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New Azo Polymers and Their Applications to High Density Optical Memory Devices

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Introduction

In recent years, there have been increasing interests in photoresponsive polymers for optical holography, optical information storage, and integrated optics. Furthermore, since they show a strong potential as information recording media for data storage and retrieval, they have been the subjects of a number of papers. So far azobenzene, spiropyran, fulguid and their derivatives as a photo-responsive group sensitive to light have been introduced into the side chain of the polymers.1 They induce the change of optical birefringence and absorbance under irradiation of a linearly polarized light. Among them, especially, azo molecules are much faster than the other photoresponsive groups in the sensitivity to the light. 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 and also investigated their applications to reversible optical information storage media through a photoisomerization of the azobenzene group, a photochromophore, using a two (or four) wave mixing technique.

In this work we will report the synthesis and characterization of these photo-responsive azo polymers and also describe their applications to high density optical memory devices.

Experimental

As optical recording media, novel poly(malonic esters) were used. They was prepared by modifying the procedure we already reported 4, , which is shown in Figure 1: New thermotropic liquid crystalline (LC) malonic ester monomers (MDR1 & MCN) were synthesized by reacting in THF at 0 °C for 24 h malonvl dichloride and mesogenic alcohols such as disperse red 1 (DR1) and p-cyanoazobenzene derivative (CN). The new monomers were condensed with aliphatic dibromides (or dibromo-xylene derivatives) with different chain length such as 1,6-dibromohexane, 1,8-dibromooctane, 1,10-dibromodecane, dibromododecane in THF in the presence of sodium hydride at 65 °C for 24h to give 8 kinds of poly(malonic esters) with two azobenzene moieties in the side chains. The optical anisotropy of the polymer derived from the Ar laser in information recording step was measured by using low power He/Ne laser of 633 nm, a

Figure 1. Synthesis of poly(malonic esters) with disperse red 1 groups in the side chain.

Results and discussion

We examined the possibility of the application of the poly(malonic esters) to erasable optical data storage media through a trans-cis isomerization of azo dye by Ar laser irradiation. For a practical application, the focused linearly and circularly polarized laser beams

(pulse width: $10~\mu s$) were irradiated to write and erase bits, respectively. For this experiment, we used the schematic optic-setup reported in our previous work.⁵ Before coating the polymeric thin films, Al reflection layer was deposited onto polycarbonate substrate by sputtering to obtain higher contrast. Figure 2 shows the digital bits stored in the PDR1 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/Cm².

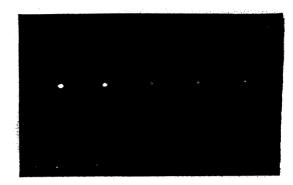


Figure 2. Digital bits stored in the PDR1 (X = p-xylene) film with power intensity of Ar ion pulsed laser (5.0, 4.0, 3.0, 2.0, and 1.0mW): pulse width, 10 μ s.

We also stored the holographic images in the PCN film. The twodimensional image was recorded successfully in the PCN film. The reconstructed images from the system were comparable to the original one as shown in Figure 3.

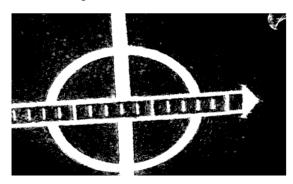


Figure 3. Holographic reconstructed image stored in the PCN film.

On the basis of the above results, we found that the poly(malonic esters) containing azobenzene groups were excellent as reversible optical information recording media for data storage and retrieval.

Conclusions

Novel liquid crystalline malonic ester monomers were synthesized from malonyl dichloride and mesogenic alcohols, a photoresponsive group. The monomers were polymerized with aliphatic or aromatic dibromides in the presence of sodium hydride to give 8 kinds of novel poly(malonic esters) with two symmetrical azobenzene groups. We found that the resulting polymer films could be used as rewritable optical data storage (or holographic image) media through a photoisomerization of azobenzene group by Ar laser irradiation. The sensitivity of data recording was dependent not only on the thickness of the polymeric thin film but also on the intensity of laser beam.

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