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# MAGNETIC FIELD EFFECT ON PHOTOCROSSLINKING REACTION OF BROMO- AND CHLOROMETHYLATED POLYSTYRENE

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Photocrosslinking efficiency of bromo- and chloromethylated polystyrene sensitized by 2,4-diisopentylthioxanthone was evaluated in a thin film by measuring the gel fraction of the polymer irradiated with UV($\lambda$>330 nm) light. By the application of an external magnetic field of 70 mT, the gel fraction increases and photocrosslinking efficiency is enhanced by ≈36%.

External magnetic field effects on photochemical processes of aromatic carbonyl compounds such as benzophenone,[1,2] 1,3-diphenyl-2-propanone,[3,4] and xanthone[5] have been studied extensively in solution and in micelles with the aid of laser-photolysis technique. However, the application of the magnetic field effect to the study of polymers is very few;[6,7] Turro[7] reported the magnetic field effect on photopolymerization efficiency and the degree of polymerization of styrene initiated by 1,3-diphenyl-2-propanone in oleophillic emulsion.

Polystyrene derivatives have been extensively developed as X-ray and electron-beam resists in microlithography.[8] Among them, one of the halomethylated polystyrene, i.e., bromo- and chloromethylated polystyrene (BCMS) (Fig. 1) recently developed as an X-ray resist was found to be sensitized to UV region by the addition of some sensitizers such as 2,4-diisopentylthioxanthone (DITX) and 4,4'-bis(dimethylamino)benzophenone.[9] Under the light($\lambda$>330 nm) irradiation, DITX induces photocrosslinking reaction of BCMS, and the BCMS/DITX system functions as a negative photoresist. In the elucidation of photocrosslinking mechanism for the negative photoresists, we have for the first time observed the magnetic field effect on photocrosslinking reaction in a thin(≈0.5 μm) film of the BCMS/DITX system.

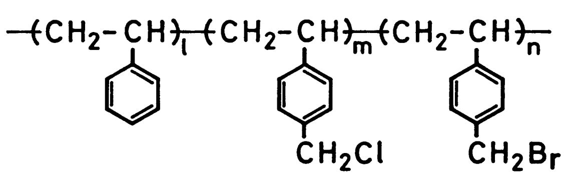

Fig. 1. Chemical structure of bromo- and chloromethylated polystyrene (BCMS) with l:m:n=24:36:40, $\overline{M_w}$ = 10.8 × $10^4$, and $\overline{M_w}/\overline{M_n}$ = 1.18.

p-Xylene solution of BCMS (10 wt%) and DITX (1 wt%) was spin-coated on a Si wafer and prebaked at 80 °C for 20 min. Photosensitive layer thus obtained (i.e., BCMS/DITX system) on a Si wafer was placed in an electromagnet and irradiated with a 450 W medium pressure mercury lamp (Ushio UM452) through a UV-33 filter in argon atmosphere. BCMS generates photocrosslinks and is insolubilized to some solvents. After developing with 2-ethoxyethanol /isopentylacetate (58:42) followed by linsing and post-baking, residual film thickness, t, was measured with an interferometer (Nikon surface finish microscope). Compared with the initial film thickness, $t_0$ (≈0.5 μm), gel fraction, G(i.e., $t/t_0$) was determined as a function of incident energy in the wavelengths longer than 330 nm. The result (i.e., characteristic curve) for the BCMS/DITX system in the absence and in the presence of a magnetic field of 70 mT is shown in Fig. 2. By the application of the magnetic field, the gel fraction increases. The incident energy at which the gel fraction reaches to 0.5, $D_g^{0.5}$, is 2500 and 1900 mJ $cm^{-2}$ in the absence and in the presence of a magnetic field of 70 mT, respectively. The sensitivity of the system (evaluated from $D_g^{0.5}$) is enhanced by ≈30% by the application of the magnetic field.

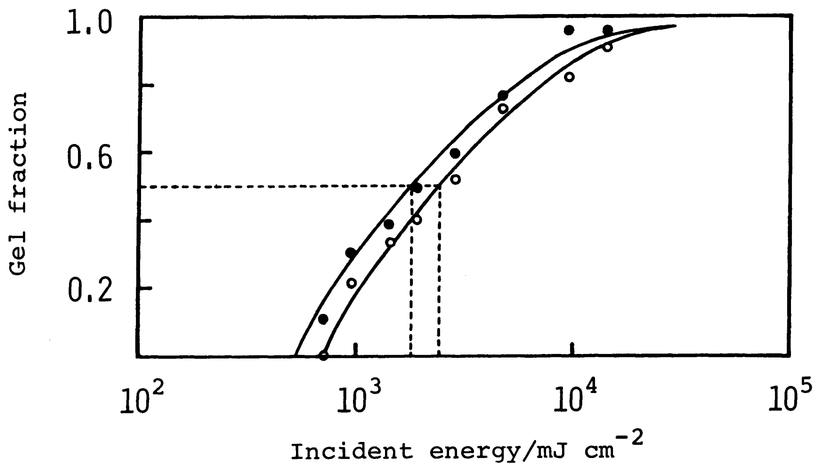


Fig. 2. Characteristic curves for BCMS/DITX in the absence of a magnetic field (o) and in the presence of a magnetic field of 70 mT (●).

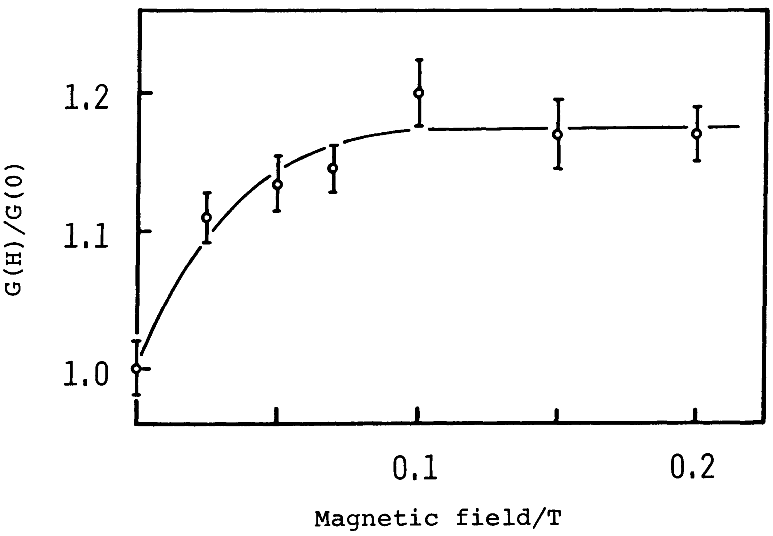


Fig. 3. Magnetic field dependence of the gel fraction of BCMS/DITX with a fixed (2.9 J $cm^{-2}$) incident energy. Probable error for G(H)/G(0) is indicated by a vertical line.

Efficiency of photocrosslink formation, $\phi$, is evaluated according to the following equation;[10]

$$\phi = r \cdot d / 2.303 \cdot E_g \cdot D \cdot \overline{M_w},$$

where $E_g$ is the gel point exposure (in Einstein $cm^{-2}$), D, the optical density (i.e., absorbance) of the BCMS/DITX film of thickness, r, and specific gravity, d, and $\overline{M_w}$, the weight-average molecular weight of BCMS ($10.8 \times 10^4$). Assuming d≈1, $\phi$ is calculated to be 0.002. By the application of the magnetic field of 70 mT,

$E_g$ value decreases to 73%, hence the efficiency of photocrosslink formation increases by ≈36%.

Magnetic field dependence of the gel fraction, G(H), of BCMS/DITX with a fixed incident energy (2.9 J $cm^{-2}$) is plotted in Fig. 3 where the probable error for G(H)/G(0) is estimated from a set of experimental values of the gel fraction in the presence and in the absence of an external magnetic field. The gel fraction increases as the magnetic field increases up to ≈0.1 T. The magnetic field effect on the gel fraction saturates at ≈0.1 T to be G(H)/G(0) ≈1.17.

The magnetic field effect on the efficiency of photocrosslink formation can be understood qualitatively by the following radical pair model (Scheme 1).

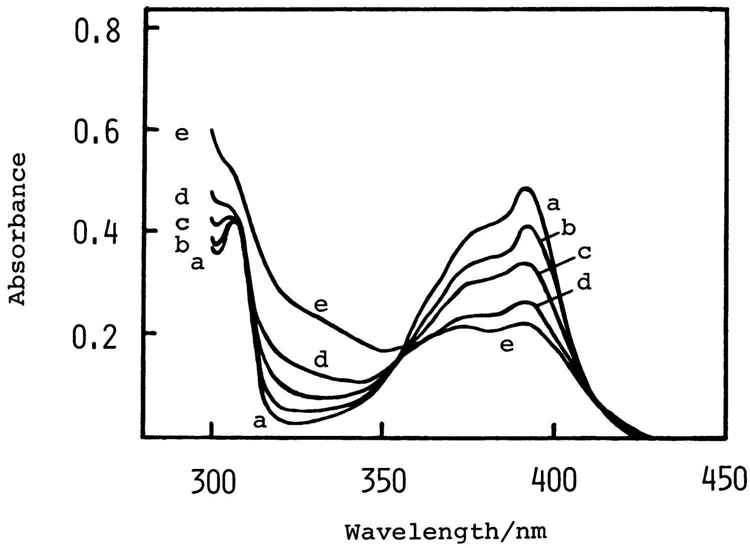


Fig. 4A. UV absorption spectra of the BCMS/DITX film irradiated with a medium pressure mercury lamp through a UV-33 filter for (a)0, (b)4, (c)14, (d)44, and (e)104 min.

$$DITX \xrightarrow{h\nu} {}^1(DITX) \rightarrow {}^3(DITX)$$

$${}^3(DITX) + P_nH \rightarrow {}^3(DITXH\cdot \ \cdot P_n) \downarrow\uparrow {}^1(DITXH\cdot \ \cdot P_n)$$

$${}^3(DITXH\cdot \ \cdot P_n) \rightarrow \text{Escaping radicals} \downarrow \text{Crosslinking}$$

$${}^1(DITXH\cdot \ \cdot P_n) \rightarrow \text{Recombination or Cage reaction}$$

Scheme 1.

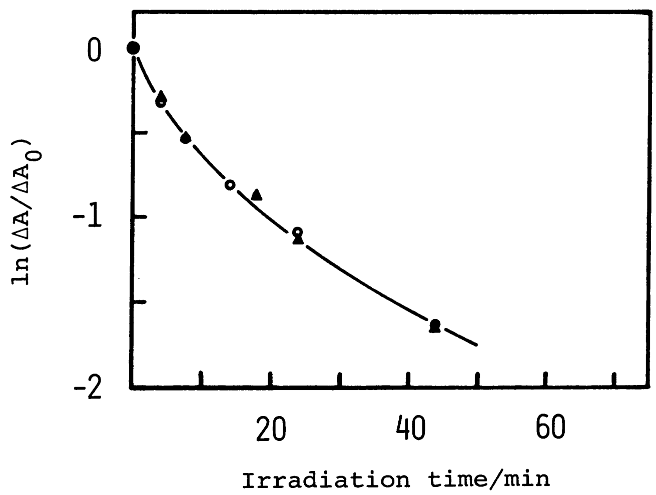


Fig. 4B. Dependence of absorbance, ΔA (=A(t)-A(t=104 min)) at 391 nm on UV(λ> 330 nm) irradiation time in the absence of a magnetic field (o) and in the presence of a magnetic field of 0.1 T (▲).

DITX in the triplet state abstracts a hydrogen atom from the BCMS polymer ($P_nH$) (α-hydrogen of the polymer may supposedly be abstracted) to form a triplet radical pair between the ketyl radical (DITXH·) and the polymer radical ($P_n$·). The triplet radical pair can convert to the singlet radical pair which subsequently undergoes recombination or cage reaction. The triplet radical pair can generate escaping free radicals which eventually induce crosslinking of the polymer. By the application of a magnetic field, conversion rate between the triplet and the singlet radical pairs decreases,[3] and consequently the efficiency of the crosslink formation increases. Actually, the rate of the photobleaching of DITX measured with UV absorption spectrum at 391 nm (Fig. 4) is not affected by the application of a magnetic field of 0.1 T, supporting that the magnetic field influences the radical pairs. From the fact that the magnetic field effect saturates at a low magnetic field (≈0.1 T) (Fig. 3), it is suggested that the hyperfine induced triplet-singlet mixing of the radical pair is effective for the BCMS/DITX system.

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