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Photoinduced chirality in achiral liquid crystalline polymethacrylates containing bisazobenzene and azobenzene chromophores

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Abstract

One new liquid crystalline polymer containing bisazobenzene, poly[4-{(2-methacryloyloxyethyl)oxy}-4′-(4-nitrophenylazo)azobenzene] (PM2BAN), and two liquid crystalline polymers containing azobenzenes with spacers of two and six methylene units, poly[(4-(4′-nitrophenylazo)phenyloxy)*x*-methylene methacrylate] (PM*x*AN, $x = 2, 6$), were synthesized and characterized. The level and rate of photoinduced chirality were studied in films of the achiral polymers by irradiation with one handed circularly polarized light (CPL) at 442 nm. The results of circular dichroism (CD) suggest that left-CPL induces left helical arrangements of the polymers and right-CPL reverses the resulting arrangements into right helices. Photoinduced chirality in film of PM2BAN is increased with the increase of irradiation time. However, the level and rate of photoinduced chirality in film of PM2BAN are lower than those in films of PM*x*AN ($x = 2, 6$) at similar irradiation time. Compared with PM2AN, photoinduced CD values are higher in PM6AN. The results are discussed in terms of interactions between azobenzene chromophores and circularly polarized light.

Keywords: Bisazobenzene-based polymer; Helical arrangement; Liquid crystalline; Photoinduced chirality; Azobenzene chromophore

1. Introduction

The induction of helical polymers has been the subject of intensive research due to the potential application of these materials in chiroptical switching and reversible optical storage [1–4]. Optically active polymers containing chiral groups and azobenzene chromophores show well-pronounced CD signals in the region of the absorption of azobenzene chromophores, demonstrating that the chiral center induces predominant helical arrangements for polymers both in film and in solution [5]. Moreover, helical arrangements of one sense can be presented in polymers without chiral moieties or chiral additives through helix-sense-selective polymerization [6]. Optically active helical polymers without chiral groups or chiral additives would be useful to clarify the relation between the helical structure and the chiroptical properties.

Recently, Nickolova et al. reported for the first time that large circular anisotropy was induced in films of achiral liquid crystalline azopolymers by irradiation with one handed CPL [7]. It was believed that liquid crystallinity was an essential factor for the polymers to exhibit such behavior. Iftime et al. reported a reversible chiroptical switch was induced between two chiral arrangements in films of achial liquid crystalline polymers by irradiation with opposite handed CPL [8]. In copolymers, circular dichroism was induced not only for azobenzene chromophores but also for nonphotoactive mesogens due to cooperative motion of side chains [9]. It was believed that a new chiral ordered arrangement could be produced by the rotation of the azobenzene chromophores induced by CPL as well as the transfer of angular momentum from the CPL to the azobenzenes [8,10,11]. Moreover, Ivanov et al. demonstrated that chirality could be photoinduced in achiral amorphous azopolymers after they were irradiated with LPL [12]. More recently, Kim et al.

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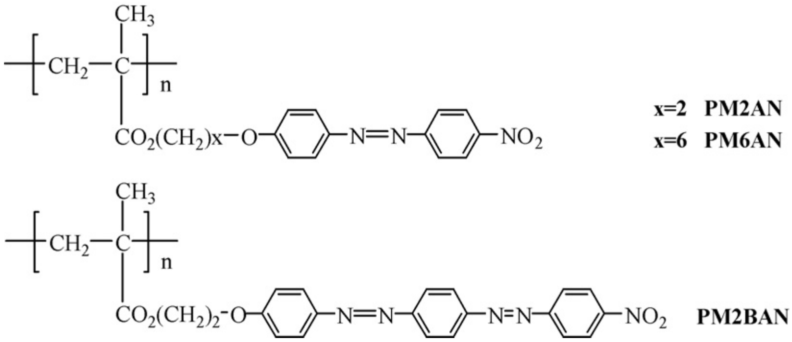


Scheme 1. Chemical structure and abbreviations of the polymers in this study.

reported that chirality could be induced in amorphous azopolymers by irradiation with one handed elliptically polarized light (EPL) [13]. However no chirality was induced in film of amorphous azopolymers by irradiation with CPL [14]. Nikolova et al. reported that photoinduced chirality was related to the rotation of the azimuth of EPL passing through azopolymers. CPL can be changed into EPL by the presence of liquid crystalline polymers due to birefringence [15].

It is shown that the level of photoinduced birefringence depends strongly on the type and size of azobenzene groups [16]. Bisazobenzene-based polymers are distinguished for their high anisotropy of molecules that can lead to large photoinduced ordered arrangements when compared to azobenzene-based polymers. The photoinduced birefringence per azobenzene structure in bisazobenzene-based polymers was five times larger than that in azobenzene-based polymers [16]. And photoinduced birefringence in bisazobenzene polymers was more stable than that in azobenzene polymers.

Recently, there has been a growing interest in the optical properties of bisazobenzene-based polymers [17–21]. In this paper, we report the synthesis and photoinduced chirality of achiral polymer (PM2BAN) containing bisazobenzene chromophore. To the best of our knowledge, no study concerning photoinduced chirality in bisazobenzene-based polymers was reported now. For comparison, photoinduced chirality in azobenzene-containing polymers (PM2AN and PM6AN) with different spacers was investigated. The structures of the synthetic polymers are shown in Scheme 1. The chiroptical properties of the polymers in films are investigated in detail by CD spectroscopy.

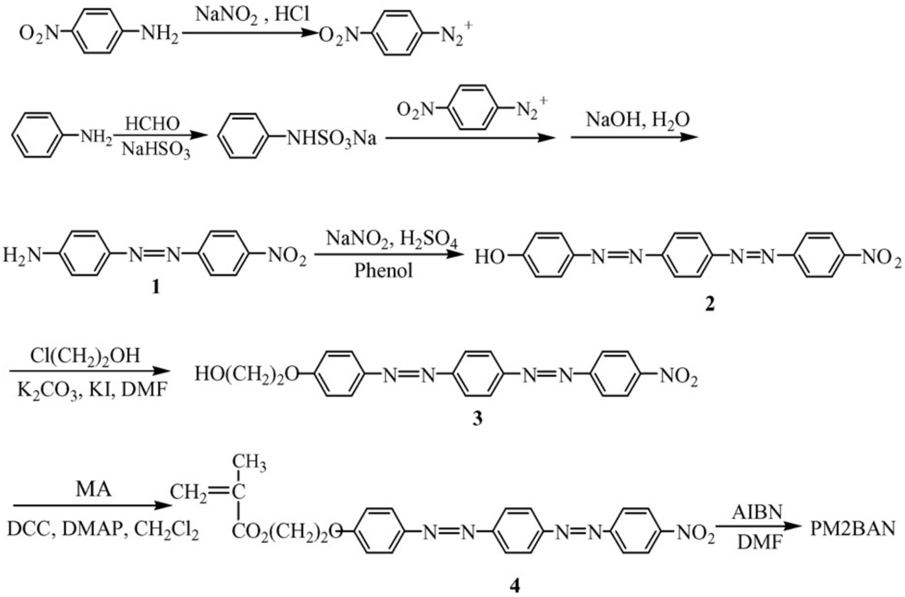
2. Experimental

2.1. Materials

Methacrylic acid, dichloromethane and DMF were purified before use. 6-Chloro-1-hexanol (Aldrich) and 2-chloroethanol were used without further purification. AIBN was crystallized from ethanol before use. Other solvents and reagents were used as received.

2.2. Synthesis of bisazobenzene-based monomer (M2BAN)

The synthetic route for M2BAN is shown in Scheme 2.



Scheme 2. Synthetic route of PM2BAN.

2.2.1. *4-Amino-4′-nitroazobenzene (**1**)*

20.7 g of 4-nitroaniline was dissolved in a solution of 37.5 ml of concentrated hydrochloric acid and 150 ml of water. The mixture was cooled to 0 °C in an ice-water bath, then a solution of 10.3 g of sodium nitrite in 50 ml of water was added dropwise. The resultant solution of diazonium salt was stirred for 30 min at 0–3 °C. Another solution of 21.7 g of $NaHSO_3$ dissolved in 5.3 g of formaldehyde and 40 ml of water was stirred for 30 min at 50 °C. Then the solution was heated to 60 °C and 14.0 g of aniline was added. After cooled to 0 °C, the resultant solution was added to a solution of 100 g of sodium acetate in 500 ml of water. The above solution of diazonium salt was added into this solution within 30 min. The reaction mixture was stirred at room temperature for 8 h. The precipitate was collected by vacuum filtration and washed with water. The crude product was added to a solution of 13.5 g of sodium hydroxide in 13.5 ml of water. The reaction mixture was refluxed for 2 h. The resultant solution was neutralized to alkalescence by adding 5% HCl. The precipitate was collected by vacuum filtration and recrystallized from DMF/H_2O (1/1, v/v). Compound **1** was obtained as crimson crystals. Yield: 79%, mp: 230–233 °C. IR (KBr pellets, υ in cm^{-1}) υ: 3403(ν_{NH}), 1605, 1587, 1505, 1462($\nu_{C=C}$, Ar).

2.2.2. *4-Hydroxy-4′-(4-nitrophenylazo)azobenzene (**2**)*

24.2 g of 4-amino-4′-nitroazobenzene was dissolved in a solution of 16.3 ml of concentrated sulfuric acid in 300 ml of water, then the mixture was stirred for 10 h at 70 °C. The reaction mixture was cooled to 0 °C, and then 6.9 g of sodium nitrite in 50 ml of water was added slowly. The resultant solution was stirred for 30 min at 0 °C and for an additional 4 h at 25 °C. After cooled to 0 °C, a solution of 9.4 g of phenol and 4.0 g of sodium hydroxide in 50 ml of water was added slowly. The resultant solution was stirred for 10 h at 25 °C. The precipitate was collected by vacuum filtration and recrystallized from DMF/H_2O (1/1, v/v). Compound **2** was obtained as mahogany solid. Yield: 84%, mp: 169–171 °C. IR (KBr pellets, υ in cm^{-1}) υ: 3504(ν_{OH}), 1600, 1588, 1500, 1461 ($\nu_{C=C}$, Ar).

2.2.3. *4-Hydroxyethyloxy-4′-(4-nitrophenylazo) azobenzene (**3**)*

To a mixture of 6.94 g of 2, 2.76 g of potassium carbonate, 0.03 g of potassium iodide (as catalyst) and 70 ml of DMF, a solution of 2.45 g of 2-chloroethanol in 10 ml of freshly distilled DMF was added dropwise. The resultant mixture was stirred for 72 h at 120 °C. Then the solution was cooled to room temperature, poured into 500 ml of water. The precipitate was filtered off and recrystallized from DMF/H_2O (1/1, v/v). Compound **3** was obtained as brown solid. Yield: 70%, mp: 131–133 °C. IR (KBr pellets, υ in cm^{-1}) υ: 3504(ν_{OH}), 2925(ν_{CH}), 1602, 1584, 1501, 1458($\nu_{C=C}$, Ar).

2.2.4. *4-{(2-Methacryloyloxyethyl)oxy}-4′-(4-nitrophenylazo)azobenzene (**4**)*

To a solution of 1.72 g of methacrylic acid, 1.22 g of 4-dimethylaminopyridine (DMAP), 3.91 g of compound **3** and 50 ml of dry CH_2Cl_2, a solution of 6.18 g of *N*,*N*′-dicyclohexylcarbodiimide (DCC) in 20 ml of dry CH_2Cl_2 was added dropwise at room temperature. The mixture was stirred for 72 h at 30 °C. The resulting mixture was filtered with suction and repeatedly washed with water, 1.2 M HCl, 5% aqueous $NaHCO_3$, H_2O, in that order. Dried over Na_2SO_4 and evaporated. Brown crude product was purified by column chromatography (silica gel, $CHCl_3$: MeOH = 9:1, v/v), followed by recrystallization from chloroform/methanol (9/1, v/v) to yield brown crystals. Yield: 60.5%, mp: 138–140 °C.

^1H NMR (in $CDCl_3$, δ in ppm) δ: 8.07(d, 4H, Ar), 7.98 and 7.93(dd, 4H, Ar), 7.52(d, 2H, Ar), 7.04(d, 2H, Ar), 6.16 and 5.60(ss, 2H, CH_2=C), 4.55 and 4.32(mm, 4H, $-OCH_2CH_2O-$), 1.96(s, 3H, $-C=C-CH_3-$). IR (KBr pellets, υ in cm^{-1}) υ: 2926(ν_{CH}), 1721($\nu_{C=O}$), 1633($\nu_{C=C}$), 1600, 1583, 1499, 1454($\nu_{C=C}$, Ar), 1250(ν_{C-O}).

2.3. *Polymerization*

Polymerization was carried out as follows: 0.5 g of monomer and 6 mol% of AIBN (relative to the monomer) were dissolved in 5 ml of freshly distilled DMF. The mixture were introduced into a glass tube, then submitted to four freeze–pump–thaw cycles under nitrogen and heated at 70 °C for 72 h. The polymerization mixture was added dropwise into 100 ml of methanol. The precipitates were filtrated, dissolved in 5 ml of THF, and reprecipitated into 100 ml of methanol. This procedure was repeated three times until the unreacted monomer was completely removed. Finally, the polymer was dried under vacuum at 50 °C to constant weight.

PM2BAN: ^1H NMR (in DMSO, δ in ppm) δ: 7.88–7.0(sss, 12H, Ar), 4.25 and 4.00(mm, 4H, $-OCH_2CH_2O-$), 1.68(s, 2H, CH_2-C-CH_3), 1.15(s, 3H, CH_2-C-CH_3). IR (KBr pellets, υ in cm^{-1}) υ: 2925(ν_{CH}), 1729($\nu_{C=O}$), 1597, 1584, 1499, 1454($\nu_{C=C}$, Ar), 1249(ν_{C-O}).

Polymers (PM*x*AN (x = 2, 6)) were synthesized according to the previous literature [22]. Properties of the synthetic polymers are reported in Table 1.

2.4. *Preparation of thin film*

Thin films (about 150–200 nm) were obtained by spin-coating solutions of the synthetic polymers in cyclopentanone (c = 0.02 g/ml) onto clean quartz slides and subsequently dried at 50 °C under vacuum for 2 days. Samples were heated above clearing temperature and then annealed at a temperature just below the LC-isotropic phase transition temperature to yield a polydomain phase.

Table 1
Properties of polymers in this study

Polymers	Conversion (%)	Mn ($\times 10^4$)[a]	PDI	Xn
PM2BAN	51	0.7	1.23	15
PM2AN	68	1.5	1.64	42
PM6AN	66	1.9	1.72	46

[a] Data come from GPC using THF as eluent.

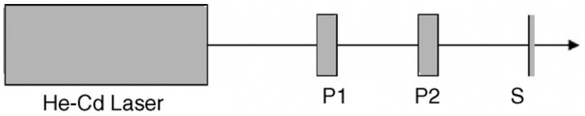


Fig. 1. Experimental setup for photoinduced chirality in the polymeric films. He–Cd laser: 442 nm; P1: Glan prism; P2: λ/4 waveplate; S: sample.

2.5. Measurements

The average molecular weights and polydispersity indices (PDI) of polymers were estimated by gel permeation chromatography (GPC) in THF on a Waters 150C GPC using polystyrene as standards. Phase transition temperatures were measured on a Perkin Pyris-1 DSC under nitrogen atmosphere (heating rate: 20 °C/min, cool rate: 100 °C/min). UV–vis spectra of films of polymers were recorded at room temperature on a Shimadzu UV-2401PC. Circular dichroism spectra were measured on a Jasco J-810 spectropolarimeter. Film thickness was determined with a Tencor Alpha-step 500 surface profilometer. All the polymeric films were irradiated with left CPL at 442 nm (360 mW/cm^2) at room temperature at first. After irradiation, CD spectra were recorded. Then the irradiated films were exposed to right CPL. The polarimetric setup used to investigate the photoinduced chirality in the films is shown in Fig. 1.

3. Results and discussion

3.1. Mesomorphic properties of the polymers

Phase transition temperatures were determined by DSC measurement. Fig. 2 displays the second DSC heating curves for the polymers. The DSC thermogram of PM2AN reveals a glass transition at 96.5 °C and a phase transition at 212.3 °C, respectively. Similar to PM2AN, a glass transition at 61.1 °C and a first-order transition at 160.6 °C are displayed in the DSC trace for PM6AN with longer spacer ($n = 6$). Lengthening the spacer from two to six methylene units reduces the glass transition temperature (T_g) about 35 °C, an effect often observed in side chain liquid crystalline polymers (SCLCP) [23], and which is due to the plasticization effect of longer alkyl spacer. The increased spacer in PM6AN can dilute the interactions between azobenzene chromophores, thus depressing the clearing temperature (T_i). Moreover, PM6AN with a longer spacer have a greater degree of freedom for the mesogens to move in the isotropic state and thus increasing entropy changes (ΔS), the result would be also a decrease of T_i due to T_i is determined by the ratio of enthalpy changes (ΔH) to ΔS [17]. PM2BAN exhibits three phase transitions at 166, 203 and 230 °C, respectively. It is known that the higher the length/diameter ratio of the bisazobenzene chromophore is, the higher the order parameter (as well as birefringence) will be. As a result, PM2BAN containing three-ring mesogens are more favored in a LC environment. Therefore the occurrence of LC phase is pronounced for PM2BAN containing two azobenzene groups. Compared with PMxAN ($x = 2, 6$), T_g and T_i are higher in PM2BAN. Such behavior can be explained as follows: the interactions between bisazobenzene groups are stronger than those between azobenzene groups, which restricted the intramolecular and intermolecular movements of chain segments as well as the conformational changes of the backbone. As a result, higher T_g was exhibited in PM2BAN with respect to PM2AN. Moreover, bisazobenzene mesogens are tend to exhibit higher ordered phase, which results in higher T_i.

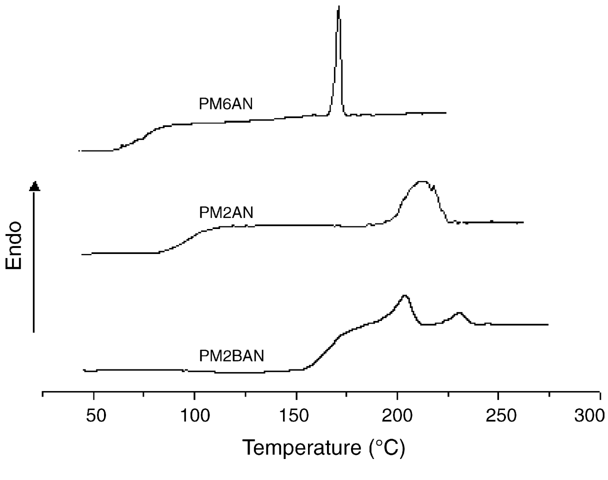


Fig. 2. The second scan DSC thermograms of PMxAN ($x = 2, 6$) and PM2BAN.

3.2. UV–vis spectra of polymers in films

The UV–vis spectra of the polymers (PM2AN, PM6AN and PM2BAN) in films prepared on quartz slides exhibit three absorption bands in 200–600 nm spectral region (Fig. 3), centered at about 460, 360 and 240 nm, respectively. The absorption bands located between 400 and 500 nm are related to the combined contributions of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition of the azobenzene chromophores. The absorption edge observed between 300 and 400 nm are related to the $\pi \rightarrow \pi^*$ electronic transitions of the azobenzene chromophores. The absorption bands located between 250 and 300 nm are due to the aromatic rings. It can be seen that PM6AN exhibits a maximum absorbance (λ_{max}) at shorter wavelength (362 nm) in compar-

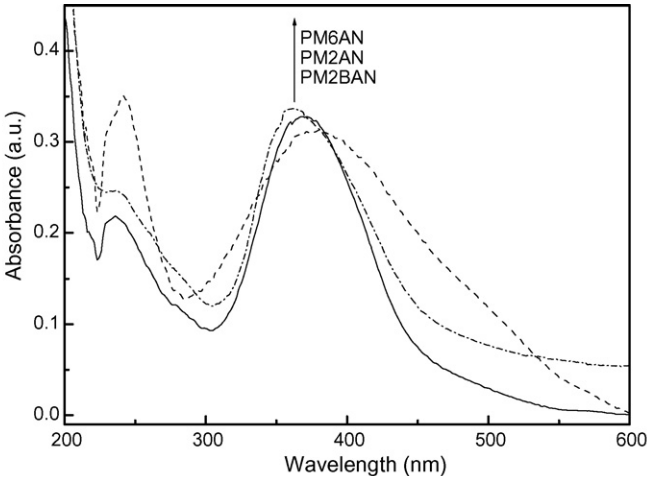


Fig. 3. UV–vis spectra of the polymers in films. PM6AN (dashed dotted line), PM2AN (solid line), PM2BAN (dashed line).

ison with PM2AN (370 nm). A blue-shift connected to the $\pi \rightarrow \pi^*$ transition band with respect to the spacer is attributed to the electrostatic dipole–dipole interactions between neighboring azobenzene chromophores [24–26]. PM2BAN exhibits λ_{max} at longer wavelength (380 nm) in comparison with PM2AN (362 nm). This is attributed to the larger conjugated system of the bisazobenzene chromophore that increases the π-electron delocalization and lowers the energy of the $\pi \rightarrow \pi^*$ transition.

3.3. Photoinduced chirality in films of polymers

Two films of PM2AN and PM6AN were irradiated with left-CPL at room temperature for 30 min. After irradiation, CD spectra were recorded. Upon irradiation with left-CPL, the initial achiral films of PM2AN and PM6AN become chiral as observed by CD spectra (Fig. 4, solid line). The asymmetric pairs of CD bands located at 415 and 520 nm with a crossover at 470 nm are observed not only for PM2AN but also for PM6AN. It can be assigned to a superposition of a split CD cotton effect due to $n \rightarrow \pi^*$ electronic transition of the azobenzene chromophore (in correlation with the UV–vis spectra) that caused by the cooperative dipolar interactions between the neighboring azobenzene chromophores. This is generally associated with the existence of an ordered helical arrangement with a prevailing handedness. Here, the photoinduced CD value at 518 nm for PM6AN is about 30 times larger than that for PM2AN. Furthermore, two negative CD bands located at about 315 and 273 nm, related to the $\pi \rightarrow \pi^*$ electronic transition are displayed in film of PM6AN. Results of CD spectra of PM2AN and PM6AN suggest that photoinduced helical arrangements of whole or at least some segments of the polymer backbone, are existed both in PM2AN film and in PM6AN film. The level of photoinduced chirality in film of PM6AN is higher than that in film of PM2AN. This indicates a more ordered helical arrangement with one prevailing handedness is induced in PM6AN than that in PM2AN. The spacer between main-chain and azobenzene chromophore affects the motion of mesogens. Compared with PM2AN, reorientation of azobenzene chromophores with directions perpendicular to the irradiation light in each layer is more efficient for PM6AN.

As shown in Fig. 4, when the previously irradiated films of PM2AN and PM6AN were irradiated with right-CPL at the same spot for 45 min, the CD spectra are virtually complete mirror images of each other both for PM2AN and for PM6AN. According to the chiral exciton coupling rules [8], this indicates that left-CPL induces left-handed arrangements in films of PM2AN and PM6AN, right-CPL erases the former left-handed arrangements at first and then induces arrangements with opposite sign.

For comparison, photoinduced chirality in film of PM2BAN with two azobenzene groups was explored. Fig. 5 shows the CD spectrum of PM2BAN in film. Similar to PMxAN ($x = 2$, 6), CPL with opposite handedness induced enantiomeric arrangements in PM2BAN film. Circular dichroism was obtained both for $n \rightarrow \pi^*$ electronic transition and for $\pi \rightarrow \pi^*$ electronic transition of azobenzene chromophores. However, the level and rate of photoinduced chirality in film of PM2BAN are much lower than those in film of PM6AN. This is related to the large size of bisazobenzene groups. The process of orientation of bisazobenzene chromophores perpendicular to the light polarization requires more *trans–cis–trans* cycles and more free volume than that of azobenzene chromophores. Thus the rate of photoinduced chirality is slower in bisazobenzene-based polymers than that in azobenzene-based polymers. However, the photoinduced chirality maybe more stable in PM2BAN than that in PM2AN based on the fact that, more thermal *cis–trans* isomerizations should be taking place in PM2BAN from an ordered state to a random state. Photoinduced chirality is stable in films of PM2AN, PM6AN and PM2BAN at room temperature. No decrease of CD value is observed in the irradiated films of PMxAN ($x = 2$, 6) and PM2BAN after a month.

The level of photoinduced chirality depends on the irradiation time. The level of photoinduced chirality was investigated in film of PM2BAN by irradiation with left-CPL for different time. CD spectra of PM2BAN at different irradiation times are shown in Fig. 6. By irradiation with left-CPL for 5 or 10 min,

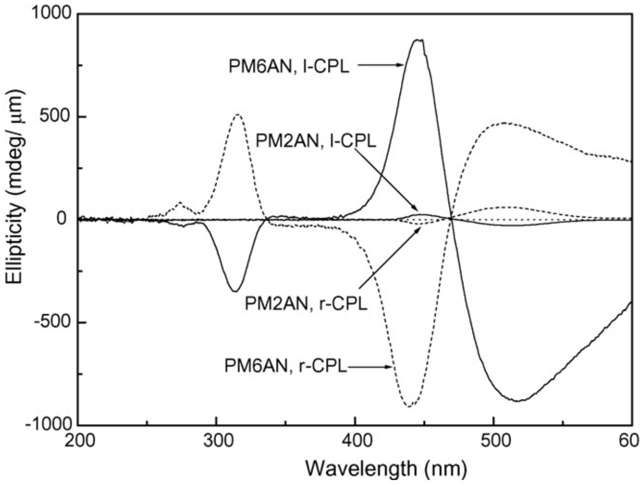


Fig. 4. CD spectra of PMxAN ($x = 2$, 6) in films. The films were irradiated with l-CPL at 442 nm for 30 min at first (solid line), and then irradiated with r-CPL at 442 for 45 min (dashed line).

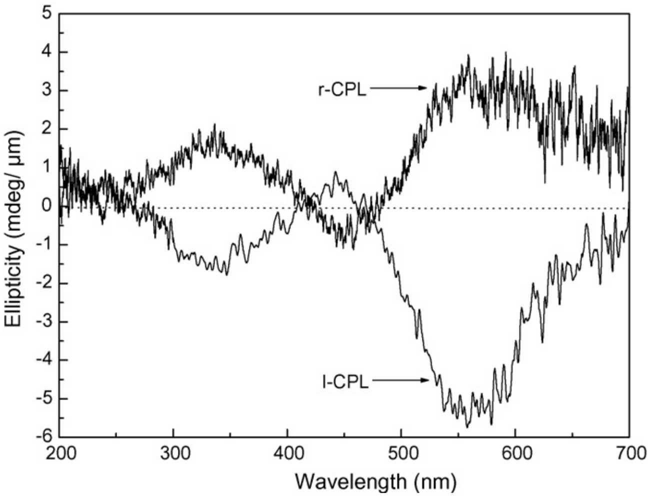


Fig. 5. CD spectrum of PM2BAN in film. The film was irradiated with l-CPL at 442 nm for 120 min at first (solid line), and then irradiated with r-CPL at 442 nm for 150 min (dashed line).

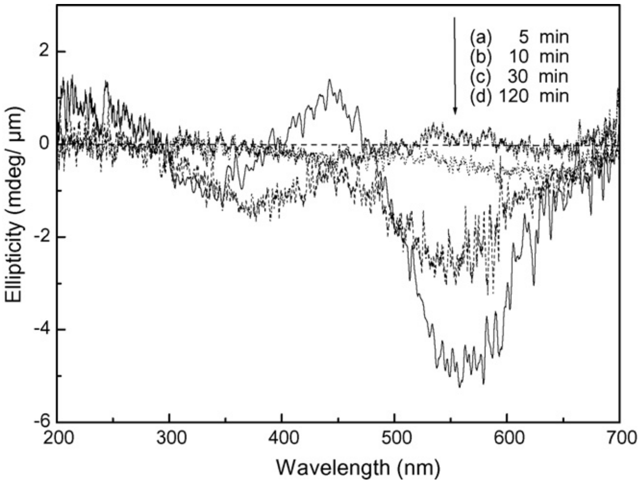


Fig. 6. CD spectra of film of PM2BAN at different irradiation times. The film was irradiated with l-CPL at 442 for (a) 5, (b) 10, (c) 30 and (d) 120 min.

no circular dichroism was obtained in film of PM2BAN. However, two negative CD bands are displayed in film of PM2BAN by irradiation with left-CPL for 30 min, indicating that a helical arrangement with one prevailing handedness was induced in PM2BAN film. A more ordered arrangement is induced in film of PM2BAN with prolonging the irradiation time from 30 to 120 min. A conclusion can be made that the level of photoinduced chirality in bisazobenzene-based polymeric film is increased with the increase of irradiation time.

As shown in Fig. 7a, it is considered that the film of azobenzene polymer can be divided into several layers. When the first layer was exposed to left-CPL, it would cause azobenzene chromophores to orient perpendicularly to the light polarization direction. Then the aligned azobenzene chromophores in the first layer would change the left-CPL into left elliptically polarized light (EPL). In the second layer, the azobenzene chromophores, upon absorbing the left-EPL, would reorient and then their dipole transition moments would be perpendicular to the long axis of the EPL. Thus the azimuth of the EPL to the next layer would change. In one word, the photoinduced helical arrangements are attributed to rotation of the azobenzene chromophores and rotation of the light as a result of the interactions between light and azobenzene chromophores. This stepwise procedure could be extended along the successive layers of the film. The polymer backbone could also move because it is linked to the azobenzene chromophores. As a result, the orientations of azobenzene chromophores and the optical axis of EPL in each layer are rotating in the same sense as the left-CPL, creating left helices in the azobenzene polymer films. When the handedness of the CPL was switched from left to right, as shown in Fig. 7b, the photoactive azobenzene chromophores in the first layer would reorient until their dipole transition moments are perpendicular to the right-CPL. Similar to the procedure of pho-

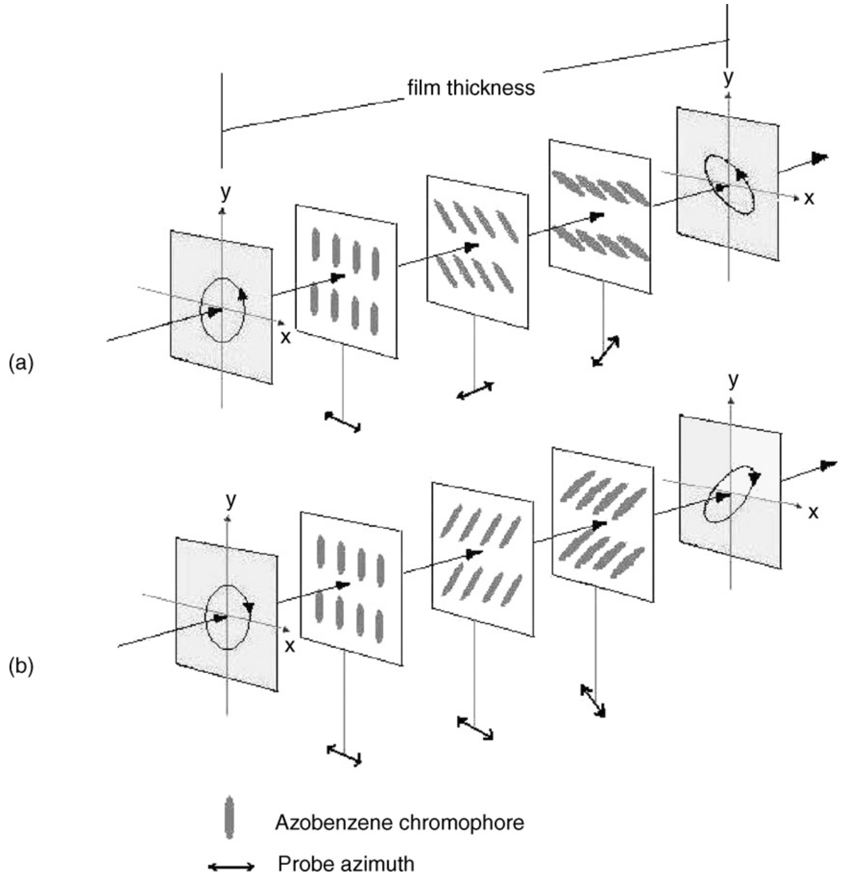


Fig. 7. Rotation of the azobenzene chromophores and rotation of the light in film as a result of the interactions between light and azobenzene chromophores. (a) Left-CPL induces left-handed helix; (b) right-CPL erases the former left-handed helix and induces right-handed helix.

toinduced helical arrangements mentioned above, right helices would be induced in the azobenzene polymer film after irradiation with right-CPL [8,11,13].

For PM2AN with spacer of two methylene units, the azobenzene chromophores could not be regarded as free from the polymer main chain; the restriction of the main chain on azobenzene chromophores makes the alignment of the azobenzenen chromophores to be difficult. While PM6AN with spacer of six methylene units, the azobenzene chromophores could be regarded as free from the polymer main chain. Therefore the alignment of azobenzene chromophores would be more efficient in PM6AN film than in PM2AN film. After irradiation with left-CPL, more helices would be induced in PM6AN film than in PM2AN film. Compared with PM2AN film, the process of orientation of bisazobenzene chromophores perpendicular to light polarization in PM2BAN film is more difficult and slower, as a result, the photoinduced chirality would be more difficult and slower.

4. Conclusions

We have reported the synthesis and characterization of bisazobenzene-based polymer (PM2BAN) and two azobenzene-based polymers (PM2AN and PM6AN) with different spacers. Circularly polarized light with opposite handedness produces enantiomeric arrangements not only for azobenzene-based polymers (PM2AN and PM6AN) but also for bisazobenzene-based polymer (PM2BAN). Long time of irradiation can enhance the level of photoinduced chirality in PM2BAN. However, the level and rate of photoinduced chirality in film of PM2BAN are lower than those in films of PMxAN ($x = 2$, 6) at similar irradiation time. Compared with PM2AN, photoinduced chirality is more efficient in PM6AN film. The level of photoinduced chirality depends on the spacer length and the type of azobenzene chromophore. We report a reversible chiroptical switch between two chiral arrangements in bisazobenzene-based polymer by change the handedness of circularly polarized light. The present results are benefit to the design of novel azopolymers for chiroptical switch applications.

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