

Preparation of Photoresponsive Oligomeric Additives for Glass-Forming Cholesteric Liquid Crystals and Helical Pitch Shift

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Oligomeric compounds consisting of photoreactive acrylates, 10-[4-(4-dodecyl-phenyl)azophenoxy]decyl acrylates, were prepared by free radical polymerization in the presence of a chain transfer agent. They are used as a reflection band shift agent for the cholesteric liquid crystals with medium molecular weight. The cholesteric liquid crystal mixed with the oligomeric material showed a selective reflection largely shifted to longer wavelength compared to that of host cholesteric liquid crystals. The reflection band shift depended on the molecular weight of oligomers. The wavelength of selective reflection was changed in response to irradiation. Rapid cooling from liquid crystalline temperature brought about a glassy film which is more stable than that composed of the monomeric compound mixture.

Key words: Azobenzene, Cholesteric Liquid Crystals, Polymer, Isomerization

1. INTRODUCTION

Cholesteric liquid crystals (CLCs) have a helical structure which reflects selectively light with particular wavelength corresponded to the helical pitch. Color devices can be achieved using this characteristic. The pitch is sensitively changed with temperature. For application the colored state has to be stabilized. We have proposed full color recording in the layer of a CLC compound in which the cholesteric alignment is frozen under the glass transition temperature[1, 2]. The CLC compound, CD8 (Fig. 1), having diacetylene with two cholesteryl groups in the both sides via alkyl spacers was used. The acetylene parts show no polymerization property in this compound. The molecular weight is about 1100 which is not large and not small. The liquid crystalline state of CD8 has fluidity similar to that of low molecular weight liquid crystals and can be frozen in glassy state by rapid cooling like polymeric materials. Image can be recorded on a CLC layer by local heating using a thermal head or the laser irradiation[3, 4]. In this method resolution of the recorded images is limited by spatial thermal conduction. For improvement of resolution, employment of photoreaction process to this system is useful. It will be faster and more sensitive for actinic light than thermal process. The utilization of CD8 doped with a photoreactive material such as azobenzene produces photo-tunable full color images based on reflection band shift in response to the photoreaction[5, 6]. This process is reversible. There is a problem that addition of a low molecular weight compound is likely to destabilize the glass state. On the other hand, increasing of molecular weight of the additive will lower miscibility to CLC.

Herein, we prepare oligomeric compounds consisting of photoreactive acrylates by free radical polymerization in the presence of a chain transfer agent to use as a reflection band shift agent. We investigate dependence

of shift of selective reflection of host CD8 on the molecular weight of oligomeric guest and stability of recorded images.

2. EXPERIMENTAL

2.1 Materials

Preparation of CD8 is previously reported. Azobenzene monomers **1** (Fig. 1) were synthesized from 4-dodecyl-4'-hydroxyazobenzenes which were prepared by the usual diazo coupling method from 4-dodecylaniline and phenol. To DMF solution (10 mL) of 4-dodecyl-4'-hydroxyazobenzene (2.17 g) and bromodecanol (1.87 g) were added potassium carbonate (1.11 g). After stirring at 80-90 °C for 12 hrs, the mixture was diluted with CH₂Cl₂, washed with water, and dried (MgSO₄). The solution was concentrated and 4-(12-hydroxydecyloxy)-4'-dodecylazobenzene (2.5 g) was purified by column chromatography (SiO₂; Ethylacetate+CCl₄). Acryloyl chloride (0.55g) was added to a mixture of the 4-(12-hydroxydecyloxy)-4'-dodecylazobenzene (2.5g) and triethylamine (0.55g) in dry CH₂Cl₂ (30 mL). After stirring at room temperature for several hours, the reaction mixture was diluted with CH₂Cl₂, washed with water, and dried (MgSO₄). The solution was concentrated and purified by column chromatography (SiO₂; CH₂Cl₂) to yield 10-[4-(4-dodecylphenyl)azophenoxy]decyl acrylate (1.70 g). Yellow crystals in 49 % yield. ¹H NMR (CDCl₃, δ): 0.88 (3H, t, -CH₃), 1.20-1.60 (30H, m, -CH₂-), 1.64 (2H, tt, -CH₂-CH₂OAr), 1.64 (2H, tt, -CH₂-CH₂Ar), 1.81 (2H, tt, -CH₂-CH₂OCO-), 2.67 (2H, t, ArCH₂-), 4.02 (2H, t, ArOCH₂-), 4.15 (2H, t, -CH₂OCO-), 5.80 (1H, dd, -CH=CH₂), 6.12 (1H, dd, -CH=CH₂), 6.39 (1H, dd, -CH=CH₂), 6.99 (2H, d, Ar-H), 7.29 (2H, d, Ar-H), 7.83 (4H, dd, Ar-H). Elemental analysis. Calcd. (wt%): C, 77.04; H, 9.78; N, 4.86. Found (wt%): C, 76.727; H, 9.66; N, 4.83.

2.2 Polymerization.

An initiator, 2, 2'-azobis(isobutyronitrile) (AIBN), obtained from Tokyo Kasei, were purified by recrystallization from EtOH. Monomer 1, AIBN (0.022 wt-ratio to monomer) and tert-dodecane thiol (tDM) (0.02, 0.2, 0.4 wt ratio to monomer) were dissolved in distilled toluene at a concentration of ca. 25 wt%, and then the mixture were placed in an ampoule tube, where tDM was used as a chain transfer agent to produce low molecular weight polymer. The solutions in the ampoules, which were degassed and then sealed, were shaken for 12 hours at 70 °C. The viscous solutions were poured into acetone or mixture of acetone and ethanol for purification of the polymeric materials. This procedure is repeated at least twice to produce polymeric materials 2, 3 and 4.

2.3 LC cell preparation.

CD8 were mixed with 1, 2, 3, 4, and 5 wt% of 1-4 and less than 0.1wt% of glass spheres with 5 μ m diameter (Nippon Shokubai) at 125 °C. The melted mixture was put between two pieces of glass slides on 125 °C Hot stage (Mettler FP82). The isotropic phase is changed to LC phase by cooling to 115, 110, 105, 100, 95 and 90°C, and then the sample was dropped into iced water at 0 °C. LC alignment is frozen into glass state by this rapid cooling process from each temperature.

2.4 Physical measurements.

Gel-permeation chromatography was conducted on a Shimadzu system comprising an LC-10ADvp pump unit, an SPD-10Avp UV detector, a CTO-10Avp column oven, and an SCL-10Avp controller. The molecular weights of the polymers were determined with reference to polystyrene standards in THF solution. Transition spectra were measured using a Hewlett-Packard UV-Vis spectrophotometer (Agilent 8453). Irradiation was conducted using an Ushio ultrahigh-pressure mercury arc through a combination of Optima color filters (WB360 and ZWB2) for 365-nm light (UV light). Photo-imaging was carried out using a Laser scanning instrument as previously reported[7].

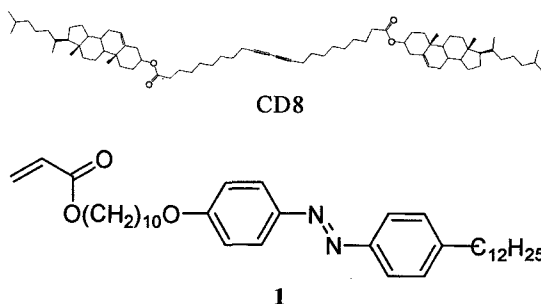


Fig. 1 Chemical structures of CD8 and 1

3. RESULTS AND DISCUSSION

3.1 Preparation of oligomers

Many compounds work well as a chain transfer agent for a free radical polymerization, but thiols are the most general. The sulfur-centered radical reinitiates another chain very efficiently. The result is a reduction of the molecular weight. Using more initiator is another way to decrease MW, but the reaction rate would increase

proportionally. Here we chose tDM for a chain transfer agent. GPC measurement for the reprecipitated materials confirmed formation of polymeric materials without monomeric component. The molecular weights based on polystyrene standard and yields are listed in Table 1. The molecular weight decreased with increasing amount of tDM, as expected. As the formula weight of a repeat unit (=monomer) is 576, polymerization degrees estimated from Mw are about 10, 14 and 26 for 2, 3 and 4. The first two compounds can be recognized as an oligomer. The dispersities (Mw/Mn) are small in all cases. The yield of these polymerizations changed from 65.8 to 26.6 % with increasing tDM.

Table I Preparation of oligomers

	Ratio of tDM/1	Yield (%)	Mw* (Mw/Mn**)
2	0.4	26.6	5500 (1.18)
3	0.2	32.1	8100 (1.17)
4	0.02	65.8	15300 (1.34)

*Mw; weight average of molecular weight; **Mn; number average of molecular weight.

3.2 Reflection band shift

Cholesteric glass films of CD8 have selective reflection of which center wavelength changing from 400 nm to 600 nm with decreasing the quenching temperature from 115 to 90 °C as shown in Fig 2. After addition of 5 wt% of 1-4 to CD8, the cholesteric glass was also formed. The center wavelength of reflection band for the films shifted to longer one than that of the pure CD8 when the quenching temperature is 90, 95 and 100 °C. At higher temperature, they show no shift. This shift is considered to be due to contribution of dynamic smectic-like domain appearing in CLC phase which is called cybotactic domain. In the case of the other additives to CD8, the relation between cybotactic contribution and longer shift of reflection has been discussed in the previous paper[8]. The mixture of monomeric compound gave the largest shift when the quenching temperature is 90°C. On quenching from 100 °C oligomer 3 gave the largest shift. The compound 4 having the largest molecular weight shows small shift on quenching from 90 and 95°C.

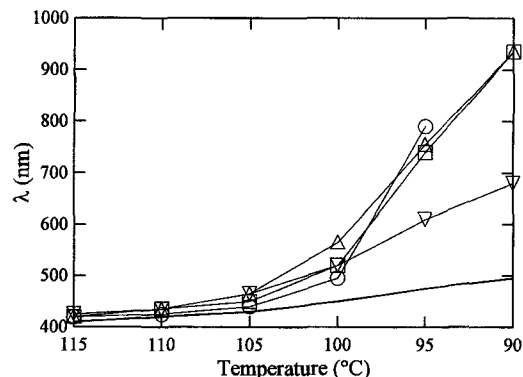


Fig. 2 Change in center wavelength (λ) of selective reflection for CD8 (solid line without markers) and for CD8 doped with 5wt% of 1(circle), 2(rectangle), 3(triangle) and 4(reverse triangle) as a function of quenching temperature.

Fig. 3 shows the concentration dependence of reflection band shift for each additive where the films are prepared by quenching from 95 °C. The shift increased with increasing concentration of additives but the relation is not linear. Excepting the case of the guest 4, the shift is enlarged more at higher concentration. Here we plotted shift values against the weight concentration, showing that quite low molar concentration of oligomers can induce large shift.

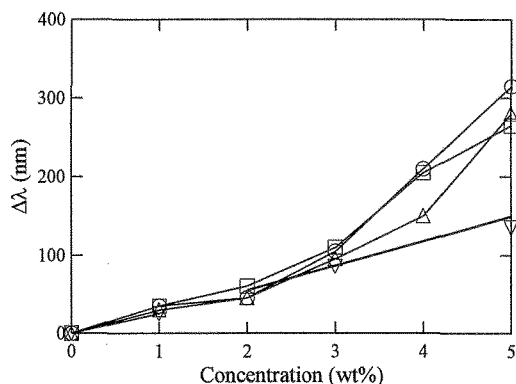


Fig. 3 Concentration dependence of reflection band shift ($\Delta\lambda$) which is estimated by subtraction from λ of CD8 with 1(circle), 2(rectangle), 3(triangle) and 4(reverse triangle) to λ of CD8. The films are prepared by quenching from 95 °C.

Irradiation of liquid crystal films containing 1-4 with UV light (366nm) induced reflection band shift to shorter wavelength. The shift is stopped upon sufficient irradiation (irradiation time; 30 seconds). We quenched these films and measured the spectra. Fig. 4 shows the center wavelength of reflection band of those films. The values are close to that of pure CD8. UV light (365nm) can be absorbed only by azobenzene moieties which can isomerize from trans to cis form by this light. The fact means that 1-4 with cis-form azobenzene have no ability to shift the reflection band.

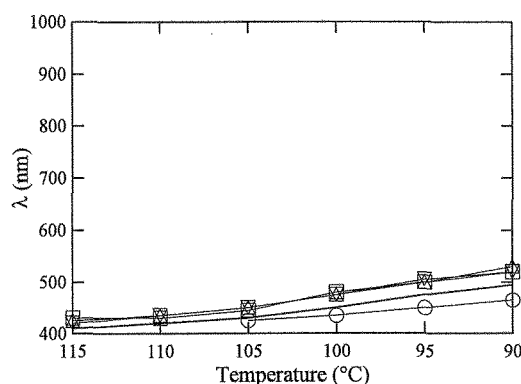


Fig. 2 Change in center wavelength (λ) of the reflection band for CD8 (solid line without markers) and for CD8 with 5wt% of 1(circle), 2(rectangle), 3(triangle) and 4(reverse triangle) irradiated with UV light (365 nm) as a function of quenching temperature.

3.3 Thermal stability of glassy film

The laser scan (325 nm) on the 1-4 containing CD8 films in a liquid crystalline state brings about a color

image. Images of queen were recorded on our samples. After fixing the image by quenching to glassy state, we heated the films to study the stability. Fig. 5 shows pictures of the films after heating for 30 min at different temperatures. After heating at 50 °C, the image was lost in the films of CD8 with 1. On the other hand, the image remains after heating at 75 °C in the films of CD8 with 3. It became turbid on the heating at 80 °C and was completely lost on heating at 85 °C. The difference in stability must be related to glass transition temperature. CD8 has glass transition temperature around 80 °C[2]. The oligomeric additives will not decrease the glass transition temperature after the mixing.

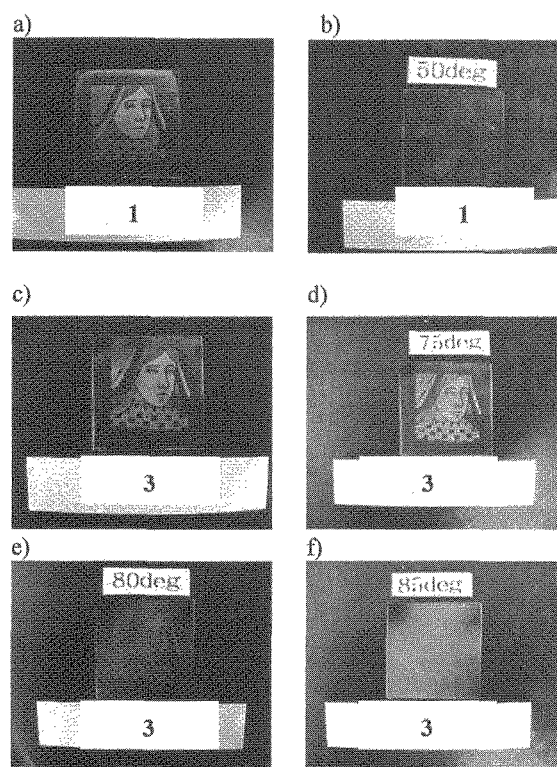


Fig.5 Pictures of images recorded on the films of CD8 with 1 before (a) and after heating for 30 min at 50 °C (b) and the films of CD8 with 3 before (c) and after heating at 75 (d), 80 (e) and 85 °C (f).

4. CONCLUSION

Oligomeric compounds consisting of photoreactive azobenzene-containing acrylates with different molecular weight are successively prepared using chain transfer agent. The molecular weight is dependent on amount of the agent. The addition of the resulted oligomer to CD8 induces a large reflection band shift comparative to addition of monomeric compound. The reflection band shift depends on the molecular weight of oligomers. The shift of the cholesteric pitch can change to zero in response to irradiation with UV light. A glassy state of oligomer-containing CD8 made by rapid cooling from liquid crystalline temperature is more stable than that doped with the monomeric compound.

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