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Photoinduced Chirality in Thin Films of Achiral Polymer Liquid Crystals Containing Azobenzene Chromophores

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ABSTRACT: Circular dichroism and circular birefringence were induced in thin films of achiral polymer liquid crystals containing 7 or 15 mol % azobenzene chromophores by irradiation with circularly polarized light (CPL). Circular dichroism was observed not only for the azobenzene moieties but also for the nonphotoactive mesogens, cyanobiphenyl groups, due to a cooperative motion. CPL with opposite handedness produces enantiomeric structures, and a chiroptical switch can be achieved by alternating irradiation with left and right CPL. The level of photoinduced chirality depends on the incorporation methods (doped or chemically bound) of the azobenzene chromophores, the amount of azobenzene units, and the sample temperature. The photoinduced circular dichroism can be erased by heating the films above the clearing temperatures or by annealing the films in the liquid-crystalline phase.

Introduction

Photochemical modulation of chiroptical properties of organic materials has been the subject of intensive research due to the potential applications of these materials in optical switching and reversible optical storage.[1] For example, polypeptides,[2−4] polyisocyanates,[5−8] and polymethacrylates[9−12] functionalized with chromophores (such as azobenzene chromophores) and chiral groups have been investigated. The photochromic effect can result in changes of the chirooptical properties (circular dichroism and optical activity) of the polymers. Reversible switching of liquid-crystalline materials between twisted and nontwisted phases by photochemical modification of the chiral dopant molecules was studied as well.[13−16]

Recently, Nikolova et al. reported the appearance of significant photoinduced optical activity in films of liquid-crystalline polyesters with azobenzene mesogens in the side chain and in films of prealigned amorphous side-chain azobenzene polymer.[17−20] In contrast to the studies mentioned above, no chiral groups are required in these systems. The only source of chirality is the irradiating light, a circularly polarized laser beam. It was thought that the light-induced reorientation of the azobenzene chromophores as well as a transfer of angular momentum from the circularly polarized light (CPL) to the azobenzenes produced a new ordered chiral phase. More recently, photoinduced circular dichroism and chiroptical switching in thin films of an achiral donor−acceptor azobenzene liquid-crystalline polymethacrylate (p**4MAN**) were investigated in our lab.[21] The formation of a supramolecular helical arrangement of smectic domains after irradiation with CPL was proposed. We also observed a circular Bragg reflection in thin films of a non-donor−acceptor azobenzene liquid-crystalline polymer (**PMAB6**) after irradiation of circularly polarized light.[22]

It is well-known that linearly polarized light can induce large linear birefringence in films of liquid-crystalline and amorphous polymers containing azobenzene groups.[23,24] One of the most interesting observations was that if only a low content of azobenzene groups was present, the nonphotoactive mesogens underwent reorientation together with the azobenzene groups, thus amplifying the effect over the limits given by the concentration of the azobenzene groups.[25,26] This is due to a cooperative motion existing between the photoactive and the inert groups. In this study, we present photoinduced chirality in thin films of liquid-crystalline copolymers with a low content of azobenzene units, and in films of a polymer liquid crystal doped with a low-molecular-weight azo dye, as comparison. The cooperative motion of the nonphotoactive mesogens, cyanobiphenyl groups, on irradiation of CPL, was investigated with circular dichroism (CD) spectroscopy, which allows identification of the circular dichroism from different functional groups. The overall optical activity was detected by measuring the optical rotation at the sodium D line.

Experimental Section

Figure 1 shows structure of the polymer liquid crystals and the low-molecular-weight azo dye dispersed red 1 (DR1) used in this study. Monomers, 4′-[(11-(methacryloyloxy)undecyl)-oxy]-4-cyanobiphenyl and 4′-[[(6-(methacryloyloxy)hexyl)-methyl]amino]-4-nitroazobenzene, were prepared using the procedure similar to the literature.[27,28] DR1 was received from Aldrich Chemical Co. and used without further purification. Polymerization was performed in dry DMF under vacuum at 60 °C for 2 days with 1−3 mol % AIBN as an initiator. Polymers were isolated by precipitation into excess methanol, purified by reprecipitation from THF solution into methanol, and finally dried to a constant weight.

The results of the characterization of the polymer liquid crystals are summarized in Table 1. Differential scanning calorimetry (DSC) measurements were done on a Perkin-Elmer DSC-6 under nitrogen atmosphere using a heating rate of 10 °C/min. The liquid-crystalline phase was determined with a polarizing microscope (Nikon E 600) equipped with a hot stage. Gel permeation chromatography (GPC) analysis was performed on a Water Associates liquid chromatograph equipped with a model R401 differential refractometer using

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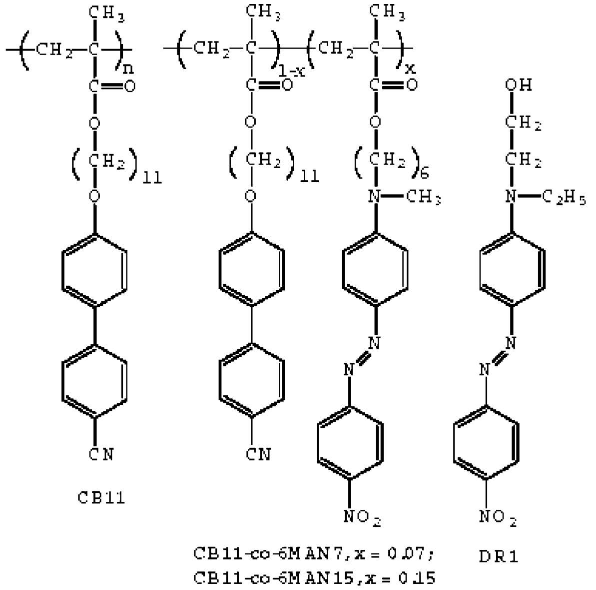

Figure 1. Structure and abbreviations of the polymer liquid crystals and azo dye used in this study.

Table 1. Molecular Weights and Thermotropic Properties of the Polymeric Systems[a]

sample	M_n	M_w/M_n	phase transition temperature (°C)	ΔH (J/g)
CB11	65 000	4.5	G 47 Sm 124 I	9.4
CB11-m-DR1			G 45 Sm 118 I	7.0
CB11-*co*-6MAN7	53 000	2.6	G 39 Sm 116 I	9.8
CB11-*co*-6MAN15	52 000	4.1	G 42 Sm 113 I	7.3

[a] M_n, number-average molecular weight; M_w, weight-average molecular weight; G, glass; Sm, smectic; I, isotropic; ΔH, change in enthalpy of Sm−I phase transition.

polystyrene as standards. The eluent was THF. UV−vis spectra were recorded on a Hewlett-Packard UV−vis spectrometer at room temperature. The content of the azobenzene units in the copolymers was calculated from the absorbance of the azobenzene group on the basis of the molar extinction coefficient.

Films were prepared by spin-coating a solution of the polymers in THF onto clean glass or fused quartz microscope slides, and their thickness was determined with a Dektak II profilometer. Samples were heated above the clearing temperature and then annealed at a temperature just below the smectic−isotropic phase transition temperature to yield a polydomain phase. Irradiation was performed at room temperature with argon ion laser beam (488 nm) that was circularly polarized. The intensity of the irradiation light was 65 or 120 mW/cm^2. Circular dichroism was measured with a Jasco J-715 spectropolarimeter. Generally, the virgin polymer films were irradiated with right CPL for 30 min at first. After irradiation, CD spectra were recorded. Then the irradiated films were exposed to opposite left CPL for 45 min. After that, CD spectra were measured again. Optical activity was measured with a Perkin-Elmer 241 polarimeter (589 nm) at room temperature.

Results and Discussion

The samples used in this study include a liquid-crystalline homopolymer **CB11**, two liquid-crystalline copolymers containing 7 and 15 mol % azobenzene units, and a mixture of **CB11** with 5 wt % (~7 mol % based on the repeating units) DR1. The azobenzene chromophore in the copolymers has a similar chemical structure to DR1. Figure 2 shows UV−vis spectra of the polymeric systems. The absorbance centered at 300 nm is due to the electronic absorption of the cyanobiphenyl groups, while the absorbance located at 500 nm for the copolymers and the mixture is assigned to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the donor−acceptor azobenzene chromophores. It is well-known that **CB11** shows a typical smectic phase.[27] The mixture and the copolymers exhibited a smectic phase as well. We observed typical focal conic textures under polarizing microscope. The relatively high phase transition enthalpy as shown in Table 1 also reveals a smectic phase characteristic of the samples.

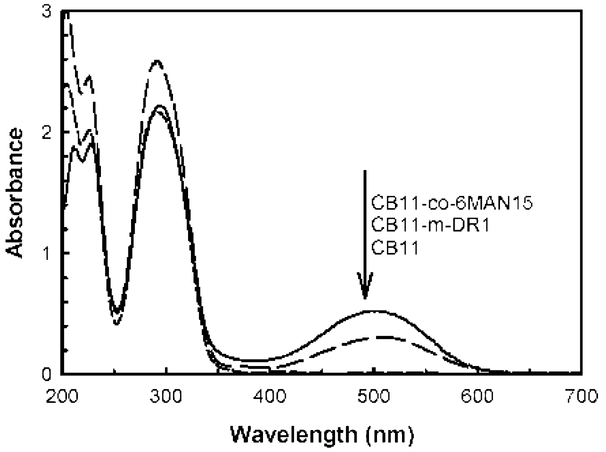

Figure 2. Absorption spectra of **CB11-*co*-6MAN15** (solid line), **CB11-m-DR1** (long dash), and **CB11** (short dash) fresh films.

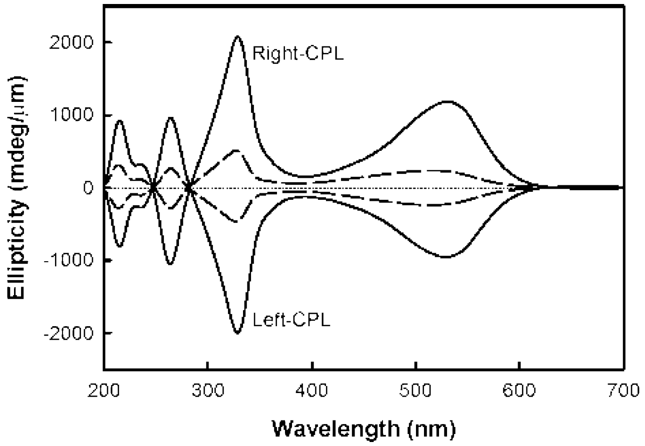

Figure 3. CD spectra of thin films of the copolymers recorded after irradiation with right and left CPL: solid line, **CB11-*co*-6MAN15**; dashed line, **CB11-*co*-6MAN7**.

First of all, photoinduced chirality was investigated in thin films of **CB11**. Two samples were exposed to right and left CPL at room temperature for 30 min. CD spectra were measured before and after irradiation. The curves observed after irradiation were exactly the same as those before irradiation. No circular dichroism was induced in the films of **CB11** by irradiation with CPL at 488 nm.

Upon irradiation with CPL, the initially achiral films of the copolymers **CB11-*co*-6MAN7** and **CB11-*co*-6MAN15** become chiral as observed by CD spectroscopy (Figure 3). The broad CD band at around 500 nm when compared to the absorption spectrum can be assigned to the $\pi-\pi^*$ transition of the azobenzene chromophore. The $n-\pi^*$ transition is also in this spectral region; it however has a much lower absorption coefficient compared with the homopolymer p**4MAN**, which exhibited a complete Cotton effect where CD bands reverse sign

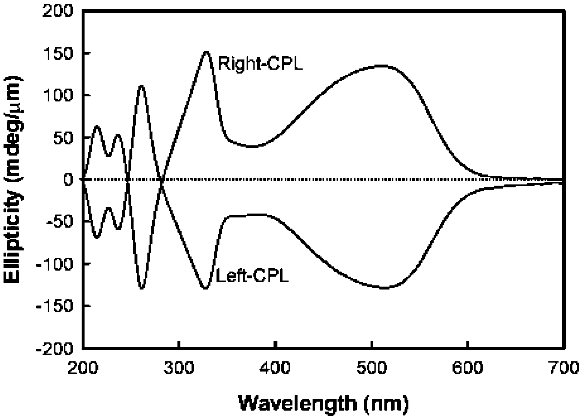

Figure 4. CD spectra of thin film of **CB11-m-DR1** recorded after irradiation with right and left CPL.

near the wavelength of the dichroic absorption maximum.[21] (The Cotton effect for circularly polarized light is analogous to spectrum of the refractive index of a substance when the spectrum includes an absorption maximum for linearly polarized light.) In the present case, the complete reversal is not observed for the azobenzene chromophore because of the large CD bands at 300 nm. These are related to the electronic absorption of the cyanobiphenyl groups; two CD bands of opposite sign, which are located at about 325 and 265 nm, were observed with a crossover point at about 280 nm. The ellipticity value of the band at 325 nm is almost twice of that at 265 nm, indicating a split CD Cotton effect originating from the electronic interactions between neighboring cyanobiphenyl mesogens. This kind of content-dependent Cotton effect was observed in polymethacrylate with azobenzene chromophore in the side chain in solution.[29] The CD bands at lower wavelength (235 and 215 nm) are due to the electronic absorption of the ester groups of the polymethacrylate.[30,31]

Chirality was induced not only for the azobenzene chromophore but also for the nonphotoactive mesogens, which reveals that the cooperative motion effect exists in photoinduced chirality process as well. A relatively low content of the azobenzene chromophore can induce chirality of the nonphotoactive cyanobiphenyl mesogens. This kind of cooperative effect is a general phenomenon in photoinduced linear birefringence by linearly polarized light.[24,25] When the chiral films produced by right CPL were exposed to opposite left CPL for 45 min, similar to the azobenzene homopolymer (p**4MAN**), virtually complete mirror images of the CD spectra induced by right CPL were observed. This indicated that (1) optical erasing of the induced circular anisotropy is possible by irradiation with CPL of opposite handedness, (2) the CPL with opposite handedness produced enantiomeric supramolecular structures, and (3) a chiroptical switching can be realized by alternating irradiation with right and left CPL. In addition, the level of photoinduced CD depends on the azobenzene content. Much higher ellipticity was detected for **CB11-*co*-6MAN15** with 15 mol % azobenzene units. After irradiation, the film was checked under a polarizing microscope. Unlike the homopolymer p**4MAN**, no or little change was observed for the film textures.

For comparison, the photoinduced chirality in thin film of **CB11** and DR1 mixture was explored. Figure 4 shows the CD spectra of the mixture **CB11-m-DR1**. Similar to the copolymers, the CD spectra induced by opposite CPL are mirror images of each other, and circular dichroism was achieved not only for the azobenzene moieties but also for the inert cyanobiphenyl groups. However, the level of photoinduced ellipticity in thin film of the mixture was lower for both the azobenzene moieties and the inert cyanobiphenyl mesogens in comparison to the copolymer with nearly the same contents of azobenzene chromophore. Furthermore, the level of the photoinduced CD in film of the mixture is almost the same for both the azobenzene groups and the cyanobiphenyl mesogens, although the polymer film has much higher contents of the cyanobiphenyl groups. In contrast, the level of photoinduced CD for cyanobiphenyl groups is much higher than that for azobenzene moieties in films of the copolymers. These results revealed that photoinduced chirality, as well as the cooperative motion, is more efficient in copolymers.

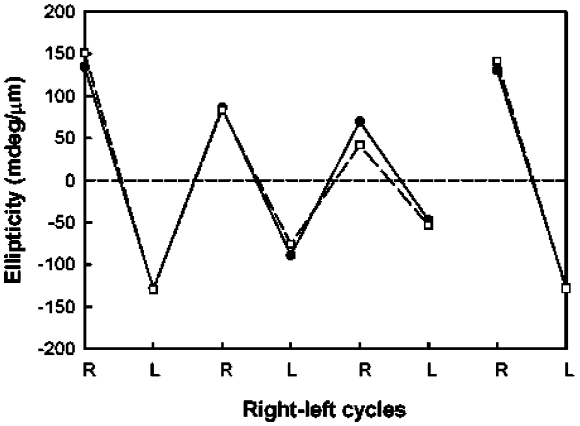

Figure 5. Optical switching of the CD at 328 nm (open squares) for cyanobiphenyl and 510 nm (full circles) for DR1 upon alternating irradiation with right and left CPL.

Chiroptical switching was explored in thin film of the mixture. Figure 5 shows the ellipticity at 328 nm for cyanobiphenyl and 510 nm for DR1 as a function of alternating irradiation with right and left CPL. Similar to the homopolymer, a chiroptical switching between the two enantiomeric supramolecular structures is possible only by alternating irradiation with left and right CPL. However, the CD for both azobenzene chromophore and cyanobiphenyl groups gradually decreases with the increase of irradiation time. Nevertheless, the initial value of the CD can be restored after thermal treatment of the sample. (The sample was heated above the clearing temperature and then annealed a few degrees below the clearing temperature to yield the polydomain state.) The reason for the apparent beaching may be due to the out-of-plane orientation of the azo dye by irradiation with CPL. Once the azobenzene groups were aligned in the propagation direction of the irradiation light, they become inactive.[32] Thermal treatment randomizes the photoinduced out-of-plane orientation. Photobleaching was observed in the thin film of the mixture after irradiation with left and right CPL for several cycles. Unlike the mixture, the copolymers show lower fatigue on alternating irradiation of right and left CPL. A little decrease of the ellipticity was observed after several cycles.

The photoinduced chirality is stable for months at room temperature. However, the induced anisotropy can be erased, either optically with opposite CPL, as mentioned above, or by heating. Heating the film above the clearing temperature of the polymer liquid crystal can erase the photoinduced CD in the mixture. Annealing the film in the liquid-crystalline phase for 1 h also

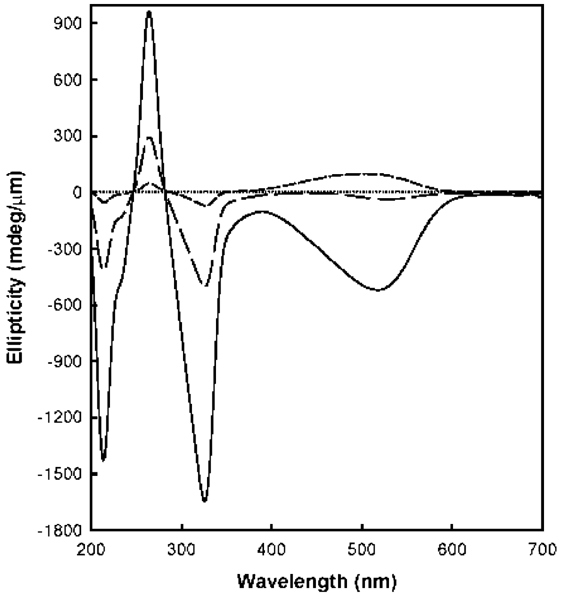

Figure 6. CD spectra of **CB11-*co*-6MAN7** recorded after irradiation a hot sample (80 °C) with left CPL for 30 min (solid line). The sample was allowed to cool to room temperature during irradiation. After that, the sample was irradiated with right CPL at room temperature for 40 min (long dashed) and 120 min (short dashed).

erased the induced CD. This indicated that the photoinduced chiral phase is not a thermally stable phase.

The consequence of photoinducing chirality at a higher temperature was investigated. A hot (80 °C) film of **CB11-*co*-6MAN7** was irradiated with left CPL for 30 min. During irradiation, the sample was allowed to cool to room temperature, which is lower than the T_g of the polymer. The sample was above T_g for only a few minutes. The CD spectrum recorded after irradiation is shown in Figure 6. The ellipticities obtained for both the azobenzene moieties and the inert cyanobiphenyl groups are much higher than those achieved at room temperature (Figure 3). The photoinduced chirality and the cooperative motion are more efficient when irradiation was performed in the liquid-crystalline phase. The cooperative motion is considered as the dipole−dipole interaction in amorphous polymers and in liquid-crystalline polymers below T_g.[33] When experiments were performed in liquid-crystalline phase, in addition to the dipolar interaction, cooperative motion of mesogens due to similar molecular shape should be taken into account. Although the photoinduced chiral order structure is not stable above T_g, cooling the sample below T_g could freeze the chirality induced in the liquid-crystalline phase, and it can be maintained for a long time.

When the chiral film was exposed to opposite right CPL for 45 min at room temperature, unlike the results demonstrated above, we could not obtain the complete mirror image of the CD spectrum generated by left CPL. The ellipticity for azobenzene groups was almost optically erased, while that for cyanobiphenyl groups still showed the negative sign although the value decreased remarkably. On continuous irradiation of right CPL for 2 h, ellipticity of opposite sign was observed for the azobenzene groups. The level of the ellipticity for cyanobiphenyl decreased again. However, it shows the same sign as the ellipticity induced by left CPL. Large CD induced in liquid-crystalline phase could not be totally eliminated by irradiation with opposite CPL at room temperature. The copolymer shows more efficient cooperative motion at the liquid-crystalline phase; however, the orientation of nonphotoactive mesogens that are not in close proximity to the azobenzene chromophore cannot be changed by irradiation with opposite CPL at room temperature. Only the azobenzene chromophores and the neighboring cyanobiphenyl mesogens switched into the opposite chiral structure. Therefore, the enantiomeric structures exist in the thin film at the same time.

Table 2. Optical Rotation of the Polymer Liquid Crystals after Irradiation with CPL

sample	left	right
CB11-*m*-DR1	−2300	+1900
CB11-*co*-6MAN7	−3100	+3400
CB11-*co*-6MAN15	−5000	+5400

Further confirmation of the photoinduced chirality was obtained by optical rotation measurements. Thick films (∼1 μm) were used in order to obtain high values. The films were irradiated with right and left circularly polarized laser beams (120 mW/cm^2) for 30 min. Table 2 lists the optical rotation of the polymer liquid crystals at the sodium D line. Opposite signs were observed due to the enantiomeric supramolecular structures induced by opposite CPL. Generally, the values obtained in these systems are much lower than those observed in azobenzene homopolymer, **p4MAN**,[21] estimated to be about 20 000 deg/cm. This is because (1) the copolymers and the mixture have a lower alignment efficiency and (2) the polymeric systems have lower mesogenic contents (∼47 wt % in our case, 64 wt % in **p4MAN**). Similar to the CD, the copolymers have higher optical activity than the **CB11-m-DR1** mixture, and the optical activity increased with the increased amount of azobenzene units. The polymeric systems show a very low absorbance at 589 nm. Therefore, by ignoring the contribution of circular dichroism to the optical rotation, we can estimate the circular birefringence using the following equation:

$$\phi = 180t\Delta n_{\mathrm{cir}}/\lambda$$

where Δn_{cir} represents the photoinduced circular birefringence, ϕ is the optical rotation, t is the thickness of the sample, and λ is the wavelength of the probe light. The circular birefringence calculated from the optical rotation at 589 nm is about 0.65×10^{-3}, 1.0×10^{-3}, and 1.6×10^{-3} for **CB11-m-DR1**, **CB11-*co*-6MAN7**, and **CB11-*co*-6MAN15**, respectively. The values are almost 1 order of magnitude lower than those reported in the literature.[17]

Conclusions

We have demonstrated that circular dichroism and optical activity were induced in thin films of achiral polymer liquid crystals with low content of azobenzene chromophores by irradiation with CPL. Circular anisotropy was observed not only for the azobenzene chromophores but also for the nonphotoactive cyanobiphenyl mesogens due to a cooperative motion, although the contents of azobenzene chromophores are as low as 7 mol %. The photoinduced circular dichroism can be erased by heating the films above the clearing temperature of the polymer liquid crystals or by annealing the films in the liquid-crystalline phase. Compared with the mixture, photoinduced chirality and the cooperative motion are more efficient in the copolymers. The efficiency depends on the content of azobenzene chromophore and on the sample temperature.

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