

Solubility control by UV irradiation of a copolymer having both photobase generating groups and photoacid generating groups

Kanji Suyama^{*a†} and Masahiro Tsunooka^{b‡}

^a Nissha Printing Co. Ltd., 3 Mibu-Hanai-Cho, Nakagyo, Kyoto 604, Japan

^b Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 593, Japan

An insoluble-soluble-insoluble contrast curve is obtained for a polymer film having both photobase and photoacid generating groups when it is developed using a polar solvent; the base groups are introduced before the acid groups.

The solubility change of polymeric material upon irradiation is a key factor in their application to photoresists because photopatterning utilizes the solubility differences between irradiated and non-irradiated polymers. Many methods have been tried to improve the solubility change upon irradiation to obtain higher sensitivity and resolution. Photoacid generators have attracted increasing attention as a catalyst for high-sensitivity photoresist systems, the 'chemically amplification' type, where generated acids catalyse the thermolyses of carbonate groups into hydroxy groups.¹ Photobase generators have also been studied, including Co-amine salt,² polymers bearing *o*-acyloxyimino (AOI) groups,³ *o*-nitrobenzoyloxycarbonyl derivatives,^{4,5} benzoyloxycarbonyl derivatives^{6,7} and formamides.⁸

We have studied the photochemical behaviour of copolymers of acryloyl acetophenone oxime (AAPO), and found that AOI groups in AAPO units transformed into pendant amino groups upon irradiation, followed by hydrolysis.^{3,9,10} On the other hand, we have also found that β -keto sulfone (β -KS) groups in phenacylsulfonyl styrene (PSSSt) copolymers were transformed into pendant sulfinic or sulfonic acid groups upon irradiation.^{11,12} From these results we expected that polymers bearing both acid and base units in the same polymer-chain would be obtained when a copolymer of AAPO and PSSSt is irradiated.

On investigation of the photochemical behaviour of a polymer bearing both units, p(AAPO-St-PSSSt) **1**, we found that **1** became soluble upon irradiation and then became insoluble on further irradiation when developed with a polar solvent. When developed with a non-polar solvent, **1** became insoluble. Here we report the dual-photoresist behaviour of **1**, Fig. 1.

Monomers were prepared as described in a previous paper,⁹ and polymerized in degassed benzene at 60 °C using 0.2 mass% of AIBN as an initiator. The resulting polymeric material was reprecipitated three times from THF-MeOH to give **1** in 39.9% yield with $M_n = 75\,000$ ($M_w/M_n = 1.66$) determined by GPC analysis using THF as eluent and polystyrene as standard. The molar ratios of the monomers in **1** were AAPO:

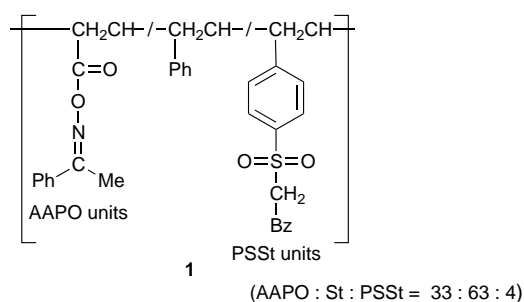


Fig. 1

PSSSt:St = 32.5:4.2:63.3, obtained from the ¹H NMR integrated area ratio. The films were prepared by spin-coating a 7.5 mass% diglyme solution on a quartz or borosilicate glass plate, followed by drying in an oven at 85 °C for 20 min. The absorbance at 254 nm was *ca.* 1.5, and the film thickness was 0.35–0.5 μm , measured by a Kosaka surface roughness meter ET-10. All irradiations were performed in air at room temperature using a Ushio UV-102 mercury lamp (100 W) without wavelength selection. The intensity of light was 3.01 mW cm^{-2} at 254 nm and 4.62 mW cm^{-2} at 366 nm, measured by an Orcs' UV-Light measure model UV-M02. After irradiation, the films were immersed into a 0.12 M HCl solution for 3 min and then in MeOH or THF for 10 min. All solutions were kept at 23 °C. UV spectra were measured by a Shimadzu UV-3100. The samples for IR spectral measurement were scratched away from the plate and measured on a Perkin-Elmer 1620.

Fig. 2 shows the relationship between the irradiation time and the normalized film thickness of **1** developed with MeOH. The dotted line shows the change of normalized film thickness, which were irradiated for a given time, HCl treated and developed with MeOH. As the irradiation time increased, the developed films became thin and dissolved completely after 2–4 min irradiation time. However, gelatinous material was obtained on the glass plate for longer irradiation times such as 10, 15 or 20 min, and it was impossible to measure the film thickness. When the films were cured at 100 °C before MeOH development, the films became hard enough to measure the thickness. In this case, the films dissolved only after 2–4 min irradiation time and became insoluble after further irradiation as indicated by the solid line in Fig. 2.

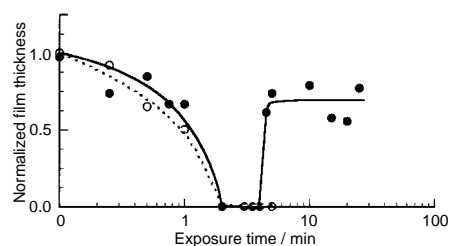


Fig. 2 Contrast curves of films of **1** developed with MeOH after HCl treatment (---○---) and MeOH after HCl treatment and curing at 100 °C (—●—)

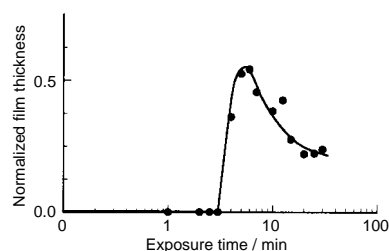
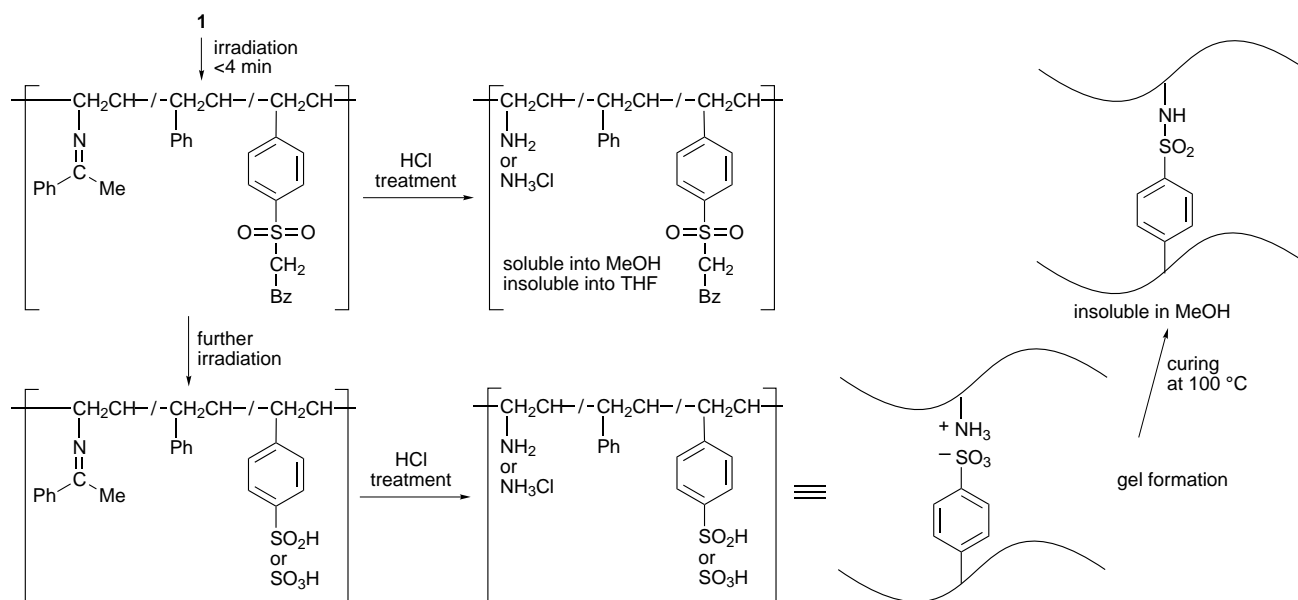


Fig. 3 Contrast curve of films of **1** developed with THF



Scheme 1 Photoreaction of 1

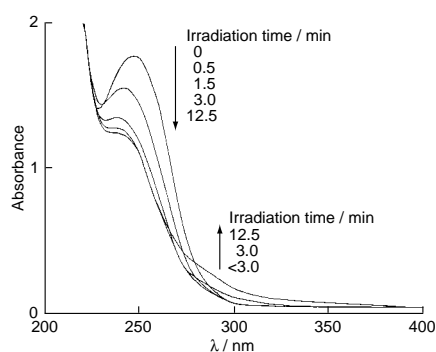


Fig. 4 UV spectral changes of film of 1 upon irradiation

This film showed a different solubility behaviour when developed with THF. As shown in Fig. 3, the film irradiated for 4 min became insoluble in THF. With longer irradiation time, the thickness of the resulting films gradually decreased. This tendency in the later stage was similar to the phenomenon found in copolymers of PSSt and styrene or MMA.¹²

Fig. 4 shows the changes of the UV absorption spectra of the irradiated films. The peak at *ca.* 250 nm decreased after less than 3 min of irradiation. Upon further irradiation, however, the decrease almost stopped, and a new band appeared in the 260–380 nm region. The latter seems to relate to the β -KS groups because this band appeared in the PSSt and styrene or MMA copolymers upon irradiation¹³ and not in those having AAPO units. The changes in the β -KS groups are thus deduced to occur after 3 min irradiation.

The structural change of this copolymer might be explained as shown in Scheme 1. Upon irradiation for less than 3 min, the AOI groups in the AAPO units decompose. The recombination of iminyl radicals and radicals on the main chain results in imino groups which are converted to amino groups by HCl treatment. At this stage the conversion of the β -KS groups appears to be very low. Upon further irradiation most of the AAPO units give imino (or amino) groups, and also β -KS groups are photo-transformed into sulfinic or sulfonic acid groups. The resulting acid groups form interaction points with amino groups, which afford intra- and inter-molecular cross-links. At this stage the film swelled in the developer. It is thus deduced that when cured at 100 °C the cross-links are transformed into sulfonamides.

The photo-decomposition of AOI groups can be explained by an effective energy transfer from β -KS groups to AOI groups, which restricts the photochemical change of β -KS groups until the AOI groups have decomposed almost completely. In fact, the sensitization of the decomposition of the AOI groups by β -KS groups was confirmed by photolysis at 366 nm. Although we used a mercury lamp without a wavelength selector as the light source for our experiments, we assumed that the energy transfer from the β -KS groups to the AOI groups is still important because the direct photolysis of AOI groups is slow compared to 1.

We thank Mr T. Takemoto, Department of Applied Chemistry, Osaka Prefecture University, for measuring the NMR spectra.

Footnotes

- † E-mail: BXE05610@niftyserve.or.jp.
‡ E-mail: tsunooka@chem.osakafu-u.ac.jp

References

- 1 *Microelectronics Technology*, ACS Symposium Series 614, ed. E. Reichmanis, C. K. Ober, S. A. MacDonald, T. Iwayanagi and T. Nishikubo, ACS, Washington, DC, 1995.
- 2 C. Kotal and C. G. Willson, *J. Electrochem. Soc.*, 1987, **134**, 2280.
- 3 K.-H. Song, A. Urano, M. Tsunooka and M. Tanaka, *J. Polym. Sci., Part C, Polym. Lett.*, 1987, **25**, 417.
- 4 J. F. Cameron and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1991, **113**, 4303.
- 5 J. M. J. Fréchet, *Pure Appl. Chem.*, 1992, **64**, 1239.
- 6 J. F. Cameron and J. M. J. Fréchet, *J. Org. Chem.*, 1990, **55**, 5919.
- 7 J. M. J. Fréchet and J. F. Cameron, *Polym. Mater. Sci. Eng.*, 1991, **64**, 55.
- 8 T. Nishikubo, E. Takehara and A. Kameyama, *Polym. J.*, 1993, **25**, 421.
- 9 K.-H. Song, M. Tsunooka and M. Tanaka, *J. Photochem. Photobiol. A: Chem.*, 1988, **44**, 197.
- 10 K. Suyama and M. Tsunooka, *J. Polym. Sci., Polym. Chem. Ed.*, 1996, **34**, 2181.
- 11 M. Tsunooka, H. Yanagi, M. Kitayama and M. Shirai, *J. Photopolym. Sci. Technol.*, 1991, **4**, 239.
- 12 M. Tsunooka, T. Ikehara, T. Takemoto and M. Shirai, *J. Photopolym. Sci. Technol.*, 1996, **9**, 17.
- 13 T. Takemoto and M. Tsunooka, unpublished results.

Received, 1st November 1996; Com. 6/07434K