Effects of Irradiation Conditions on Accelerated Photodegradation of Copolymers Bearing Acyloxyimino Groups

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Photodegradable polymers are very interesting from the viewpoints of applications to positive-type photoresists and degradable plastics. In the photodegradation (i.e. main-chain scission) of styrene copolymers bearing acyloxyimino (AOI) groups, we found that the photodegradation was accelerated with increasing decomposition of AOI groups. This result was explained by a lowering of glass transition temperature (Tg) of irradiated copolymers [1,2]. Upon UV irradiation to the copolymers, most of AOI groups were transformed into double bonds and alkyl imino groups, and although main-chain scissions occurred under air, an efficiency of main-chain scission based on a decomposed AOI group (β (%)) was several percent [3]. The yield of the double bonds was three times higher than that of the alkyl imino groups under nitrogen. The latter groups can be easily converted to amino groups by hydrolysis. The lowering of Tg is thought to be related with the structure change of pendant groups, especially with the change of AOI groups to double bonds. In this paper, we report relations between the formation of double bonds and the lowering of Tg.

In this experiment, an 0-methacryloyl 2-acetonaphthone oxime - styrene copolymer (MAANO(28.5)-St) was used as a copolymer bearing AOI groups. The number average molecular weight of the copolymer was 114,000 and the ratio Mn/Mw was 1.65. Copolymer films (10 - 20 μm thick) having 10 wt% benzophenone (BP) as a sensitizer were irradiated at 366 nm. The temperature of the films was kept at 40°C during irradiation. Decomposed fraction of AOI groups in a copolymer was determined by the change of absorbance at 1760 cm⁻¹ before and after irradiation. The number of main-chain scission was determined by the use of the number average molecular weights of the copolymer before and after irradiation, which were determined by GPC.

Figure 1 shows relations between amounts of double bonds (Aₒ/ₐ/ₐₒ) in irradiated films and their Tg's. With an increase in the amount of double bonds in the films, their Tg's decreased. Although the amount of double bonds increased with increasing decomposition of AOI groups.
groups under nitrogen, it stopped at about 50%-conversion of AOI groups under air and at this stage the lowering of Tg also stopped. The degree of decrease in Tg's of films irradiated under nitrogen was greater than those under air, and their lowest Tg's under nitrogen and air were 20 and 30°C, respectively. Thus, it is apparent that the formation of double bonds played a very important role on the lowering of Tg's of copolymer films.

Figure 2 shows effects of pre-irradiation on an efficiency of main-chain scission (β (%)). The abscissa in Figure 2 means the conversion of AOI groups by the pre-irradiation under nitrogen or air. Efficiencies in the Figure were determined by the use of the films irradiated further under air and the conversion of AOI groups by the post-irradiation was 10-20%. It can be seen that the efficiencies depend on the degree of the pre-irradiation. Especially, in the case of the copolymer films preirradiated under nitrogen, the increase of efficiencies was remarkable. From these data, we can conclude that the increase of efficiencies depends on the formation of double bonds, which induces the lowering of Tg of the copolymers. Further details are now under investigation.

Acknowledgement. This work was supported in part by a Grand-in Aid for Scientific Research (No. 63550690) from the Ministry of Education, Science and Culture of Japan.

References