation containing as a non-degradable crosslinker.

Fig. 1. Chemical structures of crosslinkers used in this study.

2. Experimental

Butyl acrylate (BA, Wako, Osaka, Japan) was purified with neutral alumina column prior to use. ITX was recrystallized from hexane. Trimethylolpropane trimethacrylate (TMPTMA, TCI) and tetrahydrofuran (THF, Kishida Chemical, Osaka, Japan) were used as received. DBzM and TBzM were prepared as described previously [4]. The chemical structures of photolabile crosslinkers and TMPTMA are shown in Fig. 1.

Formulations composed of BA, a crosslinker, and ITX were kept at 80 °C for 1 h to obtain homogeneous mixtures. After cooling and bubbling with nitrogen gas for several minutes, the formulations were subjected to rheological measurement by using a Thermo Scientific HAAKE MARSIII rotational rheometer.

The irradiation setup was consisted of upper 20 mm^φ parallel plate and quartz bottom plate with 365 nm LED light source. Formulations were set between the plates with 50 μm gap and applied an oscillation with a frequency at 1 Hz under a constant strain amplitude at 25 °C. After 15 seconds from the start of the measurement, 365 nm light with the intensity of 41 mW/cm² was introduced through the quartz bottom plate.

Obtained polymer films were soaked in THF for 10 min at room temperature. Insoluble fraction was calculated as weight ratio before and after the soaking.

3. Results and Discussion

Figure 2 shows the rheological parameter changes for a formulation containing BA, TMPTMA, and ITX on irradiation. Storage (G'),

Fig. 2. Changes of G' (—), G'' (---), and $|\eta^*|$ (····) for the formulation composed of BA / TMPTMA / ITX = 10000: 10: 1 (mol / mol). 365 nm light was irradiated during the measurement.

loss (G'') moduli, and absolute value of complex viscosity ($|\eta^*|$) increased with an increase in irradiation time. The rheological parameters reached plateau, and G' and $|\eta^*|$ became 30,000 Pa and 5,000 Pas, respectively. The obtained film was slightly sticky and adhesive. These results suggest that photopolymerization was initiated by free radicals generated from ITX on irradiation to form networked structure. However, the decrease in the rheological parameters was not observed in this case.

When TBzM was used as a crosslinker, different behavior of rheological measurement was observed as shown in Fig. 3. G' and $|\eta^*|$ values became 40,000 Pa and 6,000 Pas for 10 min, respectively, which were higher compared to Fig. 2. After that, the rheological parameters began to decrease gradually, and G' and $|\eta^*|$ became 26,000 Pa and 4,200 Pas, respectively. These results suggest that predominant process was photopolymerization in the early stage, and photodegradation in the later stage. The film irradiated for 60 min showed lower viscosity than that irradiated for 10 min, and the film was stickier and more flexible compared to that obtained from TMPTMA in Fig. 2.

Fig. 3. Changes of G' (—), G'' (---), and $|\eta^*|$ (····) for the formulation composed of BA / TBzM / ITX = 10000: 10: 1 (mol / mol). 365 nm light was irradiated during the measurement.

The solubility of the irradiated films in THF is summarized in Table 1. The insoluble fraction of the film containing TMPTMA showed little change in spite of irradiation time. On the other hand, that containing TBzM was 85 % on irradiation for 10 min, although that reduced to 53 % after 60 min irradiation. These results suggest that the networked structure of polymers containing TBzM

Table 1. Solubility of irradiated films in THF.

Formulation	Insoluble fraction (wt%)	
	Irradiation for 10 min	Irradiation for 60 min
BA / TMPTMA / ITX	85	82
BA / TBzM / ITX	85	53

were degraded, which are consistent with those obtained in Fig. 3

Similar measurement was performed for the formulation containing DBzM instead of TBzM. However, photopolymerization was very slow, and the little increased in rheological parameters was observed. Also, photopolymerization of BA in the absence of ITX did not proceed on irradiation, even in the presence of crosslinkers.

Based on the above results, plausible reaction mechanism is illustrated in scheme 1. In the primary step, irradiated 365 nm light is absorbed by ITX. The excited ITX generates free radicals, probably by abstracting hydrogen atom from the system, although this process will be inefficient in the absence of hydrogen-donating molecules such as amines [10].

In the presence of TBzM, triplet energy transfer from the excited ITX to TBzM can be expected, because it has already known that thioxanthene-9-one derivatives sensitize the photolysis of *O*-acyloxime moiety [9,11]. During the photolysis, some TBzM might generate iminyl radicals which initiate the polymerization. Because the propagation reaction is much faster than that of the photodegradation, the former process was predominant before the gelation.

Once the gelation occurred, the diffusion of BA, TBzM, and ITX was highly restricted, and the concentration of BA decreased. Therefore, actually the rate of the propagation became much lower, and scission of polymer chains proceeds mainly.

Scheme 1. Plausible mechanism of photo-induced polymerization and degradation.

4. Conclusion

We investigated the rheological changes for formulation composed BA, a crosslinker, and ITX without solvent during irradiation at 365 nm.

When TMPTMA was used as a crosslinker, rheological parameters increased on irradiation, although the reduction of the parameter was not observed. However, in the formulation containing TBzM, remarkable changes in the rheological parameters were confirmed. The formation and degradation of networked structure were evidenced by their solubility changes. These results indicate that the technique used in study is useful for understanding photofunctional materials.

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5. References

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