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Yang-Kyoo Han ^a, Hai-Sub Na ^a & Cha-Hwan Oh ^b

^a Department of Chemistry, Hanyang University, Seoul, 133-791, Korea

^b Department of Physics, Hanyang University, Seoul, 133-791, Korea

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Synthesis of New Poly(Malonic Ester) Containing Disperse Red 1 and its Applications to Optical Data Storage

YANG-KYOO HAN^a, HAI-SUB NA^a and CHA-HWAN OH^b

^a*Department of Chemistry, Hanyang University, Seoul 133-791, Korea; and*

^b*Department of Physics, Hanyang University, Seoul 133-791, Korea*

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New poly(malonic ester) with two symmetrical azobenzene groups was synthesized by the reaction of novel liquid crystalline malonic ester monomer with disperse red 1 with 1,6-dibromohexane. The resulting polymer was found to be excellent as reversible optical information recording media for data storage and retrieval through a trans-cis isomerization of the azobenzene units by Ar laser irradiation and thermal process.

Keywords: novel LC monomer; disperse red 1; optical data storage

INTRODUCTION

In recent years, there have been increasing interests in photoresponsive polymers for optical holography, optical information storage, and integrated optics¹. Furthermore, since they show a strong potential as information recording media for data storage and retrieval, they have been the subject of a

number of papers. For an example, with irradiating either linearly polarized or unpolarized light, optical information can be written, erased, and rewritten on liquid crystalline or amorphous polymer films containing azobenzene group. The information is stored by optically induced dichroism and birefringence.

In this study, we synthesized new poly(malonic ester) and investigated its application to optical information storage media.

EXPERIMENTAL

As shown in Figure 1, new thermotropic liquid crystalline(LC) malonic ester monomer (MDR1) was synthesized by reacting in THF at 0 °C for 24 h malonyl dichloride and disperse red 1. It was then condensed with 1,6-dibromohexane in THF in the presence of sodium hydride at 65 °C for 24 h to give poly(malonic ester) (PDR1) with two symmetrical disperse red 1, a photoresponsive group². The polymeric thin films were cast from the polymer solution (5 wt%) in CHCl₃ onto a glass plate for 30 seconds using a spin coater.

RESULTS AND DISCUSSION

Phase Transition Behavior.

MDR1 showed enantiotropic behavior in which LC phase appears at 117 and 86 °C, respectively, on both heating and cooling cycles by DSC. It, however, showed a typical smectic batonnet texture only on a cooling cycle (96 °C) by optical polarizing microscope (Figure 2). On the other hand, the resulting PDR1 (λ_{max} : 464 nm) exhibited only isotropization temperature (76 °C) on a heating cycle without a mesophase. Its glass transition temperature (T_g) was about 50 °C.

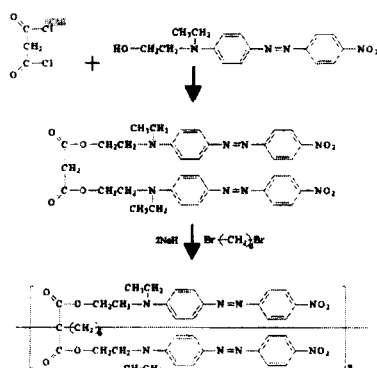


FIGURE 1. Synthesis of PDR1.

FIGURE 2. LC texture of PDR1.
(See Color Plate VI at the back of this issue)

Application as Information Storage Materials³

Writing process for optical data storage is as follows. The polymeric thin film was heated above the melting temperature of the polymer and then immediately quenched below T_g at which isotropic phase was frozen. The homogeneous film was placed between two crossed polarizers, and linearly polarized Ar laser (488 nm) with a intensity of 15.4 mW/cm^2 was irradiated onto the sample. The resulting transmitted intensity, which results from the optical birefringence of the polymer, was measured by low-power Ga/As laser (probe beam: 847 nm) through the crossed polarizers.

As a result, Figure 3 shows a writing and relaxation profile on the polymeric films with the irradiation time. When the laser is turned on, the transmitted intensity increases up to about 20 min and then remains constant. This means that the azobenzene groups, which is unoriented initially within the isotropic phase (no transmission), are aligned perpendicular to the plane of laser polarization through a trans-cis isomerization of azobenzene group.

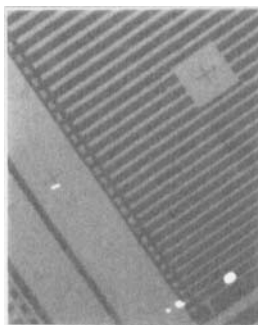
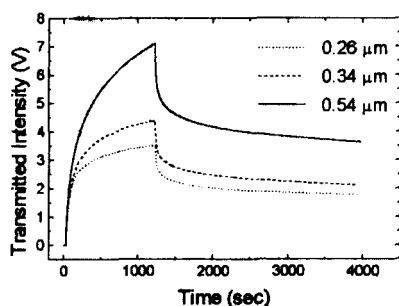


FIGURE 3. Writing and relaxation profile. FIGURE 4. Image pattern stored in PDR1. (See Color Plate VII at the back of this issue)

Such an orientation gives rise to high transmission. On the other hand, the transmitted intensity rapidly decreases within the first few minutes and then remains constant for a long time, when the writing laser is turned off. The recorded data can be erased (no transmission of the probe beam) by heating over the melting temperature of the polymer and it is possible to rewrite the information by repeating the write-in process described previously.

Figure 4 shows a representative photograph of the analog image pattern stored in the polymeric film.

Acknowledgments

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