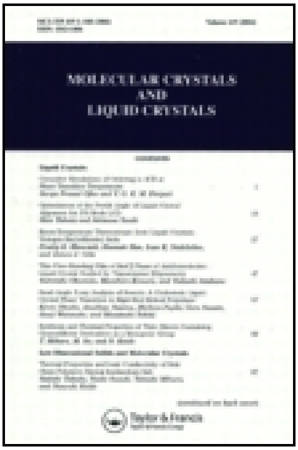

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Holographic Recording of Azobenzene-Functionalized Liquid Crystalline Linear Telomers

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Optical storage properties of azobenzene-functionalized liquid crystalline telomer B and telomer D were investigated by holographic measurements. Both of the telomers are linear with different molecular structures. Linearly and circularly polarized Ar^+ laser of 488 nm was used to inscribe holographic gratings on the telomer films prepared by spin coating from their solutions in THF. Higher diffraction efficiency was obtained from telomer B compared to telomer D under identical experimental conditions. This may be due to lower glass transition temperature and rigidity of structure of telomer B. Diffraction efficiencies of 9% and 4% were obtained from telomer B and telomer D film, respectively by irradiation of linearly polarized Ar^+ laser ($200\,mW/cm^2$) for 15 minutes. The stored information in telomer films was seemed to be stable for long time under dark at room temperature.

Keywords: azobenzene-functionalized LC telomer; diffraction efficiency; holography; photoisomerization

INTRODUCTION

Azobenzene functionalized polymers are known as azo-polymers are interesting and potentially useful materials for optical applications [1–6]. Holographic recording has been usually performed in azopolymers with polarized blue light. High diffraction efficiencies, associated with changes in refractive index as well as with surface modulation

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have been reported [7–9]. Red light induced holographic storage in a liquid crystalline side chain cyano-azobenzene polymethacrylate at room temperature was reported by E. Lörincz *et al.* [10]. They obtained stable gratings under simultaneous irradiation with interference pattern created with two coherent linearly polarized red light beams and unpolarized UV (around 350 nm) light. The basic mechanism involved in grating formation is the reversible *trans* → *cis* photoisomerization of azobenzene chromophores. When a film of these materials is exposed to an interference light pattern with wavelength near the absorption band of the chromophores, its surface undergoes a controlled topographical modification. *trans*-Azobenzene molecules are rod-like shaped similar to that of liquid crystal molecules. On the other hand, *cis*-azobenzene molecules obtained by photoisomerization with irradiation of UV light have bent shape different from that of liquid crystal molecules. The bent structure causes a large effect on molecular arrangements of azobenezene molecules. However, *cis*-azobenzene molecules are thermodynamically unstable compared to their *trans*-form. Therefore, a thermal relaxation process occurs in the dark even at room temperature. The two states of azobenzene molecules have distinct absorption spectra which allow reversible storage of data.

When illuminated with a polarized light of appropriate wavelength, azobenzene groups undergo a reversible *trans* → *cis* → *trans* photoisomerization and an associated orientational redistribution of the chromophores (perpendicular to the polarization direction). Andruzzi *et al.* reported the production of holographic gratings of azobenzene-functionalized side-chain polymethacrylates using Ar^+ laser of 488 nm [11].

Recently we have reported the formation of SRGs on azobenzene functionalized poly 6-[4-(4′-propoxyphenylazo)phenoxy]hexylacrylate), poly 3AB6Ac film by irradiation of linearly and circularly polarized Ar^+ laser (488 nm) through photomask [12–13]. In that case, deep and regular film surface deformation was produced only by circularly polarized Ar^+ laser depending on illumination intensity and exposure time. The undertaken study makes evidence of holographic recording with longer stability. To the best of our knowledge, no work has been done on holographic recording of azobenzene functionalized telomers. In this article, we report the holographic gratings of azobenzene functionalized liquid crystalline linear telomers by irradiation of Ar^+ laser (488 nm) through photomask. The influences of several experimental parameters are also being studied and will be published in forthcoming articles. The advantages of holographic storage are: large data density/capacity, better reliability, fault and damage tolerance, high transfer rates, short access time, high durability and low cost.

EXPERIMENTAL

Telomer B and Telomer D were synthesized by free radical telomerization of 6-[4-(4′-methoxyphenylazo)phenoxy]hexylmethacrylate, MAB6Mc with benzylthiol and dodecanethiol, respectively in presence of AIBN as initiator in DMF at 60°C for 48 h. The detailed synthesis of monomer, MAB6Mc and telomers was described elsewhere [14]. Gel permeation chromatography (GPC) analyses using tetrahydrofuran, THF as eluent revealed molecular weights and polydispersity indexes of the telomers. Differential Scanning Calorimetry (DSC) experiments were performed on a Seiko instrument SSC-5020 equipped with computerized data elaboration system. The experiments were run on 10–20 mg telomer sample at a temperature rate of 10°C per minute. Polarizing optical microscopy (POM) observations were made with Olympus BHSP polarizing microscope equipped with a Mettler FP 80 hot stage controlled by Mettler unit. The heating and cooling cycles were performed at a rate of 10°C $\min^{-1}$.

Telomer films of good optical quality were prepared on glass plate by spin-coating the solution of telomer in THF. The films were then dried at room temperature. Thicknesses of the films were estimated by UV/V is spectroscopic measurements. Special care was taken to obtain homogeneous films with equal thickness for all samples. Photoisomerization of telomer films was carried out by using a 500 W high pressure Hg lamp (Ushio SX-UI 5000) equipped with a cut filter (Sigma, UTVAF-35U) for UV irradiation (365 nm), and a 500 W Xe lamp (Ushio SX-UI 500XQ) equipped with a cut filter (Sigma, DIF 50s-GRE) for visible light irradiation. Ar^+ laser at 488 nm was used for holographic experiments and He-Ne laser (633 nm) was used as probe light for measuring the first order diffraction efficiency.

RESULTS AND DISCUSSIONS

Figure 1 shows the chemical structures of telomer B and telomer D. Although both of the telomers are linear, they are different in their molecular structures. Characterizations of the telomers are presented in Table 1. Molecular weights and polydispersity indexes of both the telomers are almost similar. Telomer B exhibited lower glass transition temperature than telomer D as shown in Table 1.

The UV/visible absorption spectra of the telomers showed a strong absorption at around 360 nm corresponding to π-π^* transition of *trans*-azobenzene moiety and a weak absorption at about 450 nm which originated from n- π^* transition. Both the telomers showed reversible *trans* → *cis* photoisomerization by UV and visible light irradiation,

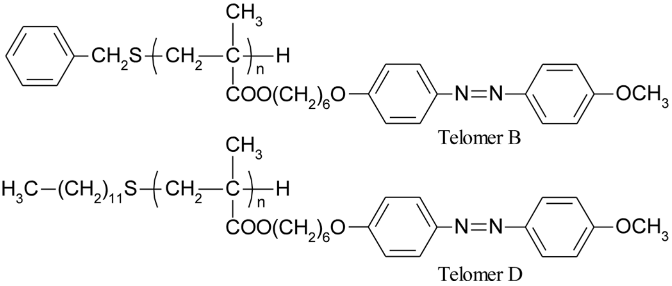

FIGURE 1 Chemical structures of telomer B and telomer D.

respectively. A little absorbance at around 488 nm was found in the UV-Vis absorption spectra of the telomer films. Therefore, Ar^+ laser of 488 nm was used to inscribe holographic gratings on the telomer films.

The instrumental set up for holographic grating formation on telomer films by irradiation of polarized Ar^+ laser through photomask is shown in Figure 2. Both linearly and circularly polarized Ar^+ laser were used. Holographic gratings formed on telomer films were characterized by measuring the first-order diffraction efficiency (η) which is defined as the ratio of the intensity of the diffraction beam (I) to that of the incident beam (I_0) as expressed by the following equation

$$\eta = \frac{I}{I_0} \tag{1}$$

Figure 3 shows the diffraction efficiencies of telomer B and Telomer D induced by irradiation of linearly polarized Ar^+ laser (200 mW/cm^2) as a function of irradiation time. The formation of holographic gratings on azopolymer films largely depend on intensity of laser power and thickness of film. The value of diffraction efficiency induced by linearly polarized Ar^+ laser was increased and decreased with an increase in time. As we explained in our previous article, by irradiating linearly

TABLE 1 Characterization of Telomer B and Telomer D

Compound	M_n	M_w	M_w/M_n	Thermal phase transition behavior
Telomer B	6000	11000	1.8	G 64 S 86 N 128 I
Telomer D	7000	14000	2.0	G 71 S 88 N 124 I

M_n-Number average molecular weight; M_w-Weight average molecular weight; G-Glassy; S-Smectic; N-Nematic; I-Isotropic.

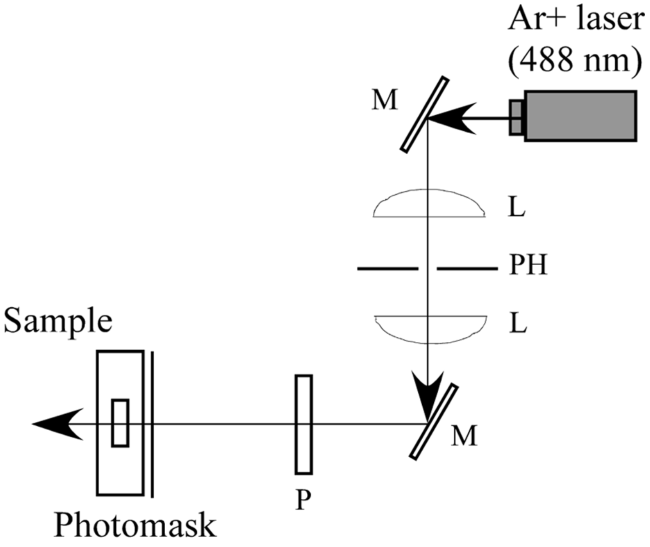

FIGURE 2 Instrumental setup for grating inscription on azo-telomer films. M: Mirror; L: Lens; PH: Pinhole; P: Polarizer.

polarized light only molecular orientation is caused by reversible *cis* → *trans* → *cis* photoisomerization, but no mass transfer takes place. That's why the changes in diffraction efficiencies of the telomers by irradiating linearly polarized Ar^+ laser were very faster. After

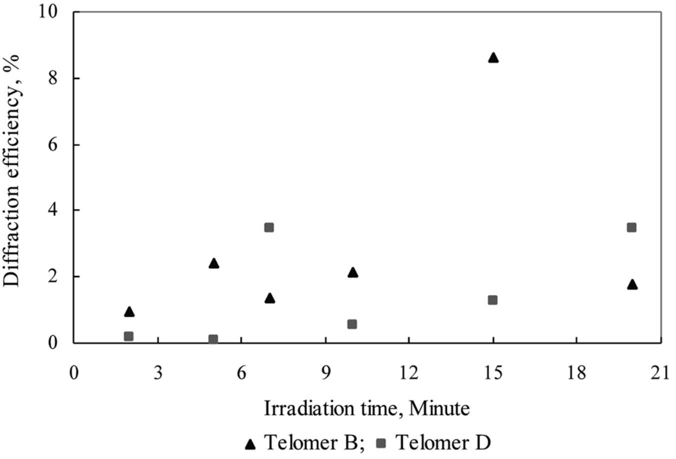

FIGURE 3 Diffraction efficiencies of telomer B and telomer D films induced by linearly polarized Ar^+ laser ($200\,mW/cm^2$) as a function of irradiation time.

irradiation, azotelomer molecules orient perpendicular to the polarization direction of irradiated light. Diffraction efficiencies as high as about 9% and 4% were obtained from telomer B and telomer D film, respectively with a thickness of about 400 nm by irradiation of linearly polarized Ar^+ laser with 200 mW/cm^2 intensity for15 minutes only.

On the other hand, in case of irradiating circularly polarized Ar^+ laser, diffraction efficiencies of both telomer B and telomer D increased very slowly with an increase in irradiation time (Fig. 4). Diffraction efficiencies of about 6% and 3% were obtained from telomer B and telomer D films having thickness of about 400 nm by irradiating circularly polarized Ar^+ laser with an intensity of 200 mW/cm^2 for 15 minutes. High order diffraction was found clearly with increasing diffraction efficiency.

Telomer B showed faster and better holographic properties compared to telomer D. Glass transition temperature of telomer B is lower than that of telomer D as shown in Table 1. Moreover, considering the

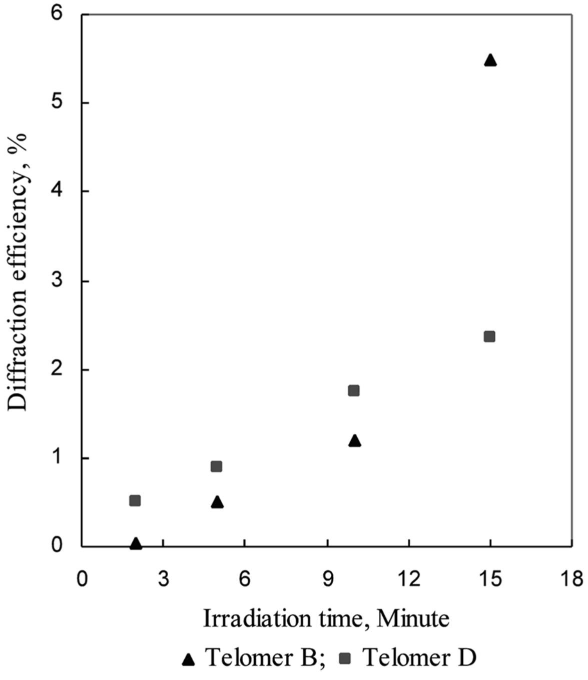

FIGURE 4 Diffraction efficiencies of telomer B and telomer D films induced by circularly polarized Ar^+ laser (200 mW/cm^2) as a function of irradiation time.

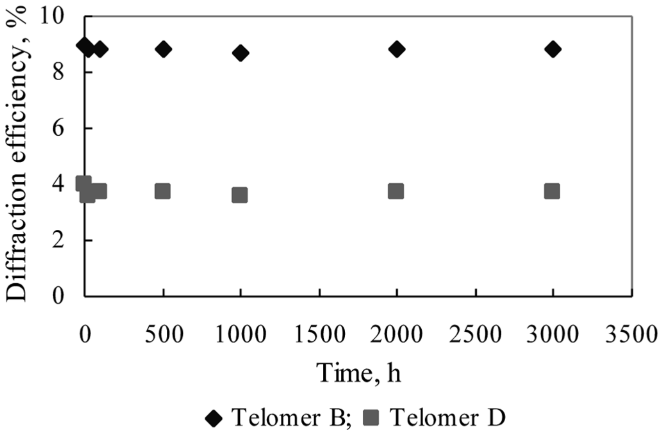

FIGURE 5 Time dependencies of holographic recordings of telomer B and telomer D.

structures of both telomers it is evident that the structure of telomer B is more rigid than that of telomer D. Therefore, it is assumed that the lower glass transition temperature and rigidity of structure of telomer B contribute to yield higher diffraction efficiencies than that of telomer D. Rheological properties may also be related to its better and faster photoresponsive properties. Polarized optical microscopic observations revealed the formation of holographic gratings on telomer films.

The time dependencies of diffraction efficiencies of telomer B and telomer D after linearly and circularly polarized Ar^+ laser irradiation were also studied at room temperature. Figure 5 shows the time dependencies of telomer B and telomer D films after irradiating linearly polarized Ar^+ laser. Diffraction efficiencies decreased a little initially. It may be due to *cis* → *trans* thermal back isomerization, but after a certain time it seemed to be constant under dark at room temperature for long time. These results revealed that the period of record of both telomer B and telomer D films are high and they can be potential candidates for various diffractive instruments.

CONCLUSION

Azobenzene functionalized liquid crystalline telomer B and telomer D have been synthesized and used for holographic recording. By irradiation of linearly and circularly polarized Ar^+ laser (488 nm) through photomask these telomers showed high diffraction efficiencies. The telomer films exhibited faster and higher diffraction efficiencies in shorter time by linearly polarized Ar^+ laser. Diffraction efficiencies of about 9% and 4% were obtained from telomer B and telomer D film, respectively by irradiation of linearly polarized Ar^+ laser for 15 minutes only. Telomer B showed higher diffraction efficiencies compared to telomer D under identical experimental conditions. It is assumed that this is due to the lower glass transition temperature and rigidity of structure of telomer B. The holographic recordings of the telomer films are also seemed to be very stable at room temperature.

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