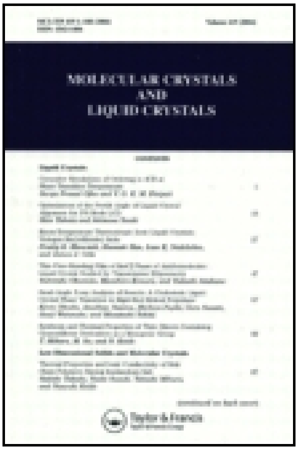

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Light Controlled Birefringence of Liquid Crystalline Polymer Bearing an Azo Chromophore

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Light Controlled Birefringence of Liquid Crystalline Polymer Bearing an Azo Chromophore

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Mesogenic and azo monomer were synthesized and copolymerized to get liquid crystalline copolymer such as polymethacrylate (CP I). Another copolymer (CP II) was prepared with methylmethacrylate using the same azo monomer used above. Trans-cis isomerization of two copolymers was observed under UV-irradiation. The stability of photoinduced birefringence in CP I was found better than that of CP II.

Keywords: liquid crystalline copolymer; photoisomerization; photoinduced birefringence

INTRODUCTION

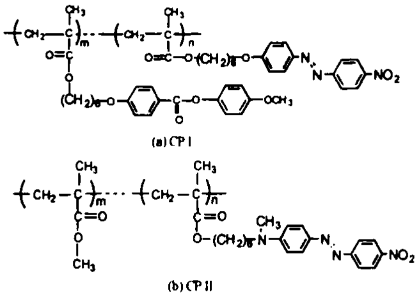
Photoresponsive polymers are being intensely investigated over last two decades, which can be attributed to both fundamental and applied significance[1-4]. A large number of studies have been concentrated on the photoinduced birefringence of the polymers containing the azobenzene group. These materials are found to possess unique optical properties. There is constantly increasing attention in the field of optical data storage and holographic applications. In the present study mesogenic/azo copolymer was synthesized by using the mesogenic comonomer and the azobenzene containing monomer. Another copolymer was prepared with methylmethacrylate (MMA) using the same azo monomer. The comparative behavior of two copolymers was studied in terms of their trans-cis isomerization and photoinduced birefringence.

EXPERIMENTAL

4-methoxyphenyl-4'-methacryloyloxy hexyloxy benzoate (M I) and 4-nitrophenyl azophenyloxy-N-methylhexyl methacrylate (M II) were synthesized. Copolymers were prepared by radical polymerization under azobisisobutyronitrile. Red polymers were collected by reprecipitation from THF into ethanol. Yield was calculated around 10-20%.

RESULTS AND DISCUSSION

The synthesized copolymer structures are shown in Figure 1. CP I consists of M I and M II units whereas CP II consists of M II and MMA instead of M I. The copolymers are dark red in color and soluble in tetrahydrofuran, dimethylformamide, dioxane, chloroform etc. Table I shows the comonomer feeding ratio, copolymer composition, molecular weight, and polydispersity. CP I is liquid crystalline and CP II is totally amorphous in nature. The glass transition temperatures of CP I and CP II were found to be 37 and 108°C respectively. CP I showed the nematic-to-isotropic transition behavior at 72°C, which was also confirmed by optical microscopy. Azo aromatic groups can undergo reversible trans-cis isomerization around the azo linkage when irradiated under the wavelength close to λ_{max}. During irradiation the absorbance at λ_{max} decreases due to conversion of trans isomer to cis isomer. The rate of reverse reaction is so fast that all cis forms were converted to trans forms even at room temperature. In the case of films of CP I and CP II the absorbance at 475nm varied under irradiation. Without light, the absorbance was recovered to initial value. In Figure 2, the absorbance at 475nm were illustrated with the change of the irradiation time in CP I. We integrated the each spectrum with the 0.5 sec. interval. The rate of trans-cis photoisomerization in CP I is almost close to that in CP II.


(a) CP I

(b) CP II

FIGURE 1 Structures of the copolymers used for this study.

Table 1 Composition and molecular weight of two copolymers.

Sample	Feeding Ratio (mol/mol) M	II	Composition (mol/mol) M	II	Molecular Weight (M_n)	Polydispersity
CP I	1(M I)	1	3 (M I)	1	9012	2.2357
CP II	1(MMA)	1	5 (MMA)	1	14328	2.5934

Using the films of two copolymers, we investigated the photoinduced birefringence under 532nm light irradiation. Under this wavelength, photoisomerization can be induced. Initially, the transmittance was observed to be zero without light irradiation under crossed polarization. We irradiated the light at 45^0 angle between the polarization of the pump beam and analyzer optic axis. At this angle, the transmittance reached to the maximum value. The transmittance increased during irradiation and without light, it decreased gradually. The residual transmittance can give us information about long-term durability for optical data storage. Finally, the signal was erased using the circularly polarized beam to randomize the molecular orientation of azo group. In this phenomenon, we found the stability of CP I is better than that of CP II although the glass transition temperature of CP I is much lower than that of CP II. It can be thought that the stability of birefringence was strongly dependent on the liquid crystallinity, geometrical hindrance, and dipole-dipole interaction rather than on glass transition temperature.

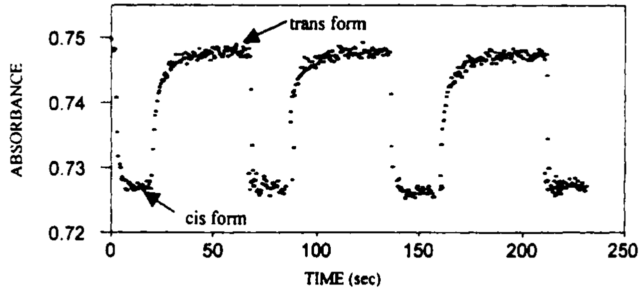


FIGURE 2 Change of absorbance at 475 nm due to trans-cis photoisomerization in CP I.

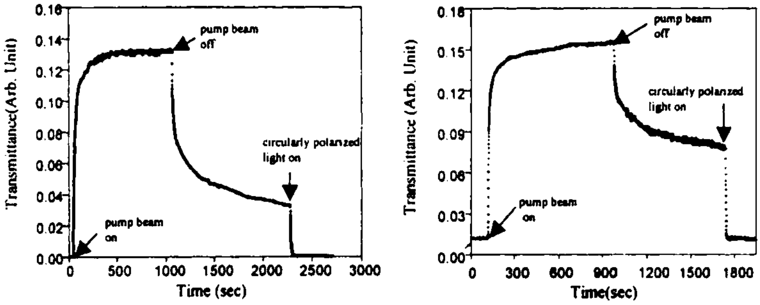


FIGURE 3 Change of transmittance in CP I and CP II due to photoinduced birefringence.

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