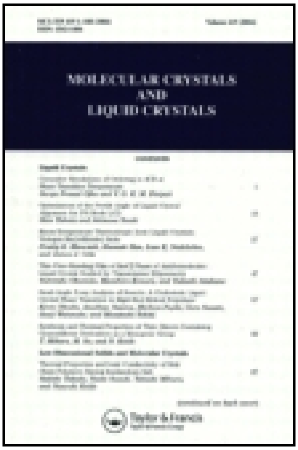

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Photo-responsive Polymers and their Applications to Optical Memory

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Photo-responsive Polymers and their Applications to Optical Memory

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We synthesized photo-responsive azo polymers from novel malonic ester and silicate ester monomers having two symmetrical azobenzene groups in the side chain. The possibility of their applications as reversible data storage media was investigated utilizing optical data recording techniques. As a result, the azo polymers had very excellent stability and resolution of the stored data as well as the sensitivity to pump beam. The polymeric thin films also could be used as erasable digital data materials for a practical use by an Ar ion pulse laser (pulse width: 10 μs). In addition, the polymeric thick films (500–1000 μm) from new monomer and methyl methacrylate showed good angular selectivity for holographic memory by using optical two wave mixing technique.

Keywords: angular selectivity; data resolution; data storage stability; digital data bit; holographic memory; photo-responsive azo polymers

INTRODUCTION

Recently photo-responsive polymers with chromophore groups have attracted much attention in optical data storage, optical holography, and integrated optics [1,2]. Furthermore, since they show a great potential as recording media for data storage and retrieval, they have been the subjects of a number of papers. So far azobenzene,

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spiropyran, fulguid and their derivatives as a photo-responsive group, which is sensitive to light, have been introduced into the side chain of the polymers. They induce the change of optical birefringence and absorbance under irradiation of a linearly polarized light. Especially, azo dye molecules are much more sensitive to the light than any other photo-responsive groups [3,4], That is why azo containing polymers are mainly used as electronic materials. We, therefore, have extensively studied on the synthesis and characterization of novel liquid crystalline polymers with two symmetrical azobenzene groups in the side chain. Moreover, we investigated their applications to reversible optical information storage media through a photoisomerization of the azobenzene group, a photochromophore [5,6].

As a series of our works, the present work reports the synthesis of photo-responsive polymers from new malonic ester and silicate ester liquid crystalline monomers and their applications to data storage media for optical memory.

EXPERIMENTAL

As optical recording media, novel poly(malonic esters) [7] and poly-(silicate ester) [8] were prepared by the procedure already reported (Fig. 1). New thermotropic liquid crystalline (LC) malonic ester monomer (MDR1) was synthesized through reacting in THF at 0°C for 24 h malonyl dichloride and disperse red 1(DR1). It was then condensed with 1,6-dibromohexane or α, α'-dibromo-*p*-xylene in THF in the presence of sodium hydride at 65°C for 24 h to give poly(malonic esters) with two symmetrical DR1, a photoresponsive group. On the other hand, silicate ester monomer (MSi-DR1) was synthesized by reacting 3-methacryloxypropylmethyldichlorosilane and DR1 in methylene chloride at room temperature for 48 h. The monomer MSi-DR1 was polymerized with a radical initiator at 60°C for 72 h to produce homopolymer (PSi-DR1) and copolymers with different composition ratio. The results for polymerization are listed in Table 1.

The polymeric thin films were cast from the polymer solution (5 wt%) in $CHCl_3$ onto a glass plate for 30 seconds using a spin caster. The thickness of the films was controlled by varying the spin speed and the concentration of the polymer solution. We also prepared the polymeric thick films from the LC monomer (MDR1 or MSi-DR1) and methyl methacrylate (MMA) to carry out a fundamental experiment for holographic memory: the novel LC monomer was dissolved in the MMA solution including radical initiator AIBN and then the mixed monomer solution was charged into the reaction plate, which is made from two glass plates, through a syringe. The plate was placed

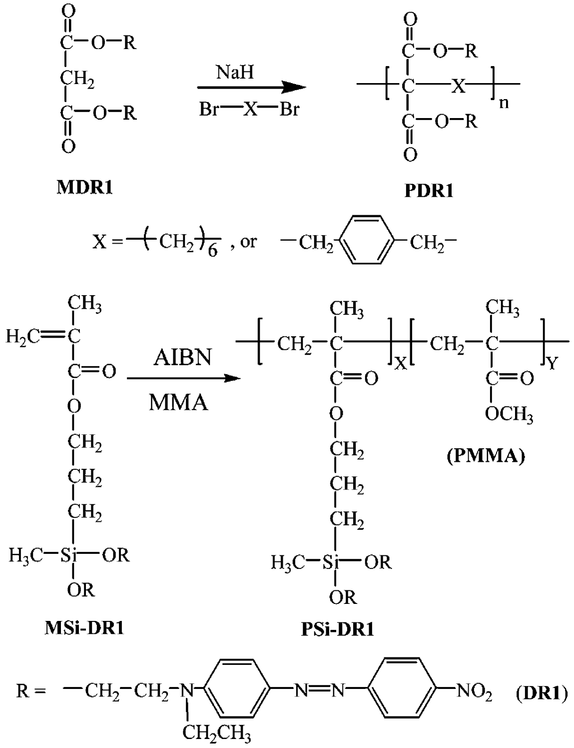


FIGURE 1 Synthesis of novel photo-responsive polymers with DR1 group in the side chain: poly(malonic esters), PDR1; poly(silicate esters), PSi-DR1.

in an oven and polymerized for 72 h at 60°C to obtain a thick film. The film thickness (500–1000 μm) is determined by the thickness of rubber band used as a spacer between the glass plates.

TABLE 1 Polymerization Results for the Homopolymer (PSi-DR1) and the Copolymers

Polymer	Copolymer composition[a] MSi:MMA	Conversion (%)	M_w	T_g (°C)	Initial decomposition temperature[b] (°C)
PSi-DR1	100:0	65	6500	47	195
PSi-PMMA-1	57:43	73	11600	68	208
PSi-PMMA-2	19:81	81	18700	76	221
PSi-PMMA-3	3:97	79	25800	93	245

[a] calculated from the characteristic peaks of ^{1}H-NMR spectra.
[b] Temperature of 1.0% weight loss in TGA thermogram.

The prepared polymers showed maximum absorbances (λ_{max}) around 465 nm in UV-VIS absorption spectra due to the stable trans conformation of azobenzene. On the basis of the UV-VIS results, linearly polarized argon laser with 488 nm was used as a pump beam to record optical data in the polymeric thin films. The optical anisotropy of the polymer derived from the pump beam in a write-in step was measured by using low power Ga/As laser of 847 nm, a probe beam. For holographic memory, Nd-YAG laser with 532 nm was used as reference and object beams.

RESULTS AND DISCUSSION

Phase Transition Behavior

The new malonic ester monomer MDR1 showed enantiotropic behavior in which LC phase appeared at 117 and 86°C on both heating and cooling cycles by DSC. It, however, was observed to show a typical smectic batonnet texture only on a cooling cycle (96°C) by means of optical polarizing microscope (OPM). On the other hand, the poly(malonic esters) (PDR1) obtained from the MDR1 and dibromide compounds had no mesophase. The PDR1-6 having six methylene units (X: $-(CH_2)_6-$) in the polymer backbone exhibited only isotropization temperature (76°C) on a heating cycle without a mesophase. Its glass transition temperature (T_g) was about 50°C. In addition, introducing a rigid p-xylene unit instead of flexible methylene group into the polymer backbone enhanced T_g (96°C) of the corresponding polymer (PDR1-p-Xylene). The weight average molecular weights of the PDR1 polymers were in the range of 5,000 to 15,000, which were controlled by polymerization time.

In addition, MSi-DR1 monomer also showed monotropic behavior in which LC phase appeared at 80°C on cooling cycle of DSC. It, however, had a typical smectic batonnet texture on both heating (76–87°C) and cooling cycles (87–65°C) by OPM. The homopolymer (PSi-DR1) and copolymers with MMA exhibited only the melting temperature on a heating cycle without any mesophase.

Application to Optical Data Storage Media

The application of the prepared photo-responsive polymers as optical data recording media was performed according to our previous literature [6,7]. As a result, Figure 2 shows writing, relaxation, and erasing profiles for the PDR1 thin films with irradiation time: When the polarized argon laser was turned on, optical birefringence rapidly increased

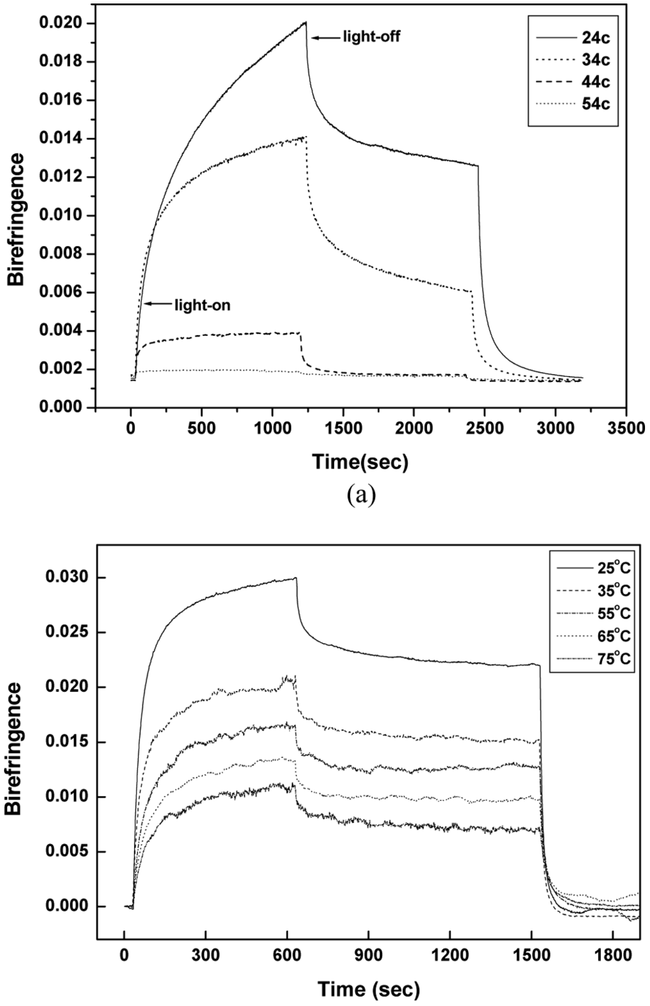


FIGURE 2 Writing, relaxation, erasing processes with temperature: (a) PDR1-6 and (b) PDR1-p-xylene thin films.

in a write-in process. This means that polymer chains were aligned perpendicular to the plane of laser polarization through a trans-cis isomerization of azobenzene group incorporated into the polymer. Such an orientation gives rise to high transmission of the probe beam during a read-out process. However, the value of birefringence caused by the high transmission rapidly decreased about 20% within the first few minutes and then maintained a certain value, when the writing laser was turned off. The stored data also can be easily erased by a circularly polarized Ar laser. In the experiments, the optical birefringence (Δn) derived from the film was calculated from the transmitted intensity of the probe beam measured in a read-out process and the transmitted intensity I can be expressed as

$$I = I_0 \sin^2\left(\frac{\pi \Delta \mathrm{nd}}{\lambda}\right) \sin^2(2\theta)$$

where, I_0 and λ is the incident power and the wavelength of the probe laser, d is the thickness of the film, and θ is the angle between the polarization angle of the pump beam and the optic axis of a polarizer used in the read-out process [5]. The measurement was carried out at $\theta = 45^\circ$ to obtain the highest transmitted intensity from the equation.

On the other hand, the stored information (high birefringence) was drastically decreased as the ambient temperature was increased. Such decay was quite rapid in the PDR1-6 with flexible methylene group in the polymer main chain. As shown in Figure 2(a), especially, the recorded data was erased completely when the temperature went up to the T_g (50°C) of the film. Thus, we introduced a rigid group like *p*-xylene unit instead of the methylene group in the main chain to enhance the storage stability of the data with temperature. In the case of the PDR1-*p*-xylene film, the recorded data was very stable up to 75°C, as shown in Figure 2(b). It indicates that the stability of the optical data is closely related to the T_g of the film using as recording material. To investigate the capability of the film as a rewritable medium, we also performed the reversibility of the data for a write-erase-rewrite process. As a result, the PDR1 film exhibited excellent property as an erasable material as shown in Figure 3.

For a practical application, the focused linearly and circularly polarized laser beams (pulse width: 10 µs) were irradiated to write and erase bits, digital data, respectively. For this experiment, we used the schematic optic-setup reported in our previous work [7]. Before preparing a polymeric thin film, Al reflection layer was deposited onto a substrate material using a sputtering method in order to obtain higher contrast. Figure 4 shows the digital bits of a 0.5 µm size stored in the PDR1-*p*-Xylene thin film. The resolution of the bits was getting better with increase in the power intensity of the pulsed laser beam from 1.0 to 5.0 mW/Cm^2. On the other hand, irradiating the circularly polarized Ar laser can erase the digital data and repeating the write-in process also can rewrite them.

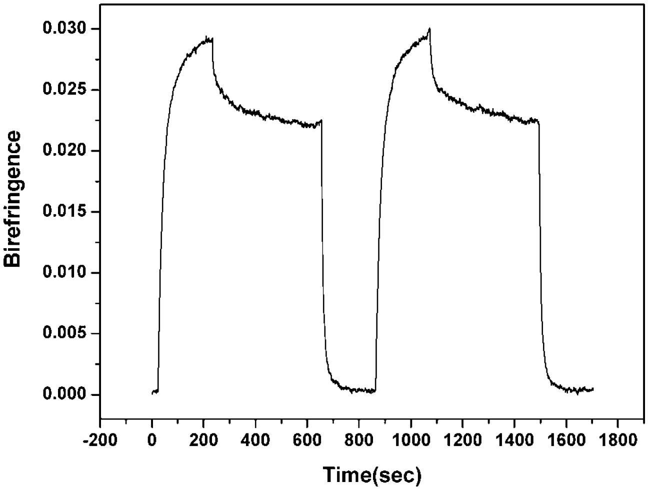


FIGURE 3 Reversibility of the data storage for the PDR1-p-Xylene.

On the basis of the above results, we found that the poly(malonic esters) with DR1 as a chromophore were excellent as reversible media for data storage and retrieval. However, their high crystallinity and poor solubility make it difficult to prepare the corresponding thick

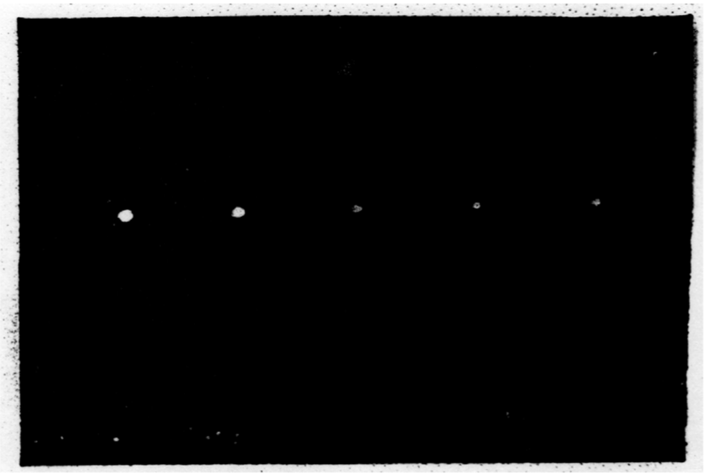


FIGURE 4 Digital bits (0.5 μm) stored in the PDR1-xylene film with the power intensity of Ar ion pulsed laser (5.0, 4.0, 3.0, 2.0, and 1.0 mW): pulse width, 10 μs.

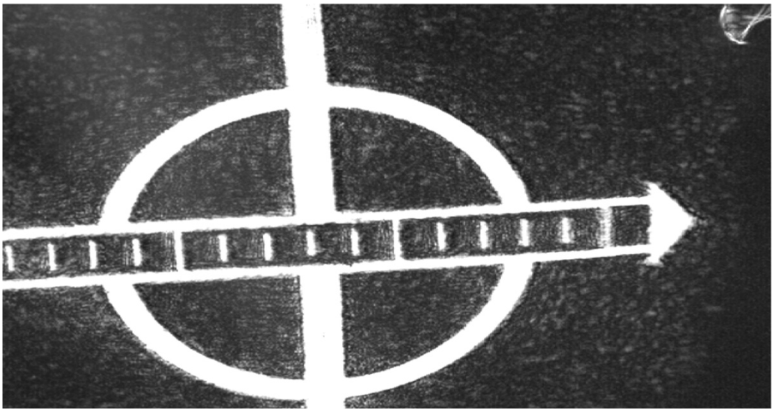


FIGURE 5 Holographic image (1.0 × 2.0 μm) inscribed in the polymeric MDR1 thick film.

film. Thus we made the thick film (530 μm) from the LC monomer MDR1 (5 wt% vs. MMA) and the MMA to examine the possibility of application as a holographic device. Figure 5 shows the hologram image (1.0 × 2.0 μm) stored in the MDR1/PMMA blend typed thick film using a two wave mixing optic-setup for holographic memory [7]. High concentration of the MDR1 in the blend thick film is needed

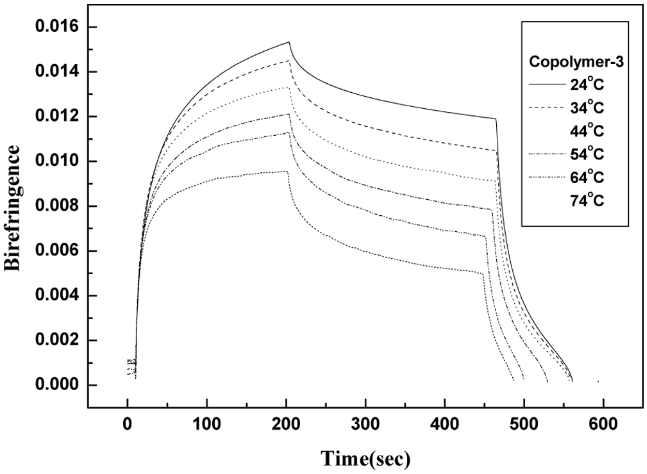
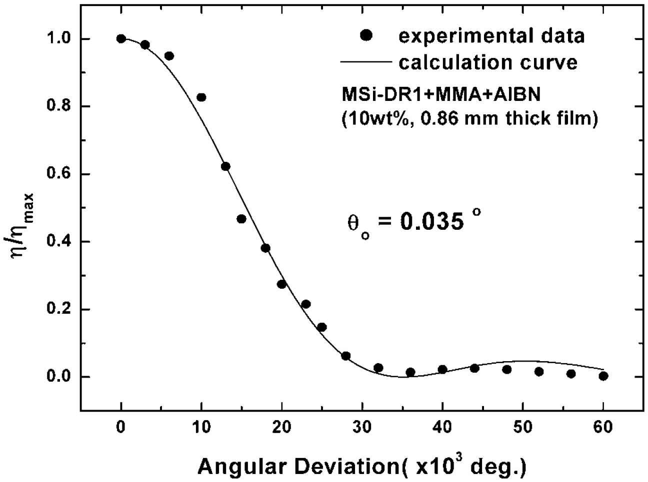


FIGURE 6 Influence of temperature on the data storage for the copolymer PSi-PMMA-3.

to improve both resolution and diffraction efficiency of the image inscribed in the thick film. However, it was impossible to prepare the thick film including the MDR1 of more than 5 wt% because of its poor solubility against the MMA.

Therefore, we synthesized new acrylate typed monomer MSi with two symmetrical azobenzene groups in the side chain to enhance both content and solubility of the photo-responsive monomer. The monomer was polymerized in the presence of radical initiator to produce corresponding homopolymer and copolymers with different MSi composition, which are summarized in Table 1. Figure 6 is a writing-relaxation-erasing profile of the digital data with temperature for the copolymer thin film (PSi-PMMA-3). The result was similar to the trend of the PDR1-*p*-Xylene film. The recorded data also was very stable up to the T_g of the copolymer-3. Based on these results, we prepared the copolymer thick film (860 μm) with the MSi of 10 wt% in terms of the MMA for holographic memory device utilizing the special reaction plate. The resolution of the holographic image was better than the one inscribed in the MDR1-PMMA blend thick film.



$$\frac{\eta}{\eta_{max}} = \sin c^2(\pi\Delta\theta / \Delta\theta_R) = \left(\frac{\sin(\pi\Delta\theta / \Delta\theta_R)}{\pi\Delta\theta / \Delta\theta_R}\right)^2$$

($\Delta\theta$: angular deviation, $\Delta\theta_R$: angular selectivity)

FIGURE 7 Angular selectivity of the copolymer thick film for the holographic memory.

Figure 7 displays the angular selectivity of the copolymer thick film, indicating how many images we can store per unit volume. The thick film had good angular selectivity of 0.035° angle [9]. It shows a strong potential of the film as a volume hologram material.

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