Visible Light Crosslinking of Polymeric Photobase Generators Using Ketobiscoumarins

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INTRODUCTION
The utilization of photo-generated base is a recent topic in the field of imaging and UV-curing processes.[1] The base can catalyze crosslinking reactions to form networks and alter the polarity from hydrophobic to hydrophilic.

Acyloxyimino (AOI) groups are one of the photochemically base-generating groups and are transformed into primary amino groups on irradiation as shown in Scheme 1.[2] Other base-generating groups, carbamoyloxyimino (COI) groups, are also found to be transformed into amino and hydrazino groups on irradiation.[3-6] These photo-transformations were accomplished by mid-UV light including i-line from conventional mercury lamp.

Because visible light is desired in curing systems that damage of substrates should be avoided such as dental use, we had attempted the photolyses of AOI and COI groups using benzoquinonylsulfanyl compounds as a sensitizer that absorbs light longer than 400 nm.[7] We succeeded in the photolyses, and the generated basic groups made films insoluble in tetrahydrofuran (THF) after post-exposure bake (PEB). However, the degree of photo-decomposition was low.

In this communication, we report the effect of another family of sensitizers, ketobiscoumarins,[8-12] on the photolysis of pendant AOI and COI groups. The solubility change of polymer films is also examined.

EXPERIMENTAL
IR and UV spectral measurements were performed using a Jasco FTIR410 and a Shimadzu 2400PC spectrometers, respectively.

7,7'-Dihydroxy-3,3'-ketobiscoumarin (HKC) and 7,7'-bis(diethylamino)-3,3'-ketobiscoumarin (AKC) were prepared from corresponding salicylaldehydes and dimethyl 1,3-acetonedicarboxylate as described in literature.[8] 7,7'-Didecanoxy-3,3'-ketobiscoumarin (DKC) were prepared from HKC and bromodecane as literature[12]: mp: 129.5 ~131 °C (lit.[12] 130 -131 °C).

2-Benzylsulfonyl-1,4-benzoquinone (QBS)

Scheme 1. Photo-transformation of pendant AOI and COI groups.
[13], acetophenone O-acryloyloxime (AAPO)[2], and acetophenone N-methacryloyloxyethyl-carbamoyloxime (AMCO)[5] were obtained as described previously. Styrene (St) and THF were distilled before use.

The polymerization condition and characterization of polymers were described in a previous report[7]. The number average molecular weights for p[AAPO(27)-St] and p[AMCO(34)-St] were 88,000 and 124,000, respectively.

Films were prepared by coating THF solutions of the polymers and sensitizers onto silicone plates. The amount of sensitizers were [sensitizer] : [AOI or COI groups]= 1 : 8 (mol/mol). The thickness of films was about 0.5 µm, which was measured by a Nanometrics Nanospec/AFT M3000 interferrometer.

Irradiation was performed by an Ushio UM-102 medium-pressure mercury lamp (100 W) through a Toshiba UV-39 filter at room temperature in air. Light intensity was 2.5 mW/cm² when measured by an Orc UV-M02 photometer with a detector UV-42 (sensitive to 320-480 nm region). PEB was carried out on a Koike Precision Instrument HM-15G hot plate for 10 min in air.

Development was performed by soaking the irradiated films in THF for 10 min at room temperature. Normalized thickness of polymer films was obtained from ratios of thickness before and after the development.

RESULTS AND DISCUSSION

Fig. 1 shows UV-visible spectra for sensitizers used here. AKC has the greatest molar absorption coefficient at 436 and 405 nm, while DKC has little absorption at 436 nm. Ketobiscoumarins showed little change on irradiation in THF solutions or polystyrene matrixes, while QBS decomposed rapidly as previously reported.[7]

In the presence of these ketobiscoumarins, pendant AOI groups decomposed on irradiation with visible light. Fig. 2 shows the IR spectral changes for p[AAPO(27)-St] films on the irradiation in the presence of DKC. The decrease of peaks due to C=O stretching band at 1760 cm⁻¹ and C-O-C stretching bands at 1120 cm⁻¹ in AOI groups were observed.

Along with the photolysis of AOI groups, a
peak at 1605 cm\(^{-1}\) due to ketobiscoumarins decreased. A peak around 380 nm in UV-visible spectrum also decreased. These results indicate that ketobiscoumarins reacted during irradiation.

Similar behavior was observed in the presence of HKC and AKC. The photolysis of AOI groups in the presence of sensitizers is compared from the changes of peaks at 1760 cm\(^{-1}\) in Fig. 3. The rate of photolysis was in the order DKC >> HKC > AKC > QBS, which was different from the order of absorbance around 430 nm.

After irradiation, films were still soluble in THF. However, they turned insoluble after PEB. Fig. 4 shows the degree of insolubilization versus irradiation time for p[AAP0(27)-St] films in the presence of additives. The degree of the insolubilization was in the order DKC > HKC > AKC, which was the same order of photo-reactivity observed in Fig. 3. This result indicates that the degree of insolubilization depended on the generation of pendant amino groups.

The above photochemical and solubility properties were also observed for polymers bearing COI groups. Fig. 5 shows the IR spectral change for p[AMCO(34)-St] films in the presence of DKC. The decrease was observed for peaks at 1735 and 1505 cm\(^{-1}\) due to C=O and N-H stretching in COI groups, respectively. From the comparison of the rate of photolysis, the effects of ketobiscoumarins were in the order DKC > HKC > AKC > QBS as shown in Fig. 6.

Concerning to solubility, films of p[AMCO(34)-St] became insoluble in THF only on irradiation as shown in Fig. 7.

PEB was effective for the enhancement of insolubilization for AMCO polymers. At higher temperature of PEB, another factor of crosslinking, the generation of isocyanate groups from COI groups on heating, should be considered.[6] In fact, the degree of the insolubilization after PEB at 120 °C was a little different, where HKC was the highest. These results suggest the formation of crosslinking between hydroxy groups and isocyanate groups.
The reason of higher efficiency of DKC compared to AKC is not clear at present. The difference in triplet energy level (Et) might be the reason, because Et for DKC (239 kJ/mol for 7,7’-dimethoxy-3,3’-ketobiscoumarin [8]) is higher than AKC (Et = 213 kJ/mol [8]), thus more effective energy transfer to AOI (Et = 250 kJ/mol [14]) and COI (Et = 250 kJ/mol [14]) groups can be expected.

In conclusion, both AOI and COI groups were photo-decomposed with visible light in the presence of ketobiscoumarins. The photochemical formation of basic groups made polymer films insoluble in THF with PEB treatment.

REFERENCES