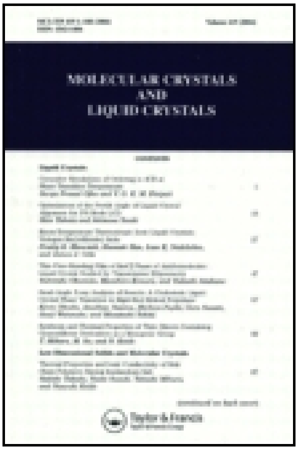

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Studies on Synthesis, Thermal and Photochemical Properties of Liquid Crystalline Telomers

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Studies on Synthesis, Thermal and Photochemical Properties of Liquid Crystalline Telomers

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Liquid crystalline (LC) telomers have been synthesized and their thermal as well as photochemical properties are reported. The effects of telogen content on the degree of telomerization and molecular weights of the telomers were also studied. The molecular weights of the telomers were found to decrease with an increase in the telogen content in the telomerization. Isotropization temperatures of the telomers from liquid crystalline to isotropic phase were determined as a measure of the stability of the telomers which showed that stability depends on its molecular weight and structure of the telogen. The telomers also showed fast photoresponsive properties due to the disorganization of the uniaxial molecular orientation caused by the trans-cis photoisomerization of the azobenzene groups.

Keywords: liquid crystalline telomers; photoisomerization; uniaxial molecular orientation

INTRODUCTION

Telomers with controlled molecular weights and predetermined functionalities (chain end structures) are synthesized by telomerization [1,2]. The typical telomerization includes a chain transfer agent which is called telogen whose fragments define the telomer extremities, a monomer and a catalyst as a free radical initiator. Liquid crystalline (LC) polymers consist of two components: mesogenic moieties and

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polymer chain moieties. Properties of the LC polymers mainly depend on chemical structures of mesogenic groups, spacers, main chains, length of spacers and so on [3]. The molecular weights of the LC polymers influence significantly their LC behaviors [4–8]. Blumstein et al. investigated the effects of molecular weight on the phase transition behavior of the fractionated main chain type LC polymers. They revealed that the stability of LC states was enhanced with an increase in the molecular weight resulting in an increase in both the phase transition temperature and the order parameter [4]. Ikeda et al. also described that phase transition temperatures as well as changes in enthalpy at the phase transition from LC phase to an isotropic phase increased with an increase in the molecular weight of side chain type LC polymers, corresponding to an increase in the stability of LC phases [8]. One of the causes of the effects of molecular weight on the LC behaviors is the presence of non-mesogenic end groups which is attached to the end of main chains through initiating the polymerization, because the relative content of the non-mesogenic end groups in the polymers becomes more with decreasing the degree of polymerization.

Tamaoki reported thermal- and photo-mode full color recording by the use of cholesteric solid films of dicholesteryl esters having molecular weight of about 1000 [9]. Characteristics of the cholesteric solid films of the dicholesteryl esters are rapid responses of the switching compared to the polymeric materials, but shows high stability of the switched state similar to the polymeric materials. Therefore, to study the effects of molecular shape and molecular weight on the stability and the response of the LC materials to external stimuli will be significant for the applications of LC materials to various optical devices.

EXPERIMENTAL

Telomers were synthesized by the reaction of 6-[4-(4′-Propoxyphenylazo)phenoxy]hexylacrylate, 3AB6Ac with telogens; 1-dodecanethiol, benzylthiol, azothiol (3AB6SH) in the presence of azobisisobutyronitrile (AIBN) as initiator and were termed as telomer Dn, telomer Bn and telomer An, respectively. Thermal properties of the telomers were examined by means of differential scanning calorimetry, DSC and polarizing microscopic observation. Molecular weights of the telomers were determined by gel permeation chromatography, GPC. Solid films of the telomers were prepared by spin coating of the telomer solutions in THF. The photoisomerization of azobenzene group was carried out by using a 500 W high pressure Hg lamp equipped with a cut filter for UV irradiation (365 nm) and a 500 W Xe-lamp equipped with a cut filter for visible light irradiation. Changes in transmitted light intensity of a He-Ne laser were monitored with a photodiode when the films were irradiated under UV light.

RESULTS AND DISCUSSION

The conditions of synthesis and characteristic parameters of the homopolymer of 3AB6Ac and telomers were given in Table 1. The molecular weights of the homopolymer were 7000 (**Mn**) and 8600 (**Mw**) determined by GPC. Introduction of the telogens, **DS** and **BS** in the telomers was identified by NMR spectra and XPS spectroscopy. The peak intensity corresponding to sulfur in the XPS measurements increased with increasing the telogen fed to the telomerization solution. Figure 1 shows the effect of telogen content on Mn of the telomers. It was observed that the molecular weights of the telomers decreased with an increase in telogen content during telomerization. So, the molecular weight of the telomer can be controlled easily by varying the amount of the telogen. In addition, Mn of the telomers was dependent on the structure of the telogens. Namely, different telogens contribute to yield telomers of different molecular weights even though the telogen content was the same. Phase transition temperatures were

TABLE 1 Conditions of Synthesis and Characterization of Homopolymer and Telomers

	3AB6Ac mmol	Telogen mmol	AIBN mg	Ti °C	DP	NMR Mn	GPC Mn	GPC Mw/Mn
P	1.5	0	10	128	17		7000	1.22
D1	1.5	0.25	10	111	6.7	2500	4400	1.24
D2	1.5	0.50	10	98	5.5	2000	3600	1.18
D3	1.5	0.75	10	89	4.1	1500	3100	1.14
D4	1.5	1.00	10	85	3.8	1300	2500	1.13
D5	1.5	1.50	10	78	2.9	1000	2400	1.15
B1	1.5	0.125	10	121	11	2600	4400	1.30
B2	1.5	0.25	10	109	8.6	1500	3500	1.26
B3	1.5	0.50	10	103	7.4	1300	3000	1.22
B4	1.5	1.00	10	99	2.8	1100	2800	1.10
A1	1.5	0.125	10	128	11		4300	1.36
A2	1.5	0.25	10	129	7.6		3100	1.36
A3	1.5	0.50	10	120	7.2		2900	1.29
A4	1.5	0.75	10	116	5.4		2200	1.17
A5	1.5	1.00	10	113	3.2		1300	1.53

Temperature: 60°C, Solvent: DMF 10 ml; Duration of telomerization: 48 h.

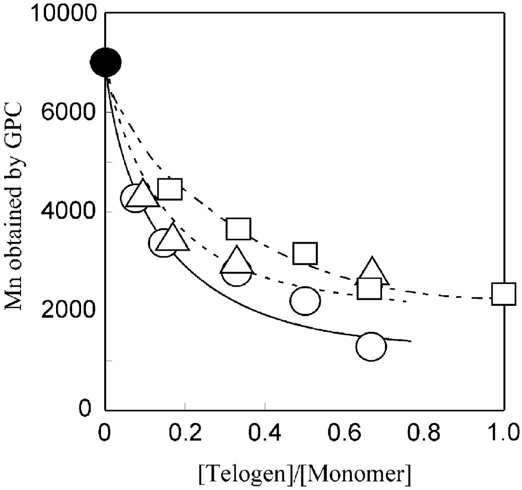

FIGURE 1 Effects of telogen contents on molecular weights of telomers ○: An, △: Bn, □: Dn, ●: Homopolymer.

determined by DSC measurement and polarized microscopic observation. It was observed that isotropization temperatures of the telomers, Ti decreased with a decrease in Mn in a similar way reported earlier [4–8] (Fig. 2). The isotropization temperature, Ti, can be

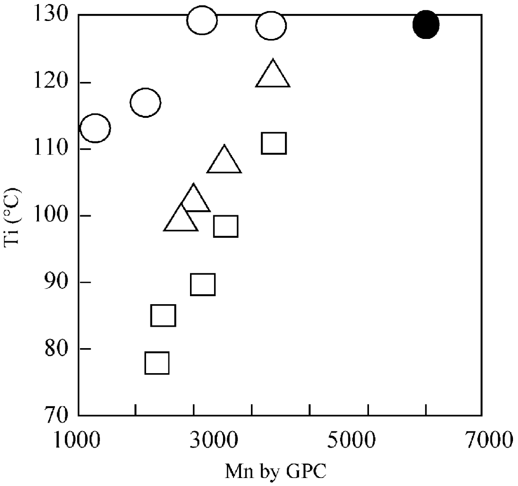

FIGURE 2 Effects of molecular weights on isotropization temperatures of telomers ○: An, △: Bn, □: Dn, ●: Homopolymer.

assumed to be a measure of stability of the LC phase. Therefore, it is noteworthy here to compare the effect of the structure of the telogens on Ti. However, the depression of Ti was dependent on the structure of the telogens. The telomer **An** showed a little effect of the Mn on Ti compared to the other telomers. The end-capping of the polymer chains with mesogenic groups may improve the stability of the LC phase even if the LC polymers have rather low molecular weight.

The telogens seemed to influence not only the stability of the LC phase, but also the morphology and crystallinity of the telomers at lower temperature range. DSC thermograms of the telomers and the homopolymer are shown in Figure 3. Three small endothermic peaks were observed on the thermogram of the homopolymer. The thermal behaviors of the telomers having Mn lower than 4000 was affected strongly by the molecular weight and the structure of the telogens. Contrary to the homopolymer, sharp exothermic and endothermic peaks were observed and the changes in enthalpy tended to increase with the decrease in Mn. The exothermic peaks appeared at lower temperatures than the endothermic peaks. Since fluidity of the telomers in this temperature range is extremely low, the exothermic and the endothermic peaks may be corresponding to the crystallization and the subsequent melting of the crystalline phase. Larger enthalpy change of the telomers with lower Mn indicates the increase in the amount of heat required to melt, meaning the increase in the crystalline domain. From this point of view, low molecular weight

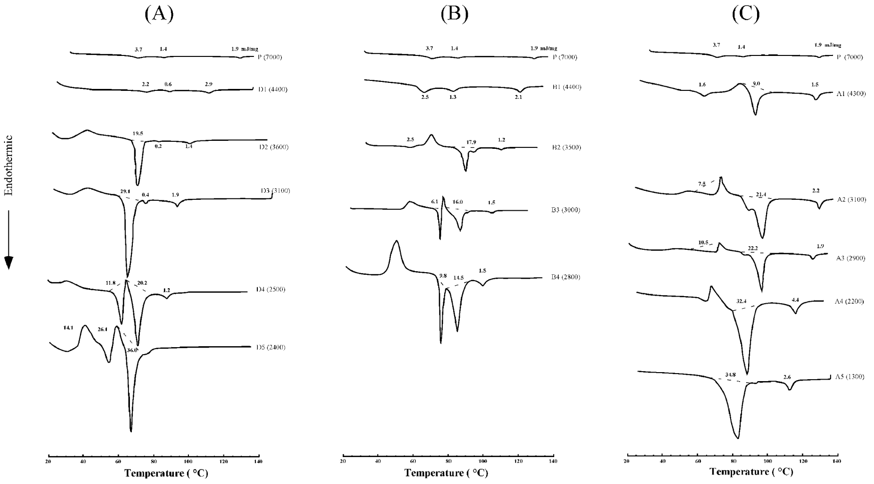

FIGURE 3 DSC thermograms of telomers having different terminal groups; Dn (A), Bn (B), An (C).

telomers possess higher fluidity and be easy to crystallize than the telomers with higher molecular weight.

On the other hand, the **An** telomers having the same groups both at the end of the main chains and in the side chains showed different thermal transition behavior from that of the telomers **Bn** and **Dn**. Large exothermic and endothermic peaks were observed at 80°C and 90°C even for **A1** with Mn of 4300, whereas no exothermic peak was observed for **D1** and **B1** with similar Mn. These results may be related to the disordering effect of non-mesogenic groups attached at the end of main chains on the molecular orientation or packing of the mesogenic groups. In the case of the **An** telomer, the mesogenic groups can be arranged in the crystalline and liquid crystalline phases easily, because of less disordering effect of the azobenzene group attached at the end of the main chains. Therefore, both crystallization peak and melting peak were observed for the telomers **An** with higher molecular weight. The structure of the telogens and molecular weight influenced the stability and the morphology of the telomers. This is interpreted in terms of the fluidity and the facility of the molecular orientation. Thus, it can be expected that the response to external stimuli will be dependent on the kind of telomers and their molecular weight.

In Figure 4A, the spectrum of **B2** in THF solution exhibits almost symmetrical band at 360 nm with a small shoulder at 380 nm. After spin coating and solvent evaporation on a quartz glass substrate, a maximum absorption of the thin films of telomers was shifted to

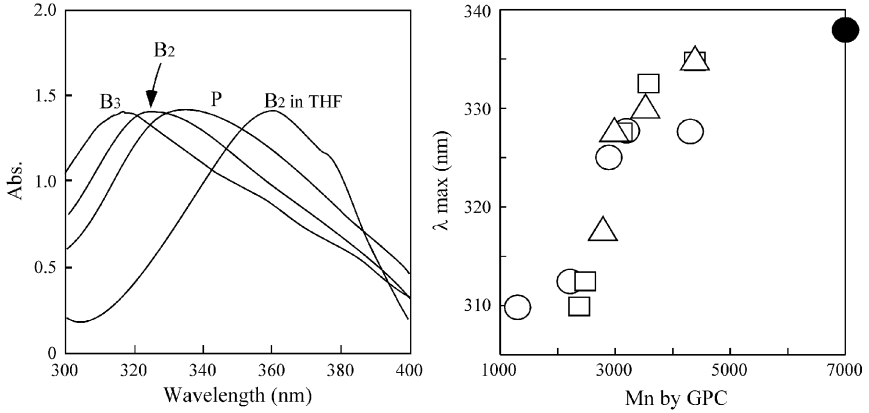

FIGURE 4 Absorption spectra of telomers (B2 and B3) and homopolymer coated on a glass substrate, and B2 in THF (Fig. A), and the effect of molecular weight on λmax of the films made from the telomers (Fig. B). ○: An, △:Bn, □: Dn, ●: Homopolymer.

shorter wavelength. The maximum wavelength of the telomers is plotted as a function of Mn in Figure 4B. The maximum wavelength is dependent on the molecular weight of the telomers, but not on the structure of the telogens. Namely, the wavelength of the maximum decreased with decreasing Mn, regardless of the structure of the telogens. Contrary to the films, the maximum wavelength of the telomers in THF solution was independent on the molecular weight. It has been reported that the polymers having azobenzene moiety as a side chain tend to associate or aggregate in a solid state [10,11]. Figure 5 shows changes in absorption spectra of **B1** in THF solution (A) and in the solid state (B) by UV irradiation. No significant difference in the absorption at longer wavelength region between in THF and in solid state was recognized. This may indicate that no strong association between chromophores occurs. DSC measurements explored that the telomers having lower Mn tended to crystallize at lower temperature. Although the crystallization and association of the chromophores may be related to the shift of the absorption band, it is not clear sufficiently.

Upon UV irradiation, the absorption decreased in the region of the $\Pi - \Pi^*$ transition around 360 nm. In the THF solution, the photoisomerization from trans-form to cis-form almost completely proceeded within 10 s by UV irradiation as can be seen in Figure 5. The yield of the trans-form at the photo-stationary state was estimated to be about 95% by NMR spectroscopy. On the other hand, the solid films became the photo-stationary state within 1 min by UV irradiation. In the case of the solid films, isosbestic points at 310 and 410 were observed

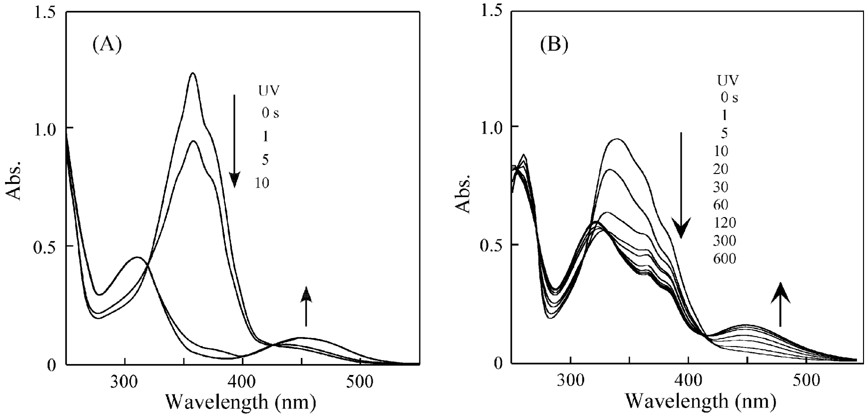

FIGURE 5 Changes in absorption spectra of B1 (Mn 4400) in THF (A) and in a solid film (B) coated on a glass plate by UV irradiation.

within 30 s, while prolonged irradiation resulted in a shift of the isosbestic points. As can be demonstrated in Figure 5, azobenzene molecules are well known to show the photoisomerization from the trans-form to the cis-form by UV irradiation. The trans-form has a rod shape which is similar to that of LC molecules, while the cis-form has a bent shape different from that of LC molecules entirely. The trans-to-cis photoisomerization of the azobenzene molecules disorganizes a structure of a LC molecular orientation and results in a depression of a phase transition temperature from a LC phase to other phases. Consequently, an isothermal phase transition can be induced photochemically [12]. The shift of the isosbestic point may be related to the transformation of the phase structures of the telomers. Therefore, it is expected that the phase transition of the telomers can be induced by means of the photoisomerization of the azobenzene groups.

Uniaxially oriented films were prepared by spin-coating the telomer solution in THF on a glass substrate coated with polyimide film and rubbed in one direction, and followed by thermal treatment. Figure 6 shows the transmitted light intensity through the uniaxially oriented film between two crossed polarizers as a function of angle between rubbing axis and polarizer axis. The transmitted light intensity (I) is expressed in this condition as follows,

$$I = \sin^2(\Pi \cdot \Delta n \cdot d/\lambda) \tag{1}$$

where, d and λ express the sample thickness and the wavelength of the monitor light (633 nm, He-Ne laser) respectively. The thickness of all the films was almost same, and it was about 200 nm. Therefore, the transmitted light intensity should be proportional to Δn, which is a measure of the uniaxial molecular orientation of the azobenzene mesogenic groups. As can be seen in Figure 6, **P** and **D1** films exhibited higher uniaxial molecular ordering compared to the others. The uniaxial molecular orientation in the solid films was achieved for **B1**-**B4** and **A1** telomers, whereas the oriented films could not be obtained from the telomers **D2**-**D5** and **A2**-**A5**. These telomers which did not give the oriented films exhibited large endothermic peaks in a range from 80 to 90°C corresponding to the melting of the crystalline phase as shown in Figure 3. Therefore, the crystallization is one of the causes interfering the uniaxial molecular orientation on the rubbed substrate.

Changes in the transmitted light intensity through the films upon UV irradiation are shown in Figure 7. In these figures, the light intensities normalized were plotted in order to compare the photochemical response property of the telomer films. The light intensity of all the films decreased upon UV irradiation. Under this experimental

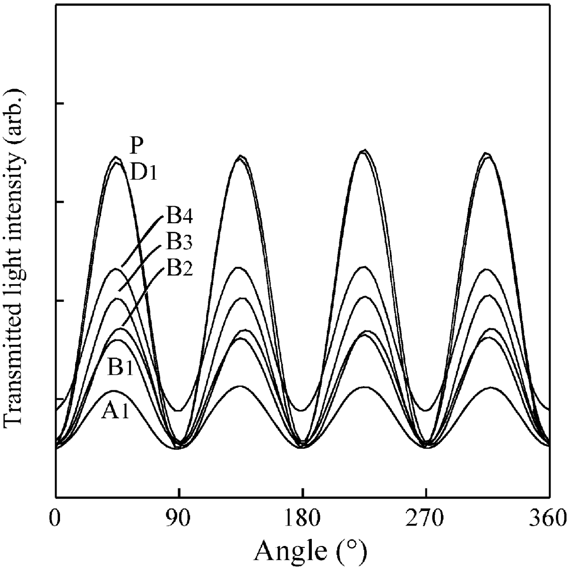

FIGURE 6 Changes in transmitted light intensity through the uniaxial films as a function of rotation angle.

condition, the light intensity is related to Δn in Eq. (1) as mentioned above. Therefore, the decrease in the light intensity demonstrates that the trans-to-cis photoisomerization results in the disorganization of the uniaxial molecular orientation. The telomers except **B4** and **A1** showed a steep decrease in the transmitted light intensity compared to the **P** film. Namely, the photo responses of these telomers are faster than the **P** film. On the other hand, the comparison of results of the telomers **Bn** reveals that the photoresponse is affected by not only the molecular weight, but also the morphology or molecular packing of the mesogenic groups. The facility of the molecular packing leading

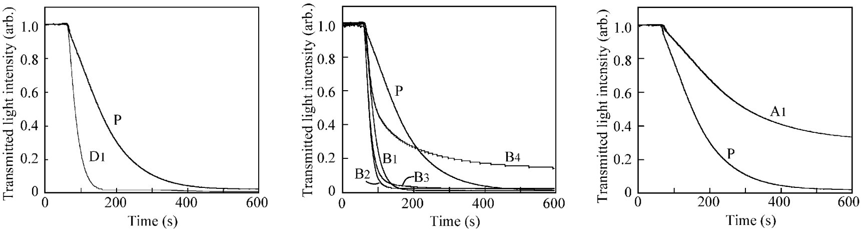

FIGURE 7 Photochemical phase transition of uniaxially oriented films by UV irradiation at room temperature.

to crystallization may cause the less photoresponse ability of both **B4** and **A1** telomers.

CONCLUSION

The molecular weight of the telomers decreased with increasing the concentration of telogens in the polymerization solution. The isotropization temperature as well as the morphology was found to be dependent on the molecular weight of the telomers. In particular, the telomers with low molecular weight or attached with azobenzene moiety at the end of the main chains tend to crystallize easily due to their fluidity and facility of the molecular packing. The uniaxially oriented films were prepared by spin-coating of the telomers in THF on the glass substrate followed by rubbing and thermal treatment. The uniaxially orientated films could not be obtained from the telomers with lower molecular weight. The precise control of the molecular orientation in the solid film was related to facility of the molecular packing, leading to the crystallization. Telomer **D1** having dodecane group at the end of the main chains was found to be suited for the uniaxial molecular orientation comparable to the homopolymer. **D1** telomer showed rapid switching by UV irradiation. The molecular weight of the telomers as well as the control of its morphology affects the molecular orientation and the photoresponsive properties of the telomers in the solid films.

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