Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 2175–2182

polymer

www.elsevier.com/locate/polymer

Synthesis, thermal and photochemical properties of liquid crystalline telomers

Md. Zahangir Alam, Tomoko Ohmachi, Tomonari Ogata, Takamasa Nonaka, Seiji Kurihara*

Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

Received 20 August 2004; received in revised form 13 January 2005; accepted 13 January 2005

Abstract

Liquid crystalline telomers have been synthesized by free radical polymerization. Their thermal as well as photoresponsive properties are reported. The effects of telogen content on the degree of polymerization were also studied. The degree of polymerization decreased with an increase in the telogen content during telomerization. Consequently, the molecular weights of the telomers decreased with the increase in the telogen content. The isotropization temperatures of the telomers from liquid crystalline to isotropic phase were determined as a measure of stability of the telomers. The stability of the telomers was found to be influenced strongly by their 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; Isotropization temperature

1. Introduction

Liquid crystalline (LC) polymers such as main chain type and side chain type consist of two components, mesogenic moieties and 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 [1]. In addition, the molecular weight of the LC polymers is known to influence significantly their LC behaviors [2–6]. 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 [2]. Finkelmann et al. synthesized LC oligomers which were composed of oligo (methylsiloxane) with mesogenic side groups and explored the effects of molecular weight on occurrence of LC phases and their thermal properties [3]. They described a steep increase in the phase transition temperature in a range of degree of polymerization from 3 to 10. In addition, the oligomers having the degree of polymerization lower than three did not show any LC phase owing to higher melting point. 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 [6]. One of the causes of the effects of molecular weight on the LC behaviors is the presence of non-mesogenic end groups which are 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.

There are also some reports on formation and properties of glassy LC materials. Chen reported the generation of circularly polarized photoluminescence from films of glass forming chiral nematic LCs [7]. Kreuzer synthesized cyclic siloxanes with 4–7 monomeric units that contained mesogenic side chain groups and investigated their glass transition temperatures with respect to comparison with linear polysiloxanes having the same degree of

---

* Corresponding author. Tel.: +81 96 342 3678; fax: +81 96 342 3679.
E-mail address: kurihara@gpo.kumamoto-u.ac.jp (S. Kurihara).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.01.033

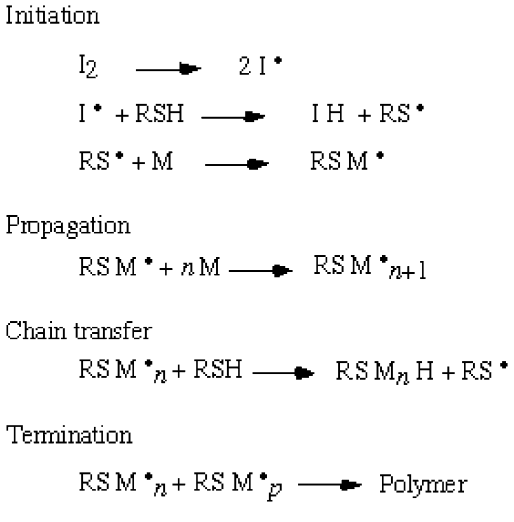
polymerization [8]. Furthermore, Tamaoki reported thermal- and photo-mode full color recordings by the use of cholesteric solid films of dicholesteryl esters having molecular weight of about 1000 [9]. Characteristics of the cholesteric solid films of the dicholesteryl esters are rapid response of the 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.

Telomerization is one of the methods for synthesis of polymers (telomers) with controlled molecular weights and predetermined functionalities (chain end structures) [10,11]. 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 as shown in Scheme 1. In this study, we synthesized telomers containing azobenzene groups by using three chain transfer agents and investigated the influence of the content of the chain transfer agents during telomerizaion on the molecular weight of the telomers and their thermal as well as photochemical properties by means of photoisomerization of the azobenzene groups.

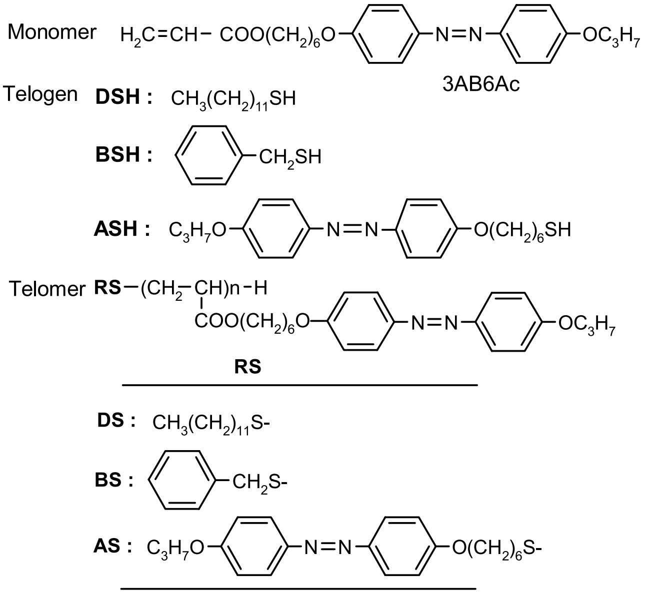
2. Experimental

2.1. Materials

Azobenzene compounds, **3AB6Ac** and **ASH** were synthesized and used in this study (Scheme 2). Two mercaptan compounds and other reagents were purchased and used without further purification.



Scheme 1. Radical telomerization.



Scheme 2. Structures of monomer, telogens and telomers.

2.1.1. Synthesis of 6-(4-(4′-propoxyphenylazo)phenoxy]hexylacrylate), ***3AB6Ac***

2.1.1.1. 4-Propoxyaniline. To a solution of 11.3 g (200 mmol) of KOH, 30 g (198 mmol) of 4-hydroxyacetanilide in 150 ml of EtOH was added 49 g (398 mmol) of 1-bromopropane. After refluxing the reaction mixture for 24 h, 75 ml of 12N-HCl dissolved in 150 ml of EtOH was added and was again refluxed for more 24 h. The reaction mixture was then poured into water and was neutralized with KOH aq. solution. The product was extracted with $CHCl_3$, washed with water, dried over anhydrous $MgSO_4$. The product obtained after removal of the solvent by evaporation was a black oily liquid in 68% yield. ^1H NMR ($CDCl_3$, δ): 1.0 (m, 3H, methyl), 1.7 (m, 2H, methylene), 3.4 (s, 2H, NH_2), 3.8 (t, 2H, CH_2OPh), 6.5–6.8 (m, 4H, aromatic).

2.1.1.2. 4-Propoxy-4′-hydroxyazobenzene. To a solution of 20 g (132 mmol) of 4-propoxyaniline dissolved in 200 ml of 4N-HCl was added 63.6 g (600 mmol) of $NaNO_2$ dissolved in 500 ml of water at 0 °C. The obtained solution was then added to a 500 ml of aq. solution of 18 g (192 mmol) of phenol and 63.6 g (600 mmol) Na_2CO_3 slowly. After stirring at room temperature for 1 h, it was neutralized with dilute HCl solution. The precipitated product was filtered, washed with water and dried under vacuum.

Yield: 89% as solid. ^1H NMR ($CDCl_3$, δ): 1.0 (m, 3H, methyl), 1.8 (m, 2H, methylene), 4.0 (t, 2H, CH_2OPh), 5.0 (t, 1H, OH), 6.9–7.9 (m, 8H, aromatic). Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 69.53; H, 6.62; N, 10.71.

2.1.1.3. 4-Propoxy-4′-(6-hydroxyhexyloxy)azobenzene. To a mixture of 12 g (48 mmol) of 4-propoxy-4′-hydroxyazobenzene, 6 g (43 mmol) of K_2CO_3 and a very minute amount of KI dissolved in 300 ml of dimethylformamide (DMF) was added 6.4 g (48 mmol) of 6-chlorohexanol. After refluxing for 72 h at 100 °C the reaction mixture was poured into 300 ml of water, extracted with $CHCl_3$, washed with water and dried over anhydrous $MgSO_4$. After removal of $CHCl_3$ by evaporation the obtained liquid was poured into water. The precipitated product was filtered and was recrystallized from methanol.

Yield: 70% as solid. ^{1}H NMR ($CDCl_3$, δ): 1.0 (m, 3H, methyl), 1.3–2.0 (m, 10H, methylene), 3.4 (m, 2H, CH_2OH), 4.0–4.1 (m, 4H, CH_2OPh), 4.4 (t, 1H, OH), 6.9–7.9 (m, 8H, aromatic). Anal. Calcd for $C_{21}H_{28}N_2O_3$: C, 70.76; H, 7.91; N, 7.86. Found: C, 70.59; H, 7.95; N, 7.95.

*2.1.1.4. 6-[4-(4′-Propoxyphenylazo)phenoxy]hexylacrylate, **3AB6Ac**.* To a solution of 9 g (25.8 mmol) of 4-propoxy-4′-(6-hydroxyhexyloxy) azobenzene and a minute amount of hydroquinone dissolved in 150 ml of THF was added 5.4 g (52.8 mmol) triethylamine and 4.8 g (52.8 mmol) acryloyl chloride slowly at 0 °C with stirring. After stirring at room temperature for 1 day the reaction mixture was poured into water. The precipitated product was collected and purified by recrystallization from ethanol.

Yield: 38% as solid. ^{1}H NMR ($CDCl_3$, δ): 1.0 (m, 3H, methyl), 1.4–2.0 (m, 10H, methylene), 4.0 (m, 4H, CH_2OPh), 4.2 (m, 2H, CH_2OCO), 5.8 (q, 1H, CH2=CH), 6.1 (q, 1H, CH2=CH), 6.4 (q, 1H, CH2=CH), 6.9–7.9 (m, 8H, aromatic). Anal. Calcd for $C_{24}H_{30}N_2O_4$: C, 70.21; H, 7.37; N, 6.82. Found: C, 70.33; H, 7.45; N, 6.85.

*2.1.2. Synthesis of 6-[4-(4-propoxyazo)phenoxy]hexane-1-thiol, **ASH***

2.1.2.1. 4-Propoxy-4′-(6-bromohexyloxy)azobenzene. To a solution of 8 g (31 mmol) of 4-propoxy-4′-(6-hydroxyhexyloxy)azobenzene, 1.8 g (13 mmol) of K_2CO_3, 0.9 g (6.5 mmol) of KI in 100 ml of methylethylketone (MEK) was added 37.8 g (155 mmol) of 1,6-dibromohexane and was refluxed for 24 h. The reaction mixture was then cooled to room temperature and extracted with $CHCl_3$, washed with water and was dried over $MgSO_4$. After removal of $CHCl_3$ by evaporation the crude product was recrystallized from ethanol.

Yield: 50% as solid. ^{1}H NMR ($CDCl_3$, δ): 1.0 (m, 3H, methyl), 1.3–2.3 (m, 10H, methylene), 3.4 (t, 2H, CH_2Br), 4.0 (m, 4H, CH_2OPh), 6.9–7.9 (m, 8H, aromatic). Anal. Calcd for $C_{21}H_{27}BrN_2O_2$: C, 60.14; H, 6.49; N, 6.68. Found: C, 60.11; H, 6.45; N, 6.58.

*2.1.3. 6-[4-(4-Propoxyazo)phenoxy]hexane-1-thiol, **ASH***

To a solution of 6.6 g (15.7 mmol) of 4-propoxy-4′-(6-hydroxyhexyloxy)azobenzene in 60 ml of EtOH, 4.2 g (17 mmol) of sodium thiosulfate pentahydrate dissolved in 20 ml of water was added. The mixture was refluxed for 6 h at 75 °C. After cooling to room temperature, an intermediate compound (Bunte salt) was precipitated. It was washed with acetone to remove Br compound. A solution of 120 ml of $CHCl_3$ and 120 ml of 1 N HCl was degassed by passing nitrogen for 20 min and Bunte salt was added to it and the resulting mixture was refluxed for 6 h at 60 °C. After cooling to room temperature the organic phase was separated and the aqueous phase was extracted with $CHCl_3$, washed with water and dried over $MgSO_4$. The crude 6-[4-(4-propoxyazo)phenoxy]hexane-1-thiol obtained by evaporation of the solvent was recrystallized from ethanol.

Yield: 50% as solid. ^{1}H NMR ($CDCl_3$, δ): 1.0 (m, 3H, methyl), 1.4 (t, 1H, SH), 1.4–1.9 (m, 10H, methylene), 2.5 (m 2H, CH_2SH), 4.0 (m, 4H, CH_2OPh), 6.9–7.9 (m, 8H, aromatic). Anal. Calcd for $C_{21}H_{28}N_2SO_2$: C, 67.70; H, 7.58; N, 7.51. Found: C 67.27; H, 7.50; N, 7.50

2.2. Procedure of telomerization

First, 0.62 g (1.5 mmol) of the monomer, **3AB6Ac** and required quantity of telogen were dissolved in 10 ml of DMF in a polymerization tube, and 10 mg (0.06 mmol) of azobisisobutyronitrile (AIBN) was added to the solution. After degassing the reaction mixture with nitrogen, the tube was sealed properly and then maintained in the water bath at 60 °C for 48 h. The reaction mixture was then poured into MeOH. The precipitated product was collected and dissolved in $CHCl_3$ again. By repeating this reprecipitation cycle several times until purity telomer was collected and dried under vacuum up to a constant weight. The telomers obtained from dodecanethiol, benzylthiol and **ASH** were termed as telomer **Dn**, telomer **Bn** and telomer **An**, respectively.

2.3. Characterization and photoresponsive behavior

Thermal properties of the telomers were examined by means of differential scanning calorimetry (DSC; Seiko SSC-5020) and polarizing microscopic observation (Olympus BHSP polarizing microscope; Mettler FP80 and FP82 hot stage and controller). The scan rate of DSC measurements was 10 °C/min of heating. Molecular weights of the telomers were determined by gel permeation chromatography (GPC; Jasco 870-UV detector at 254 nm, Shodex KF-804F column, tetrahydrofuran, THF as eluent). In addition, NMR measurements were carried out for determining the molecular weights of both telomers **Dn** and **Bn** by comparing the peaks corresponding to the telogen attached to the end of telomers and azobenzene side chain groups.

Solid films of the telomers were prepared by spin-coating using THF as solvent. The film thicknesses obtained were estimated to be about 200 nm by measuring absorbance with an UV/visible spectrometer (Shimadzu UV-1600). Photoisomerization behaviors of the telomers both in THF and in solid state were examined by monitoring changes in absorption spectra at room temperature. The photoisomerization of azobenzene group between *trans*-form and *cis*-form was performed 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. The power densities of the incident light were 58 mW/cm^2 for UV and 58 mW/cm^2 for visible light, respectively.

Uniaxially oriented films were prepared by spin-coating the telomer dissolved in THF on a glass substrate coated with polyimide film and rubbed in one direction, and by thermal treatment: the films were annealed at the reduced temperature T_{red} ($=T/T_c$, T; annealing temperature, T_c; clearing temperature) of 0.95 for 3 min, and was followed by rapid cooling to room temperature on an aluminum plate. The films thus prepared were placed between two crossed polarizers. The polarizing directions of these two polarizers were set at an angle of 45° with respect to the orientation axis of the films. Changes in the transmitted light intensity of a He–Ne laser were monitored with a photodiode when the films were irradiated under UV light.

3. Results and discussion

3.1. Thermal properties

The conditions of synthesis and characteristic parameters of the homopolymer and telomers were given in Table 1. A homopolymer of **3AB6Ac** was synthesized by polymerization in a similar manner to the telomerization without any telogen, giving the homopolymer attached with isobutyronitrile group at one or both ends of polymer main chains. The molecular weights of the homopolymer were 7000 (M_n) and 8600 (M_w) determined by GPC. In addition, the molecular weights of the telomers were also given in Table 1. Introduction of the telogens, **DS** and **BS** in to the telomers was identified by NMR spectra and X-ray photoelectron spectroscopy (XPS). The XPS measurements revealed that the peak intensity corresponding to sulfur increased with increasing the telogen fed to the telomerization solution. The molecular weights of the telomers determined by TOF Mass roughly correspond to those obtained by NMR measurements. So, it can be assumed that the number of the telogen introduced in to the telomers is one, because of higher concentration of telogens compared to the AIBN content through a chain transfer reaction as given in Scheme 1. By comparing peaks corresponding to methyl and phenyl groups in the NMR spectra of the telomers, the molecular weights of both telomers, **Dn** and **Bn** were estimated as given in Table 1. The molecular weight of the telomer **An** could not be determined by NMR measurements, because of no distinguishable peak in the NMR spectra of **An** between the azo side group and the telogen **AS**. Thus, in order to discuss the effect of the molecular weight on the thermal properties of the telomers, the molecular weights of all the telomers were determined by GPC measurements. Although there was a little difference between the molecular weights determined by NMR and GPC measurements, both molecular weights showed a similar tendency. Therefore, the molecular weight determined by GPC measurements will be suited for discussing the effect of molecular weight on the thermal properties of the telomers.

M_n of the telomers were determined by GPC as a function of the content ratio of the telogens to **3AB6Ac** fed in the telomerization solutions. It was observed that the molecular weight of the telomers decreased with increasing the telogen content. So, the molecular weight of the telomers can be controlled easily by varying the amount

Table 1
Synthesis and properties of homopolymer and telomers

	3AB6Ac, g (mmol)	Telogen, g (mmol)	AIBN (mg)	DP	By NMR	By GPC		
					M_n	M_n	M_w	M_w/M_n
P	0.62 (1.5)	0 (0)	10	17.0	–	7000	8600	1.22
D1	0.62 (1.5)	0.05 (0.25)	10	6.7	2500	4400	5400	1.24
D2	0.62 (1.5)	0.10 (0.50)	10	5.5	2000	360	4300	1.18
D3	0.62 (1.5)	0.15 (0.75)	10	4.1	1500	3100	3500	1.14
D4	0.62 (1.5)	0.20 (1.00)	10	3.8	1300	2500	2800	1.13
D5	0.62 (1.5)	0.30 (1.50)	10	2.9	1000	2400	2800	1.15
B1	0.62 (1.5)	0.015 (0.125)	10	10.8	2600	4400	510	1.30
B2	0.62 (1.5)	0.03 (0.25)	10	8.6	1500	3500	4500	1.26
B3	0.62 (1.5)	0.06 (0.50)	10	7.4	1300	3000	3700	1.22
B4	0.62 (1.5)	0.12 (1.00)	10	2.8	1100	2800	3100	1.10
A1	0.62 (1.5)	0.0425 (0.125)	10	10.6		4300	5700	1.36
A2	0.62 (1.5)	0.093 (0.25)	10	7.6		3100	3600	1.36
A3	0.62 (1.5)	0.186 (0.50)	10	7.2		2900	3700	1.29
A4	0.62 (1.5)	0.276 (0.75)	10	5.4		2200	2600	1.17
A5	0.62 (1.5)	0.372 (1.00)	10	3.2		1300	2000	1.53

Temperature, 60 °C; duration, 48 h; solvent, DMF (10 ml).

of the telogens. In addition, M_n of the telomers was dependent on the structure of the telogens. Namely, different telogens contribute to yield different molecular weights of the telomers even though the telogen content was the same. In this study, although the chain transfer constant of the telogens could not be determined, that of **ASH** having azobenzene moiety seemed to be the highest among them. The sequence of the decreasing of the molecular weight with various telogens was found as follows: **ASH** > **BSH** > **DSH**.

Phase transition temperatures were determined by DSC measurement and polarized microscopic observation. Fig. 1 shows the effects of the kind of telogens and the molecular weight of the telomers on their isotropization temperatures (T_i), which is the phase transition temperature from a LC to an isotropic phase. The isotropization temperature can be assumed to be a measure of the stability of the LC phase. Therefore, it is noteworthy here to compare the effect of the structure of the telogens on T_i. It was clearly seen that T_i decreased with a decrease in M_n in a similar way reported earlier [2–6]. However, the depression of T_i was dependent on the structure of the telogens. The telomer **An** showed a little effect of the M_n on T_i 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. On the basis of the DSC measurement and the polarized optical microscopic observation, the thermal phase transition behaviors of the homopolymer and telomers are stated in Table 2. The thermal behaviors of the telomers having M_n lower than 4000 were affected strongly by the molecular weight and the structure of the telogens. Typical DSC thermograms of the homopolymer **P** and the telomer **D3** are shown in Fig. 2. Other telomers showed almost same thermograms. Polymer **P** showed three peaks corresponding to the crystal to smectic, smectic to nematic, and nematic to isotropic phase transitions, respectively. Telomers having higher molecular weight showed similar phase transition behaviors. But, telomers having lower molecular weight showed different phase transition behaviors. The low molecular weight telomers exhibited only the crystal to nematic and nematic to isotropic phase transitions. The smectic phase of the low molecular weight telomers may be disappeared due to their high melting temperatures. Sharp exothermic and endothermic peaks were observed and the changes in enthalpy tended to increase with the decrease in M_n. 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 M_n 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 telomers possess higher fluidity and may be easy to crystallize than the telomers of higher molecular weight.

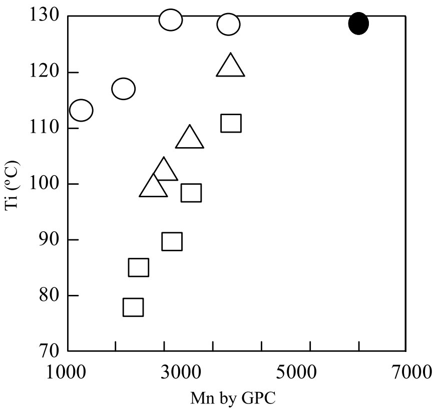


Fig. 1. Effects of molecular weights of telomers on their isotropization temperatures ○, **An**; △, **Bn**; □, **Dn**; ●, homopolymer by Kurihara et al.

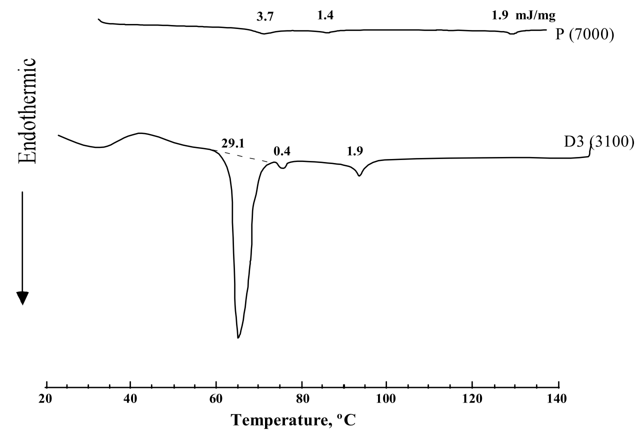


Fig. 2. DSC thermograms of polymer **P** and telmoer **D3** by Kurihara et al.

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 M_n of 4300, whereas no exothermic peak was observed for D1 and B1 with similar M_n. 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.

Table 2
Thermal phase transition behaviors of homopolymer and telomers

Compound	T_k (°C)	T_m (°C)	T_{SN} (°C)	T_i (°C)	ΔH_m (mJ/mg)	ΔH_{SN} (mJ/mg)	ΔH_i (mJ/mg)
P		80	100	128	3.7	1.4	1.9
D1		76	87	111	2.2	0.6	2.9
D2		71	83	98	19.5	0.2	1.4
D3	42	64	74	89	29.1	0.4	1.9
D4	65	72		85	32.0		1.2
D5	60	67		78	62.1		4.5
B1		66	84	121	2.5	1.3	2.1
B2	60	88		109	18.3		1.2
B3	59	83		103	22.1		1.5
B4	50	83		99	24.3		1.5
A1	83	60	94	128	1.6	9.0	1.5
A2	72	97		126	20.8		2.2
A3	73	97		120	22.2		1.9
A4	68	89		116	32.4		4.4
A5		84		113	34.8		2.6

T_k, crystallization temperature; T_m, crystal to LC phase transition temperature; T_{SN}, smectic to nematic phase transition temperature; T_i, LC to isotropic phase transition temperature; ΔH_m, change in enthalpy of crystal to liquid crystal phase transition; ΔH_{SN}, change in enthalpy of smectic to nematic phase transition; ΔH_i, change in enthalpy of LC to isotropic phase transition.

3.2. Photoresponsive properties

The structure of the telogens and the 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 Fig. 3(A), the spectrum of **B2** in THF solution exhibits the absorption maximum around 360 nm corresponding to π–π* transition. After spin-coating and solvent evaporation on a quartz glass substrate, a maximum absorption of the thin films of telomers was shifted to shorter wavelength. The maximum wavelength of the telomers is plotted as a function of M_n in Fig. 3(B). 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 M_n, 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 [12,13]. Fig. 4 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 range of the spectra between in THF and in solid state was recognized. This may indicate no strong association between chromophores. DSC measurements explored that the telomers having lower M_n 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 π–π' transition around 360 nm. In the THF solution, the photoisomerization from *trans*-form to *cis*-form almost completely proceeded within 10 s by UV

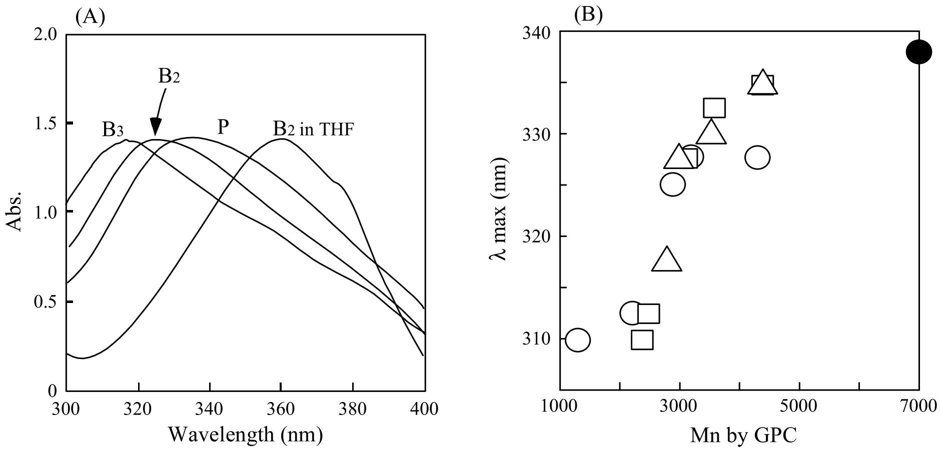


Fig. 3. Absorption spectra of telomers **B2**, **B3** and homopolymer coated on a glass substrate, and **B2** in THF (A), and the effect of the molecular weight on λ_{max} of the films made of the telomers (B). ○, **An**; △, **Bn**; □, **Dn**; ●, homopolymer by Kurihara et al.

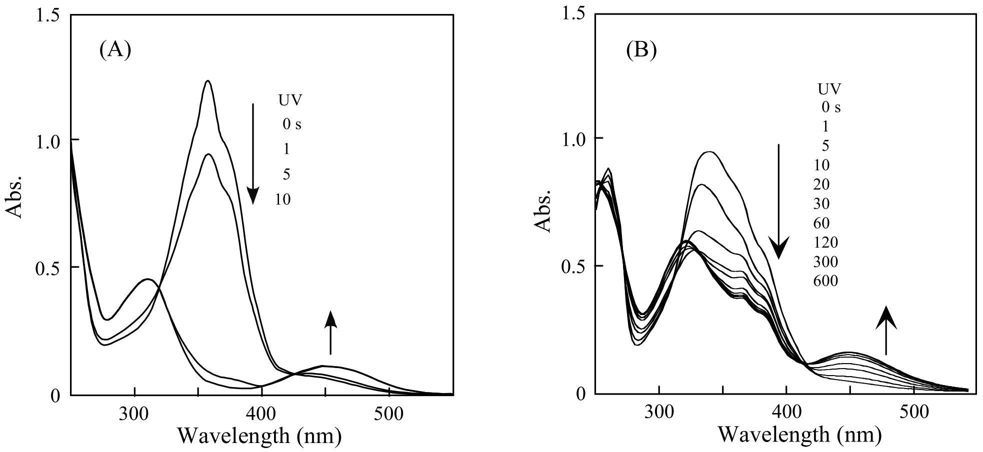


Fig. 4. Changes in absorption spectra of telomer Bl (*Mn* 4400) in THF (A) and in a solid film (B) coated on a glass plate by UV irradiation by Kurihara et al.

irradiation as can be seen in Fig. 4. 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 nm were observed within 30 s, while prolonged irradiation resulted in a shift of the isosbestic points. As can be demonstrated in Fig. 4, 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 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 the 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 [14]. 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.

In order to explore the photoresponsive properties of the telomers, uniaxially oriented films were prepared by spin-coating the telomer dissolved in THF on a glass substrate coated with polyimide film and rubbed in one direction, and followed by thermal treatment; annealing at T_{red} of 0.95 for 3 min, and subsequent rapid cooling to room temperature. Fig. 5 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,

$$I = \sin^2(\pi \Delta nd/\lambda) \qquad (1)$$

where d, 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 uniaxially molecular orientation of the azobenzene mesogenic groups. As can be seen in Fig. 5, **P** and **D1** films exhibited higher uniaxial molecular ordering compared to the others. The uniaxial molecular orientation in the solid films was achieved for telomers **B1**–**B4** and **A1**, whereas the oriented films could not be obtained from the telomers **D2**–**D4** and **A2**–**A5**. These telomers which did not give the oriented films exhibited large endothermic peaks in a range from 70 to 90 °C corresponding to the melting of the crystalline phase as given in Table 2. Therefore, 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 Fig. 6. 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 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

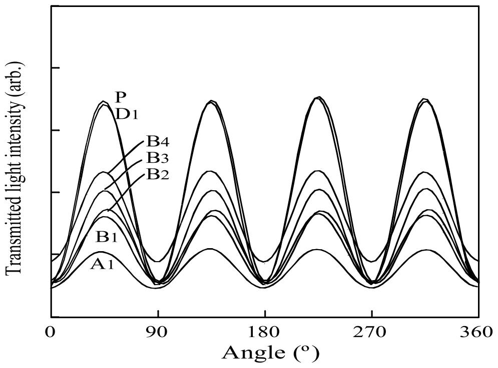


Fig. 5. Changes in transmitted light intensity through the uniaxial films as a function of rotation angle. The films were made by spin-coating and aging on the rubbed substrate by Kurihara et al.

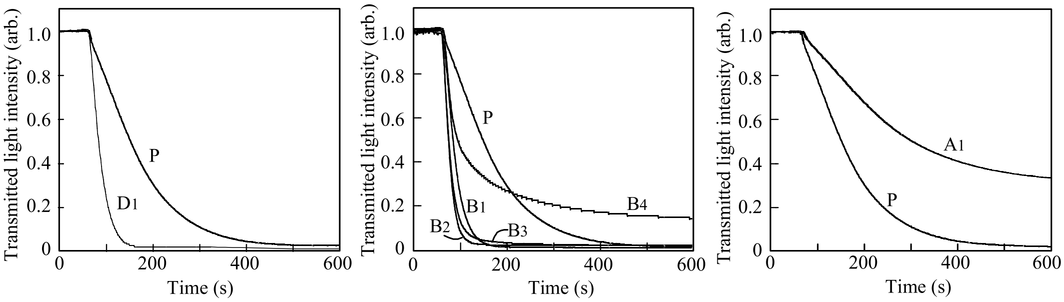


Fig. 6. Photochemical phase transition of uniaxially oriented films by UV irradiation at room temperature by Kurihara et al.

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

4. Conclusion

We synthesized telomers by the use of telogens, dodecanethiol, benzylthiol, and the azobenzene thiol derivative. The M_n of the telomers decreased with increasing the concentration of the 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. 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** containing dodecane group at the end of the main chains was found to be suited for the uniaxial molecular orientation comparable to the homopolymer. Telomer **D1** also 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.

References

[1] Plate NA, Shibaev VP. Comb-shaped polymers and liquid crystal. New York: Plenum Press; 1987.

[2] Blumstein A, Stickles EM, Gauthier MM, Blumstein A, Volino F. Macromolecules 1984;17:177.

[3] Stevens H, Rehage G, Finkelmann H. Macromolecules 1984;17:851.

[4] Zhou Q-F, Duan XQ, Liu YL. Macromolecules 1986;19:247.

[5] Zhang H, Yu Z, Wan X, Zhou Q-F, Woo EM. Polymer 2002;43:2357.

[6] Ikeda T, Horiuchi S, Karanjit DB, Kurihara S, Tazuke S. Macromolecules 1990;23:36.

[7] Chen SH, Katsis D, Schmid AW, Mastrangelo JC, Tsutsui T, Blanton TN. Nature 1999;397:506.

[8] Petri A, Bråuchle C, Leigeber H, Miller A, Weitzel H-P, Kreuzer F-H. Liq Cryst 1993;15:113.

[9] Tamaoki N. Adv Mater 2001;13:1135.

[10] Bechkok A, Belbachir M, Guyot B, Boutevin B. Eur Polym J 1999;35:413.

[11] Loubat C, Boutevin B. Polym Int 2001;50:375.

[12] Labarthet FL, Freiberg S, Pellerin C, Pezolet M, Natansohn A, Rochon P. Macromolecules 2000;33:6815.

[13] Bobrovsky A, Boiko N, Shibaev V, Stumpe J. J Photochem Photobiol A 2004;163:347.

[14] Ikeda T, Horiuchi S, Karanjit DB, Kurihara S, Tazuke S. Macromolecules 1990;23:42.