Photo-induced orientation and micropattern imaging of maleimide copolymers containing azobenzene side groups

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Summary

Photo-induced birefringence properties of azobenzene containing maleimide copolymers P[DR1PMI-*co*-St] **1** and P[DR1MSt-*co*-PMI] **2** are investigated. These polymers show reversible photo-induced birefringence and the rate parameters for the induction and relaxation processes are obtained. Photoimage patterns of the polymers with narrowest line width of 2 μm are obtained. The micro patterns are relatively stable for over a month at room temperature.

Introduction

Azobenzene is well known to undergo photo-induced *cis-trans* isomerization. Polymers containing azobenzene moieties are gaining much attention due to their intriguing optical properties such as optical nonlinearities, light-induced dichroism and birefringence.[1] A large value of the second-order molecular hyperpolarizability and noncentrosymmetric bulk ordering are expected from the azobenzene polymers which have electron donors and acceptors on the azo aromatic groups separated by conjugation. Accordingly, the azobenzene polymers with the second-order nonlinear optical properties can be utilized as practical devices, including modulators, optical frequency doublers and switches.[2] When the polymer is irradiated with a linearly polarized beam, a reorientation of azobenzene groups which

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align perpendicular to the incoming beam occurs through *trans-cis-trans* isomerization cycles.[3] These light-induced dichroism and birefringence properties allow the azo polymers useful materials for application as erasable optical memory devices, optical sensors and holographic information storage devices.

N-substituted maleimides are considered as polymerizable electron-poor ethylenic monomers and readily produce alternating copolymers with electron-rich monomers such as styrene and vinyl ether derivatives.[4] The resulting copolymers have, in general, high glass transition temperatures (T_g) and high molecular weights. Preparation of the N-substituted functional maleimide monomers are facile and the monomers, in most cases, are obtained as readily recrystallizable solids and can be stored for a long period at room temperature.
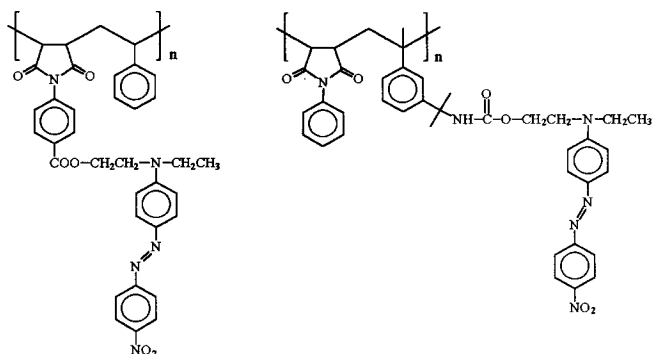
P[DR1PMI-*co*-St] **1**   P[DR1MSt-*co*-PMI] **2**

As a part of our efforts to explore a variety of functional maleimide polymers, we have investigated and now report the light-induced birefringence properties of photochromic polymers P[DR1PMI-*co*-St] **1** and P[DR1MSt-*co*-PMI] **2** shown above. The alternating copolymers **1** and **2** have a dye component, Disperse Red 1 (DR1) as an azobenzene side groups. Although many studies have been done on the birefringence properties, few articles describe the photo-induced micropattern images of azobenzene containing polymers.[5] The micropattern images of

photochemically reoriented azo polymers **2** are also described.

Results and Discussion

The alternating copolymer **1** (T$_g$: 150 °C, λ_{max} = 475nm (film)) was obtained from coupling maleimidobenzoyl chloride with Disperse Red 1 (DR1) followed by copolymerization with styrene in the presence of a radical initiator AIBN in DMF. The azo polymer **2** (λ_{max} = 475nm (film)) was prepared by polymerization of N-phenylmaleimide and 3-isopropenyl-α,α-dimethylphenylisocyanate followed by coupling with DR1. The inherent viscosities of the polymer **1** and **2** are 0.19 and 0.20 dL/g, respectively, in dioxane at 25 °C at a concentration of 0.20 g/dL. The detailed procedures for the synthesis and spectroscopic data of the azo polymers **1** and **2** will be reported elsewhere.
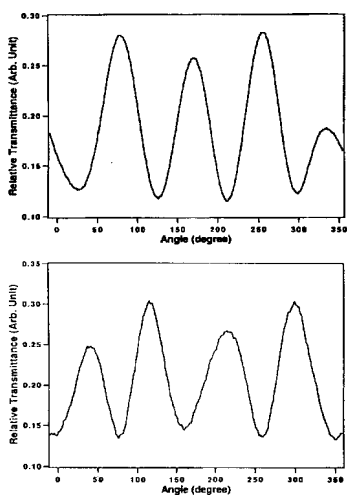

Figure 1. Bireffingence curves of azobenzene containing polymers P[DR1PMI-*co*-St] **1** (above) and P[DR1MSt-*co*-PMI] **2** (below).

In order to investigate the birefringence properties of polymers **1** and **2**, a spin-coated polymer film on a quartz slide was irradiated with linearly polarized beam using mercury lamp. The intensity of the writing beam irradiated on the polymer film was 0.46 mW/cm^2 and birefringence was induced for 10 min. A He-Ne laser (632.8 nm) was used as the reading beam which does not interfere with the absorption band of the azo group. Laser intensity was measured while rotating the polymer film around the axis of the incident beam. The results are shown in Figure **1**. As shown in Figure **1**, the relative transmittance of both polymer films varies periodically with the angle of sample rotation, indicating a photo-induced birefringence. Polymer samples

unirradiated or irradiated with unpolarized light showed no variation in transmittance according to the rotation angle of the samples. The birefringence properties of the polymer samples can also be measured by in-situ writing and reading cycles. A schematic diagram of the experimental set-up and birefringence curve of the P[DR1PMI-*co*-St] **1** are presented in Figure **2**.
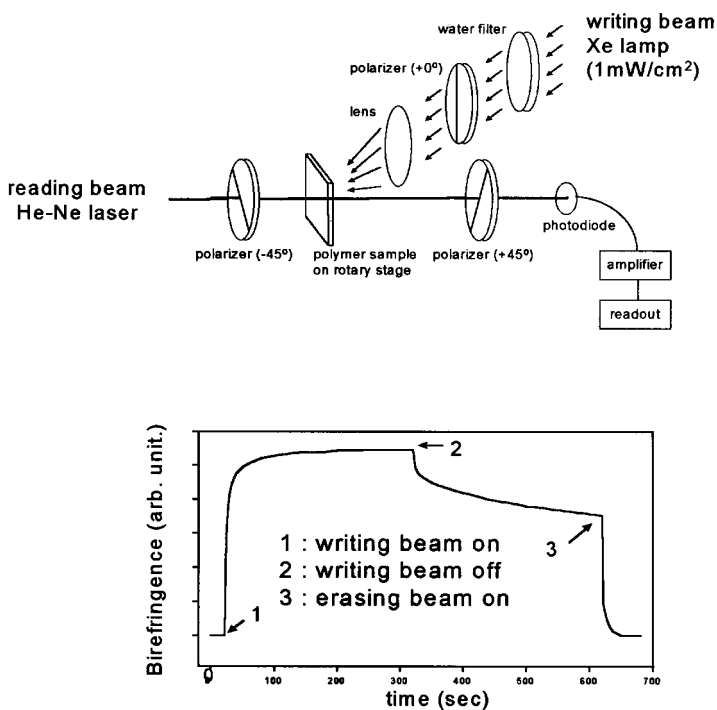

Figure 2. Schematic diagram of the experimental set-up (above) and in-situ birefringence curve (below) of P[DR1PMI-*co*-St] **1**.

The intensity of the transmitted reading beam increases sharply and reaches to the saturation when the writing beam is on. The reading beam intensity decreases when the writing beam is turned off due to relaxation of the azobenzene conformation. The relaxation curve leveled off at a constant level leading to a plateau. When the unpolarized writing beam

(erasing beam) is turned on, the intensity of the trans   mitted beam decreases to almost zero level. It is possible to repeat the cycles many times. The in-situ birefringence curves of the azo polymers **1** and **2** during the writing process are shown in Figure **3**. Growth curves can be analyzed in terms of biexponential function shown in equation 5.[6]

$$y = A[1-\exp(-k_a t)] + B[1-\exp(-k_b t)] \ \dots\dots\dots\dots\dots\dots\dots\dots\dots \ (5)$$

where k_a and k_b are the rate constants for the fast and the slow growth modes, A and B are the magnitudes of the fast and the slow growth modes, respectively.
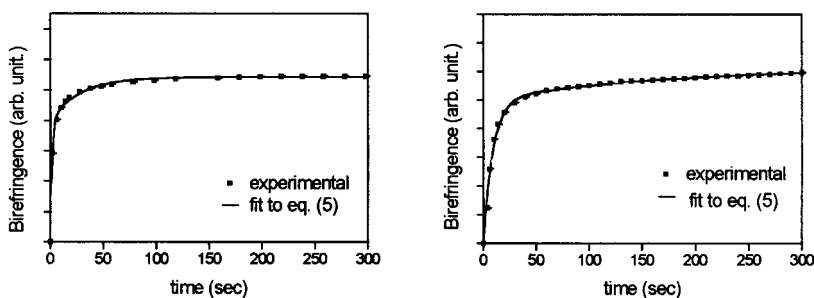

Figure 3. Photochemically induced birefringence curves for polymer **1** (left) and **2** (right).

As can be seen from the figures above, the experimental birefringence values and the calculated curves match very well. The fit parameters obtained are shown in Table **1**. The writing process consists of two components; an initial "fast mode" and a "slow mode". The parameter A_n and B_n in Table **1** represent the weighted contribution of the fast growth component with a rate constant k_a and the slow growth component with a rate constant k_b, respectively. The magnitude of k_a is governed by the quantum yield, the *trans-cis-trans* isomerization rate, and the local mobility of the azo groups.[6] The magnitude of k_b depends on the coupling interaction between the azo group and the polymer segments and the mobility of the polymer segments.[6] The values of k_a and k_b for polymer **1**

are ca. five times larger than those of polymer **2**. Since these two polymers have similar side-chain and backbone structures, it is unclear why the big differences of the values of k_a and k_b between the two polymers exist.

Table 1. Parameters obtained by fitting the birefringence growth curves in Figure **3** to equation 5.

	Polymer **1**	Polymer **2**
A	0.801	0.625
B	0.285	0.146
$k_a(s^{-1})$	0.599	0.110
$k_b(s^{-1})$	0.035	0.006
A_n	0.738	0.811
B_n	0.262	0.189

$$A_n = A/(A+B), \quad B_n = B/(A+B)$$

The dark relaxation curves of birefringence of the polymer **1** and the polymer **2** are shown in Figure **4**. The solid line is a fit to the biexponential function equation 6.
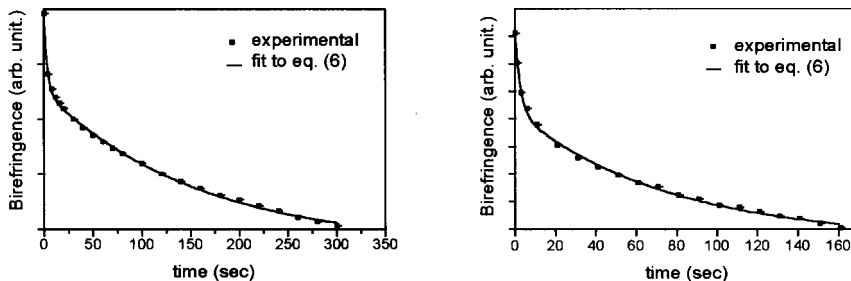

Figure 4. Dark relaxation curves of birefringence of the polymers **1** (left) and **2** (right).

$$y = C \exp(-k_c t) + D \exp(-k_d t) + E \quad \text{........................} \quad (6)$$

where k_c and k_d are the rate constants for the fast and the slow relaxation

modes. C and D are the magnitudes of the fast and the slow relaxation modes, respectively. E is the magnitudes of the unrelaxed portion and independent of time, i. e. the reserved portion of induced birefringence. The fit parameters are summarized in Table **2**. The data, similar to the growth curves, show two modes for the relaxation process. Thermal cis-trans isomerization of the side-chain azo groups would contribute to the initial "fast decay modes" while interactions between the side-chains and polymer backbones should affect the "slow process". In contrast to the growth behaviors, there is no significant difference between the birefringence relaxation rates of the polymer **1** and **2**.

Table 2. Parameters from the decay curves shown in Figure **4**.

	Polymer **1**	Polymer **2**
C	0.140	0.139
D	0.281	0.232
E	0.671	0.381
$k_c(s^{-1})$	0.299	0.369
$k_d(s^{-1})$	0.006	0.013
C_n	0.128	0.185
D_n	0.257	0.308
E_n	0.615	0.507

C_n = C/(C+D+E), D_n = D/(C+D+E), E_n = E/(C+D+E)

Local irradiation of polarized UV can produce micropatterns.[6] Figure **5** shows the photoimage patterns obtained with P[DR1MSt-*co*-PMI] **2**. The narrowest line width in the micropattern was 2 μm. Similar results were obtained with polymer 1. The micropatterns are relatively stable for over a month at room temperatures.

In summary, we have described photo-induced birefringence properties of two azobenzene-containing maleimide copolymers P[DR1PMI-*co*-St] **1** and P[DR1MSt-*co*-PMI] **2**. These polymers shows characteristic birefringence properties. In addition, light induced micropattern images of the polymers are obtained. These polymers could potentially be used in optical storage
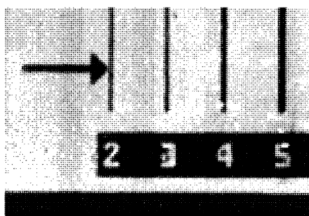
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media.

Figure 5. Image patterns stored in the thin film of the polymer **2**.

Experimental

To prepare a polymer film for birefringence measurement, a polymer solution in cyclohexanone (5 wt%) was filtered through a 0.45 μm membrane filter and then spin-coated (700 rpm) onto quartz slides. The film was dried under vacuum for 10 h at room temperature. The thickness of the film was measured by a stylus profiler (Tencor P10, Tencor Instrument). A micro-patterned photomask, a polarizer, and a UV filter C13-410, Kenko Co. were mounted on the polymer film, and irradiation was performed for 10 min. Photoimages obtained were observed under an optical microscope (Nikon OPTIPHOT2-POL) with crossed polarizers.

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