Photosolubilization of Polyolefinsulfone Containing Side-chain Oxime Ester Groups

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A novel polyolefinsulfone bearing a photobase generator in a side-chain was synthesized via radical polymerization of an olefin monomer in liquefied sulfur dioxide. The polyolefinsulfone was photochemically solubilized in an aqueous solution of 0.012 M HCl.

The design and synthesis of new photopolymers has attracted great interest in recent years. The major requirement for photopolymers is that they exhibit a chemical change that allows the irradiated parts of the polymer to be distinguished from the non-irradiated parts, usually on the basis of solubility.[1] A UV-induced change in the polarity of a polymer enhances the solubility of the irradiated parts. There have been many reports of polymer photosolubilization in which the polarity of polymers has been changed by photochemical means. Photobase-generating polymers are one such type. Photopolymers bearing photobase-generating groups are expected to be particularly applicable in photolithographic processes because their amino groups do not corrode metals.

Polyolefinsulfones contain sulfonyl groups ($-SO_2-$) in the main chain. Their practical applications include use in engineering plastics and in functional polymers such as heat-resistant polymers, adhesives, and electron beam resists.[2,3] As the sulfonyl group is a strong electron-withdrawing moiety, the neighboring methylene becomes acidic, so that the protons on the methylene can be extracted by bases, which leads to main-chain scission.[4] In this way, the addition of a base such as amine to a polyolefinsulfone solution gives rise to decomposition of the polymer. Thus, a polyolefinsulfone containing a photobase generator has potential as a photodecomposition polymer. In this study, a polyolefinsulfone possessing a photobase-generating moiety in the side chain (polyacetophenone 3-butenoyloxime sulfone) was synthesized (Figure 1), and photosolubilization of the polymer was examined. An oxime ester was chosen as the photobase-generating group;[5–13] when exposed to 365-nm light, this group is photochemically converted into an imino group, which can be changed to an amino group by adding the polymer to a dilute HCl solution (Figure 1).

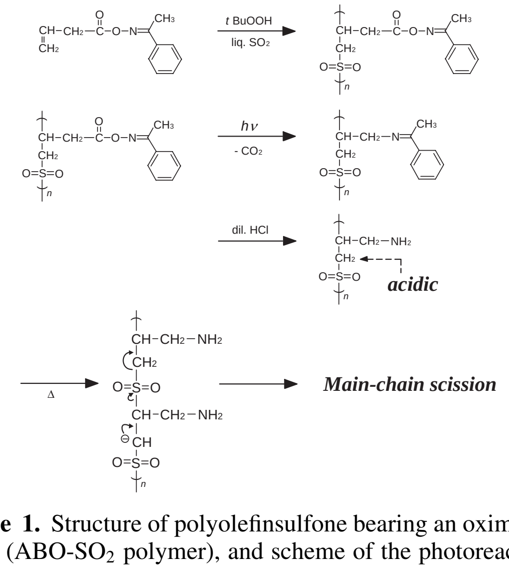

Figure 1. Structure of polyolefinsulfone bearing an oxime ester group (ABO-SO_2 polymer), and scheme of the photoreaction.

Acetophenone 3-butenoyloxime (ABO monomer) was synthesized by reaction of acetophenone oxime with 3-butenoic chloride, and then polymerized in liquefied sulfur dioxide at −13 °C by radical polymerization.[14] *tert*-Butyl hydroperoxide was used as a redox initiator. Because the stability of the sulfonyl radical is much higher than that of the vinyl radical, and the sulfur atom is positively charged, a 1:1 alternating copolymer of SO_2 and the olefin monomer is obtained. The copolymerization ratio was examined by elemental analysis.

A chloroform solution of ABO-SO_2 polymer and a sensitizer (benzophenone, 10 wt % relative to the polymer) was spin-coated on a glass plate. The thickness of the film was 1 µm. The sample film was irradiated by a 250-W super high-pressure mercury lamp with an interference filter (365 nm, 1 mW/cm^2). After irradiation, the film was immersed in 0.012 M HCl for 10 min at 80 °C. The polymer at the irradiated part was most soluble to HCl solution at 80 °C.

Figure 2 shows the UV–vis absorption spectra of ABO-SO_2 polymer film before and after irradiation. It can be seen that the absorption around 250 nm decreases with irradiation, while that of the imino group (300 nm) increases. The photochemical reaction of the oxime ester group was examined by IR absorption

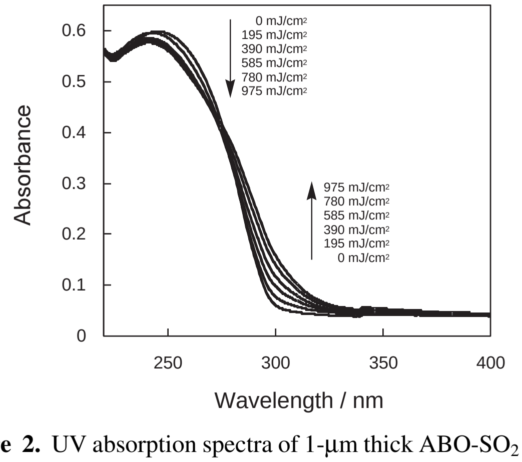

Figure 2. UV absorption spectra of 1-µm thick ABO-SO_2 polymer film with irradiation at 254 nm.

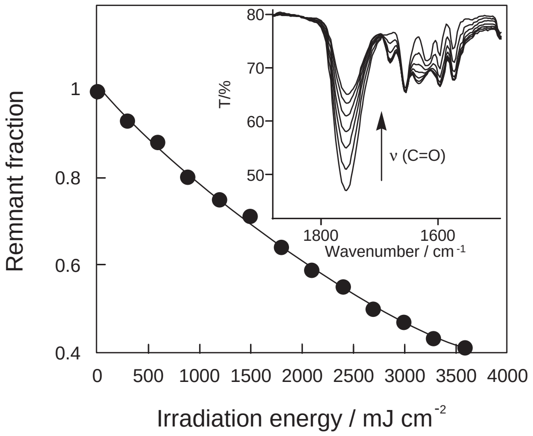

Figure 3. Remaining fraction of oxime ester groups as a function of irradiation energy. Inset shows the IR absorption spectra of the film before and after irradiation.

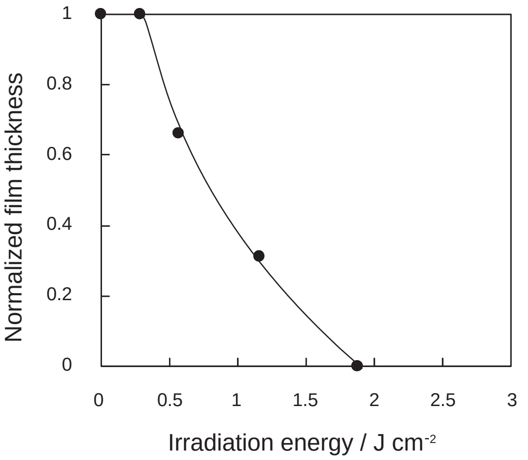

Figure 4. Thickness of ABO-SO_2 film after immersion in 0.012 M HCl at 80 °C for 10 min.

measurement (Figure 3, inset). A decrease in absorbance at $1756\,cm^{-1}$ (C=O stretching) demonstrated photoinduced decarboxylation of the oxime ester group. The fraction of oxime ester groups remaining after irradiation is plotted as a function of irradiation energy in Figure 3. A total of 60% of oxime ester groups were converted to imino groups by irradiation of 3500 mJ/cm^2.

Photosolubilization of the ABO-SO_2 polymer was also examined. After irradiation, the ABO-SO_2 polymer film was immersed in 0.012 M HCl. The film thickness was measured by atomic force microscopy (AFM); normalized film thickness is plotted as a function of irradiation energy in Figure 4. A 0.5-μm film of ABO-SO_2 polymer was completely solubilized in 0.012 M HCl by 365 nm irradiation of $1900\,mJ/cm^2$. An ABO-SO_2 polymer film with a photomask was irradiated and a photopattern was developed; Figure 5 shows a SEM image of the irradiated area. It can be seen that the irradiated area was completely dissolved, creating a sharp contrast with the non-irradiated area. The polymer at the irradiated area was dissolved in 0.012 M HCl and the molecular weight was measured by GPC. The molecular weight was decreased from 83,000 to 31,000. The reduction of molecular weight was higher than that caused by the photodecomposition of the side chain. Thus, it was supposed that the main-chain scission was induced. The solubility of the irradiated polymer was enhanced not only by the UV-induced change in the polarity of the polymer but also by the main-chain scission.

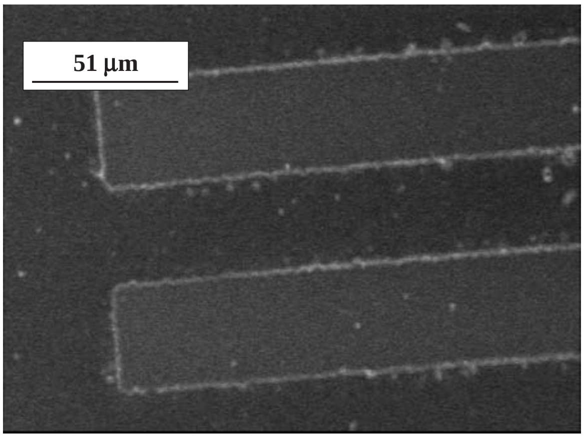

Figure 5. SEM image of micropattern formed on the ABO-SO_2 polymer film.

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References

1 A. M. Sarker, A. Mejiritski, B. R. Wheaton, D. C. Neckers, *Macromolecules* **1997**, *30*, 2268.
2 M. J. Bowden, E. A. Chandross, *J. Electrochem. Soc.* **1975**, *122*, 1370.
3 L. F. Thompson, M. J. Bowden, *J. Electrochem. Soc.* **1973**, *120*, 1722.
4 T. Shinoda, T. Nishiwaki, H. Inoue, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2760.
5 K. Suyama, S. Yamaguchi, M. Shirai, M. Tsunooka, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1708.
6 K. Suyama, Y. Miyamoto, T. Matsuoka, S. Wada, M. Tsunooka, *Polym. Adv. Technol.* **2000**, *11*, 589.
7 M. Tsunooka, T. Matsuoka, Y. Miyamoto, K. Suyama, *J. Photopolym. Sci. Technol.* **1998**, *11*, 123.
8 K. Suyama, M. Tsunooka, *J. Appl. Polym. Sci.* **1998**, *68*, 1177.
9 K. Ito, Y. Shigeru, M. Tsunooka, *Macromol. Rapid Commun.* **1996**, *17*, 203.
10 K. Ito, Y. Shigeru, Y. Kawata, K. Ito, M. Tsunooka, *Can. J. Chem.* **1995**, *73*, 1924.
11 K. Ito, M. Nishimura, M. Sashio, M. Tsunooka, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2177.
12 K. Ito, M. Nishimura, M. Sashio, M. Tsunooka, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1793.
13 K. H. Song, S. Tonogai, M. Tsunooka, M. Tanaka, *J. Photochem. Photobiol., A* **1989**, *49*, 269.
14 H. Bae, T. Miyashita, M. Iino, M. Matsuda, *Macromolecules* **1988**, *21*, 26.