Photocrosslinking Reaction of Polyimide
Containing Benzophenone Unit

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Polyimides are well known because of their excellent thermal stability, and they become important as high temperature insulation materials in the microelectronics field. Polyimide resists are one of their application and attracting much attention today.

Among them, we are interested in the photocrosslinking reaction of polyimide consisting of benzophenonetetracarboxylic dianhydride (BPDA) and 3,3'-diethyl-4,4'-diaminodiphenylmethane (EDDM), i.e. PI(BPDA/EDDM), as a part of our continuing study on the solid state reactions. We examined the photocrosslinking reaction of PI(BPDA/EDDM) and discussed the detail in mechanism, compared with its model reaction.

PI(BPDA/EDDM) films were prepared by solvent cast method from dichloromethane, followed by drying at 120 °C for 24 hours. Model compound M(BPDA/DMA) was prepared from BPDA and 2,4-dimethylaniline (DMA) by usual method. Photoirradiation was carried out with 250 W ultrahigh pressure mercury lamp or 450 W high pressure mercury lamp through a KL-35 filter.

PI(BTDA / EDDM)

M(BTDA / DMA)

In IR spectra of PI(BTDA/EDDM), a peak at 1680 cm^{-1} , which is attributed to Benzophenone carbonyl, decreases during photoirradiation. The reaction is supposed to proceed via hydrogen abstraction by excited carbonyl from ethyl group followed by recombination of radicals as shown below. Quantum yields for photocrosslinking were measured by GPC, and Arrhenius plot of the quantum yields for photocrosslinking is shown in Fig. 1.

The activation energy is quite similar to that for polyethersulfone (PESF) or polyetherimide (PEI), and is characteristic of solid state reaction. The value of the activation energy does not change around T_g , however, suggesting that the crosslinking reaction of PI(BPDA/EDDM) proceeds via different mechanism from those of PESF and PEI. It is supposed to be affected by the deactivation of carbonyl group, in other words, relaxation time of segmental motion in main chain above T_g is still longer than the life time of excited state of carbonyl group.

Hydrogen abstraction reaction of benzophenone (BP) and M(BPDA/DMA) from ethylbenzene was investigated with using HPLC and GC in order to examine the influence of imide structure of PI(BPDA/EDDM) on the reactivity of benzophenone carbonyl. The quantum yield for M(BPDA/DMA) is 0.066, which is smaller than that for BP of 0.88. The quantum yield for triplet formation was found to be unity, which is equal to that for BP. The rate constant for hydrogen abstraction by PI(BPDA/EDDM) is also smaller than that for BP. These results are supposedly due to CT character of excited state of M(BPDA/DMA).

Figure 1. Arrhenius plot of Quantum yield for photocrosslinking of PI(BTDA/EDDM).