# Magnetic Field Effect on Photocrosslinking Reaction of Directly Excited Azidomethylated Polystyrene

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## Synopsis

Gel fractions of thin films of poly(styrene-*co*-vinylbenzyl azide) (AZMS) irradiated with a low pressure mercury lamp were measured in the absence and in the presence of an external magnetic field. By the application of a magnetic field of 0.089 T, the gel fraction of AZMS decreases, and the efficiency of photocrosslink formation decreases by $\approx 20\%$, in contrast to the case of sensitized photocrosslinking of AZMS where the efficiency increases by the application of a magnetic field. Based on the photocrosslinking mechanism of directly excited AZMS, it is concluded that the singlet nitrene which is produced from the singlet excited AZMS abstracts a hydrogen atom from the AZMS polymer to form the singlet radical pair, and that the magnetic field decreases the singlet–triplet intersystem crossing rate of the radical pair.

## INTRODUCTION

Magnetic field effect on photocrosslinking reaction in polymer film was first observed with bromo- and chloromethylated polystyrene (BCMS) with 2,4-diisopentylthioxanthone (DITX) as a sensitizer.[1] In a previous paper[2] we extended the study to poly(styrene-*co*-vinylbenzyl azide) (AZMS), and found that the efficiency of photocrosslink formation of AZMS sensitized with DITX and 2-chlorothioxanthone (CTX) is increased in the presence of an external magnetic field of $\approx 0.1$ T. In sensitized photolysis, AZMS is excited to the triplet state by triplet energy transfer from the sensitizer, and the triplet azide produces the triplet nitrene. The triplet nitrene abstracts a hydrogen atom from the sensitizer and/or the polymer to generate a triplet radical pair. The magnetic field was found to decrease the triplet-singlet intersystem crossing (ISC) rate of the radical pair.[2]

To thoroughly understand the photocrosslinking mechanism of AZMS, which was originally designed for a negative-working deep UV resist in microlithography,[3] it is necessary to investigate the behavior of the singlet nitrene. The singlet nitrene can be generated efficiently by exciting the azides directly,[4,5] and the study of the magnetic field effect on crosslinking reaction through the singlet nitrene may give us a new insight into a photocrosslinking mechanism. In the present article, the magnetic field effect on the efficiency of photocrosslink formation of directly excited AZMS has been measured in thin films. The pho-

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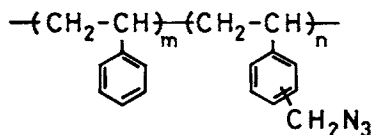
$$-(CH_2-CH)_m-(CH_2-CH)_n-$$

Fig. 1. Chemical structure of poly(styrene-co-vinylbenzyl azide) (AZMS).

tochemical behavior of the nitrene and the mechanism of the magnetic field effect have been discussed in comparison with the results of the sensitized photocrosslinking of AZMS previously reported.[2]

## EXPERIMENTAL

### Materials

AZMSs (AZMSI, AZMSII, and AZMSIII) (Fig. 1) with different monomeric ratios of styrene and vinylbenzyl azide (VBA) were prepared by copolymerization in deaerated benzene solution (50 mL) at 70°C for 30 h, with 2,2'-azobis-isobutyronitrile (0.35 g) used as an initiator. The detailed procedures of preparation and purification of AZMSs are described in the previous paper.[2] Molecular compositions and molecular weights of AZMSs were determined by elemental analysis and by high speed liquid chromatograph (Toyo Soda HLC-802UR). The results are listed in Table I. The thermal stability of AZMSs was checked by differential scanning calorimetry (DSC) (Rigaku Denki CN-8085E1). AZMSs are stable up to 200°C. Above 200°C, the azido group begins to decompose. p-Xylene (Kanto G. R. grade), used as a solvent, was purified by fractional distillation.

### Measurements

p-Xylene solution of AZMS (15 wt %) was spin-coated on an Si wafer and prebaked at 80°C for 10 min. The thin ($\approx$ 0.5 $\mu$m) film of AZMS on an Si wafer was placed in a permanent magnet (Sumitomo Special Metals Corp.), and irradiated with a 15 W low pressure mercury lamp in argon atmosphere. After developing with 2-ethoxyethanol followed by rinsing with 2–propanol and post-baking at 80°C for 10 min, residual film thickness $t$ was measured with an interferometer (Nikon surface finish microscope). Compared with the initial

TABLE I
Ratio of Monomeric Unit of VBA (%), Weight Average Molecular Weight ($\overline{M_w}$), and
Polydispersity ($\overline{M_w}/\overline{M_n}$) of the AZMS Polymer

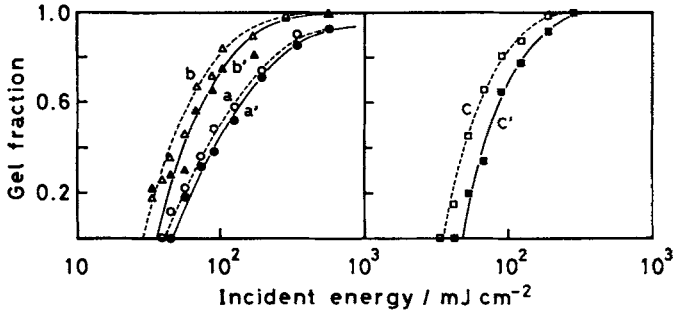|  | Ratio of VBA | $\overline{M_w}$ | $\overline{M_w}/\overline{M_n}$ |
|---|---|---|---|
| AZMSI | 9.0 | 10,300 | 1.81 |
| AZMSII | 14.7 | 12,200 | 2.26 |
| AZMSIII | 24.6 | 12,300 | 2.07 |

Fig. 2. Magnetic field effect on the characteristic curves for the sensitivity of AZMSI (curves a and a'), AZMSII (curves b and b'), and AZMSIII (curves c and c') irradiated with a low pressure mercury lamp. Magnetic field is 0 T for curves a, b, and c, and 0.089 T for curves a', b', and c'.

film thickness $t_0$, the gel fraction $G(= t/t_0)$ was calculated as a function of incident energy.

UV absorption spectra of thin ($\approx 1$ $\mu$m) films of AZMSs on quartz plates were measured with a Hitachi 200–20 recording spectrophotometer, IR spectra were measured with a Hitachi 295–10 infrared spectrophotometer, and FT-IR spectra were measured with a Nicolet 5DXB FTIR spectrophotometer.

## RESULTS AND DISCUSSION

### Magnetic Field Effect on Photocrosslinking Efficiency

Characteristic curves for the lithographic sensitivity of AZMSI, AZMSII, and AZMSIII irradiated with the low pressure mercury lamp have been measured in the absence and in the presence of an external magnetic field of 0.089 T. The results are shown in Figure 2, and lithographic sensitivities[6] $D_g^i$ and $D_g^{0.5}$ for AZMSs are listed in Table II. AZMSII shows the highest sensitivity between the three. By the application of a magnetic field of 0.089 T, sensitivity $D_g^{0.5}$ decreases by $\approx 13\%$ (from 96 to 110 mJ/cm$^2$) for AZMSI, by $\approx 20\%$ (from 51 to 64 mJ/cm$^2$) for AZMSII, and by $\approx 27\%$ (from 55 to 75 mJ/cm$^2$) for AZMSIII. The magnetic field effect of directly excited AZMS is in contrast to

TABLE II
Sensitivities $D_g^i$ and $D_g^{0.5}$, and Quantum Efficiency of Photocrosslink Formation, $\phi$, for AZMSI, AZMSII, and AZMSIII in the Absence and in the Presence of a Magnetic Field

| | $H$ (T) | $D_g^i$ (mJ cm$^{-2}$) | $D_g^{0.5}$ (mJ cm$^{-2}$) | $\phi$ |
|---|---|---|---|---|
| AZMSI | 0 | 39 | 96 | 0.25 |
| | 0.089 | 46 | 110 | 0.21 |
| AZMSII | 0 | 29 | 51 | 0.20 |
| | 0.089 | 37 | 64 | 0.16 |
| AZMSIII | 0 | 35 | 55 | 0.18 |
| | 0.089 | 48 | 75 | 0.13 |

the result (i.e., the increase in the sensitivity) observed with the sensitized photocrosslinking of AZMS/DITX and AZMS/CTX reported previously.[2]

Efficiency of photocrosslink formation, $\phi$, is evaluated according to the following equation[7]

$$\phi = rd/2.303E_gD\overline{M_w}$$

where $E_g$ is the gel point exposure (einstein/cm$^2$) and $D$ is the optical density (i.e., absorbance) of the AZMS film of thickness $r$ and of specific gravity $d$. From the $D_g^i$ value (Table II) and the absorption spectrum of the AZMS film (Fig. 3) combined with the spectral energy distribution of the mercury lamp, $E_g \times D$ value is calculated. Assuming $d \approx 1$, $\phi$ is determined as is listed in Table II. The quantum efficiency of AZMS becomes lower as AZMS contains more the VBA units. This is due to the fact that as the number of the azido group increases, the two azido groups in the same polymer chain have more chances to form azo-coupling bond intramolecularly. By the application of a magnetic field of 0.089 T, photocrosslinking efficiency decreases by $\approx 15$, $\approx 20$, and $\approx 27\%$ for AZMSI, AZMSII, and AZMSIII, respectively.

The magnetic field dependence of the gel fraction $G(H)$ of AZMSI, AZMSII, and AZMSIII at a fixed incident energy (90, 57, and 53 mJ/cm$^2$, respectively) is plotted in Figure 4. Probable error for the mean value of $G(H)/G(O)$ is indicated by a vertical line in the figure. The gel fractions of AZMSI, AZMSII, and AZMSIII decrease as the magnetic field increases up to $\approx 0.08$ T, and the magnetic field effect saturates at $\approx 0.08$ T.

## Photocrosslinking Mechanism of Directly Excited AZMS

To investigate the photocrosslinking mechanism of the AZMS polymer in thin films, IR and FT-IR spectra of AZMSs were measured under the light
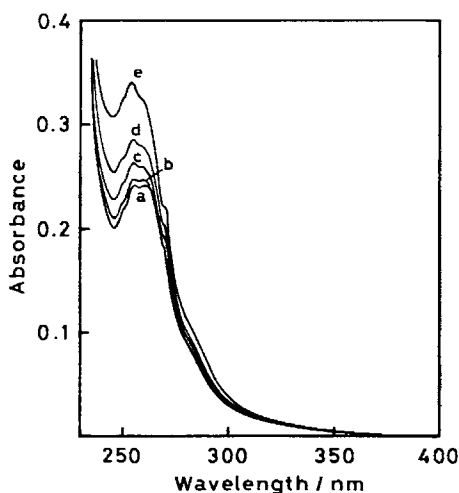


Fig. 3.   UV absorption spectra of the AZMSII film (of $\approx 0.7$ $\mu$m thickness) on a quartz plate irradiated with a low pressure mercury lamp for (a) 0, (b) 0.33, (c) 1, (d) 2, and (e) 5 min.
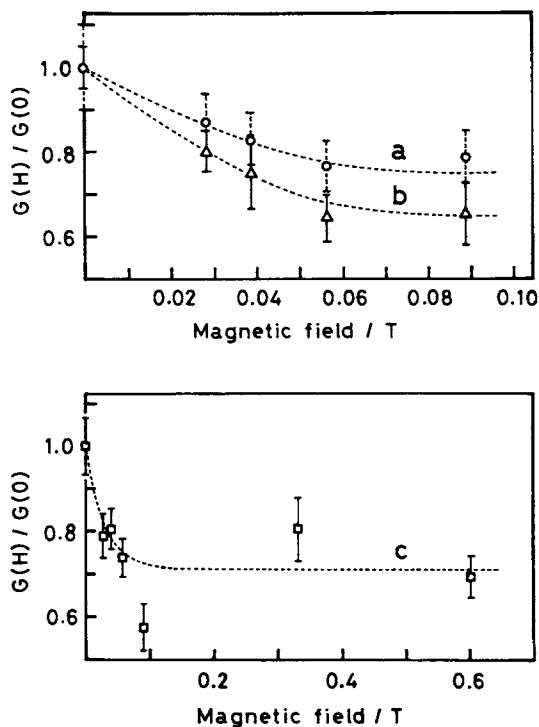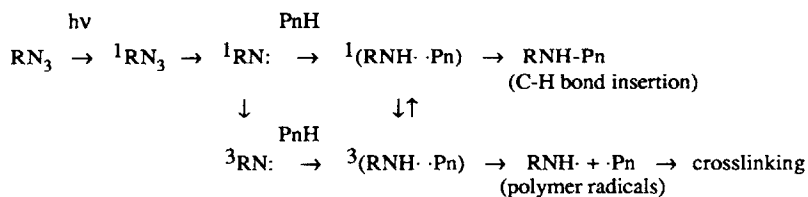
Fig. 4.   Magnetic field dependence of the gel fractions of (a) AZMSI, (b) AZMSII, and (c) AZMSIII at fixed incident energies of (a) 90, (b) 57, and (c) 53 mJ/cm$^2$.

irradiation. The 2099 cm$^{-1}$ band assigned to antisymmetric stretching vibration band of the azido group[8-10] largely decreases its intensity, revealing that photocrosslinking of the AZMS film proceeds through decomposition of the azido group.[2] Directly excited alkyl azides were reported to produce the singlet nitrene with a high (0.7–1.0) quantum efficiency[4,5] without intersystem crossing to the triplet azide.[5,11,12] Furthermore, aromatic azides in polymer matrices such as polystyrene, poly(methyl methacrylate), and poly(4-hydroxystyrene) were strongly suggested to photocrosslink polymers through C—H bond insertion of the nitrene and through a hydrogen abstraction by the nitrene to produce the primary and secondary amines as major products from the azides.[13 15]

Based on these results, photocrosslinking mechanism of directly excited AZMS is summarized in Scheme 1, where both RN$_3$ and PnH stand for the AZMS polymer:

$$\begin{array}{ccccccl}
\text{hv} & & \text{PnH} & & & & \\
\text{RN}_3 & \rightarrow & {}^1\text{RN}_3 & \rightarrow & {}^1\text{RN:} & \rightarrow & {}^1(\text{RNH}\cdot\cdot\text{Pn}) \rightarrow \text{RNH-Pn} \\
& & & & & & \quad\quad\quad\quad\quad (\text{C-H bond insertion}) \\
& & & & \downarrow & & \downarrow\uparrow \\
& & & & & \text{PnH} & \\
& & & & {}^3\text{RN:} & \rightarrow & {}^3(\text{RNH}\cdot\cdot\text{Pn}) \rightarrow \text{RNH}\cdot + \cdot\text{Pn} \rightarrow \text{crosslinking} \\
& & & & & & \quad\quad\quad\quad (\text{polymer radicals})
\end{array}$$

Scheme 1

The singlet nitrene ($^1$RN:) which is produced from directly excited AZMS (in the singlet excited state) abstracts a hydrogen atom from the main chain $C-H$ bond[15] in the AZMS polymer to form a singlet radical pair, $^1$(RNH· ·Pn). Recombination of the singlet radical pair results in $C-H$ bond insertion of the nitrene to crosslink two polymers. On the other hand, the singlet radical pair intersystem-crosses to the triplet radical pair, $^3$(RNH· ·Pn) which subsequently generates free polymer radicals. Recombination of the polymer radicals results in crosslinking of the polymer. Azo-coupling between the two nitrenes on different polymer chains[13] also crosslinks the AZMS polymer. In the case of 4-azido-4'-methoxychalcone in poly(4-hydroxystyrene) (which is called a UV resist MRL),[15] it is reported that the major products from the azide are the primary and the secondary amines, and even a small amount of solvent in polymer matrix increases the formation of the primary amine.[15] Considering the prebake condition of this work (80°C, 10 min) being comparable to that of a UV resist MRL (80°C, 20 min), it is very likely that the residual small amount of solvent in the AZMS polymer film increases the formation of the primary amine. This means that the formation of the free polymer radicals through the triplet radical pair, $^3$(RNH· ·Pn) and crosslinking therefrom become comparable to the crosslinking by the $C-H$ bond insertion of the nitrene.

By the application of a magnetic field, ISC rate between the singlet and the triplet radical pairs decreases, as is reported in the previous paper.[2] Because, in the case of directly excited AZMS, the magnetic field decreases the formation of free polymer radicals, the magnetic field effect on the efficiency of photocrosslink formation in the AZMS film is qualitatively understood on the assumption that the $C-H$ bond insertion of the singlet nitrene is less efficient than the crosslinking by the free polymer radicals. This assumption is acceptable if we consider that the $C-H$ bond insertion of the singlet nitrene is of stereospecific nature and is sensitive to the change of polymer matrix and its rigidity.[14,15] These characters may vary between AZMSs with different numbers of VBA unit. Following the same consideration, the larger magnetic field effect (i.e., the larger decrease in photocrosslinking efficiency) in AZMSs with more VBA units (Table II) is explained in terms of the less efficiency of the $C-H$ bond insertion of the nitrene due to the change of steric rearrangement of polymer chains in the vicinity of the reactive site.[14]

The fact that the magnetic field effect on photocrosslinking efficiency of directly excited AZMS is in contrast to that of the sensitized photocrosslinking gives support to the result previously reported by other authors[5,11,12] that the singlet azide does not intersystem-cross to the triplet azide as a major process.

The present study does not exclude the possibility that the singlet nitrene intersystem-crosses to the triplet nitrene and generates the triplet radical pair, $^3$(RNH· ·Pn) as a minor process.

## CONCLUSION

Photocrosslinking efficiency of directly excited AZMS is found to decrease by the application of a magnetic field of 0.089 T in contrast to the case of sensitized photocrosslinking of AZMS. From the comparison of the photo-

crosslinking mechanism of the singlet excited AZMS with that of the triplet excited AZMS, it is concluded that AZMS in the singlet excited state produces the singlet nitrene without intersystem crossing to the triplet AZMS, and that the singlet nitrene abstracts a hydrogen atom from the main chain $C-H$ bond in the AZMS polymer to form the singlet radical pair $^1(RNH \cdot \cdot Pn)$. Magnetic field decreases the ISC rate from the singlet radical pair to the triplet radical pair, suggesting that recombination of the polymer radicals is more effective in photocrosslink formation than the $C-H$ bond insertion of the singlet nitrene in the AZMS polymer film.

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