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Synthesis and Characterization of Two Chiral Azobenzene-Containing Copolymers

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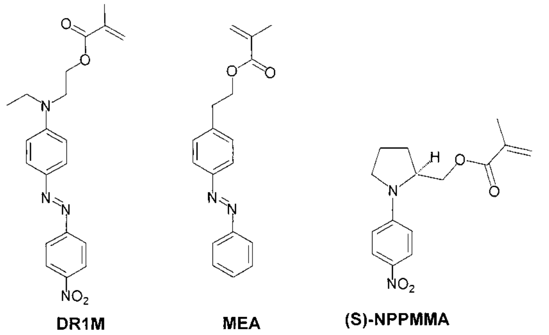
ABSTRACT: Two copolymers, poly{4′-[[[2-(methacryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene}-*co*-[(methacryloyloxy)-4-nitrophenyl-(*S*)-prolinol] (poly(DR1M-*co*-(*S*)-NPPMMA)) and poly{4-[2-methacryloyloxy)ethyl]azobenzene-*co*-[(methacryloyloxy)-4-nitrophenyl-(*S*)-prolinol] (poly(MEA-*co*-(*S*)-NPPMMA)), were synthesized and characterized. They contain side chain azobenzene chromophores (DR1 and MEA, respectively) and a prolinol-based chiral side chain group (NPP). Photoinduced birefringence, polarized absorption spectroscopy, and chiroptical properties (optical rotation and circular dichroism) in films were measured, and the results are discussed in relation to the structure of these copolymers. Cooperative motion of the chiral structural unit is observed for the photoinduced birefringence. Chirality is, however, not transmitted from the chiral structural unit to the azobenzene structural unit at the 1:1 compositions investigated here.

Introduction

Azobenzene polymers are promising materials for optical switching and digital optical storage, due to the possibility of changing the orientation of the azobenzene chromophores by irradiation with polarized light.[1] The mechanism by which birefringence is obtained in azobenzene polymer films is based on the photoinduced trans−cis−trans isomerization of the azobenzene groups, accompanied by their movement and rearrangement perpendicular to the laser polarization direction. This "written" information can be "erased" locally by irradiation with circularly polarized light or globally by heating above the glass transition temperature (T_g) of the polymer film. When azobenzene molecules are attached to ordered chiral macromolecules, the trans-to-cis isomerization of the azobenzene chromophore can induce large changes of the chiroptical properties of the macromolecule. This way, circular dichroism and optical rotatory power can be modified reversibly by irradiation of the azobenzene with unpolarized light in solution. Polymer systems, in addition to central chirality induced by an asymmetric center present in the side group, offer the possibility of helical chirality of the polymer backbone. In solution, changes in the helical structure of the polymer chain can be induced by using chiral azobenzene photoisomerizable side chains, for example in poly(α-amino acids),[2] helical polyisocyanates,[3−5] and methacrylate polymers.[6−8] Chiroptical properties in films of chiral azobenzene polymers are less studied.[9] It is also known that chirality can be photoinduced in smectic achiral azobenzene-containing polymer films simply by irradiating with circularly polarized light, following the same photoisomerization−reorientation mechansim.[10,11] Photoinduced birefringence can occur only in films, not in solution, while photoinduced chirality has been reported both in films and in solution.

The aim of this work was to investigate the linear and circular birefringence in films of amorphous copolymers containing azobenzene groups and chiral groups. Knowing that polar structural units other than azobenzene can move in concert with them to amplify the photoinduced birefringence,[12] we wanted to test whether (a) chiral groups can also undergo cooperative motion and (b) chiral groups have any influence on the potential to photoinduce chirality in the polymer film with circularly polarized light. We report here the synthesis and characterization of two copolymers, each with two different structural units: one containing an azobenzene group an another containing a chiral group. They are poly{4′-[[[2-(methacryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene}-*co*-[(methacryloyloxy)-4-nitrophenyl-(*S*)-prolinol] (poly(DR1M-*co*-(*S*)-NPPMMA), **3**) and poly{4-[2-methacryloyloxy)ethyl]azobenzene-*co*-[(methacryloyloxy)-4-nitrophenyl-(*S*)-prolinol] (poly(MEA-*co*-(*S*)-NPPMMA), **4**) (Figure 1).



POLYMERS

P-DR1M (1)
P-MEA (2)
P-DR1M-co-NPPMMA (3)
P-MEA-co-NPPMMA (4)
P-NPPMMA (5)

Figure 1. Comonomer structures and (co)polymers synthesized.

Experimental Section

Toluene and THF were dried over sodium with benzophenone indicator. Methacryloyl chloride was distilled under vacuum; triethylamine and styrene were dried over calcium hydride. They were distilled prior to use and kept in sealed

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Table 1. Polymer Characterization

polymer		M_w	PDI	T_g (°C)	$[\alpha]_D$ (DMF, $c = 0.5$)	composition (% NPPMMA)
1	pDR1M	13 200	2.40	117		
2	pMEA	69 700	2.37	78		
3	pDR1M-*co*-NPPMMA	13 400	1.77	121	*b*	49
4	pMEA-*co*-NPPMMA	22 600	2.61	110	−36	48
5	pNPPMMA	*a*	*a*	150	−24	100

[a] Not measured; the polymer is not soluble in THF. [b] Not measured; too large absorption of the probe beam (589 nm).

tubes under argon gas. The monomers were obtained as previously reported, by reaction of the corresponding alcohols with methacryloyl chloride in THF, in the presence of triethylamine.

The polymerization reactions were carried out in dry toluene (0.3 M), with 5 wt % 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. The polymerizations of DR1M and MEA were previously described.[13,14] The copolymers were synthesized as follows: A mixture of monomers (in equimolar amounts) and AIBN was loaded in an ampule, the air was removed under vacuum, and then the tube was filled with argon. Dried toluene was added under argon, and the solutions were heated at 60 °C for 2 days. The solution was then poured in methanol, the precipitate was collected, and then the polymer was purified by precipitation from DMF/methanol. The solid was dried in a vacuum oven at 70 °C overnight. The yields were 75% (polymer **3**, red solid) and 69% (polymer **4**, orange solid). The homopolymer **5** was obtained by a similar procedure (86% yield, yellow solid).

^{1}H NMR spectra of the copolymers were measured on a Bruker AC-F 200 MHz spectrometer in deuterated dichloromethane solutions. Glass transition temperatures were measured on second heating scans on a Mettler TA-30 DSC instrument equipped with a TA-3000 processor at a scan rate of 10 °C/min. UV−vis spectra of solutions and films of polymers were measured on a Shimadzu spectrophotometer. Circular dichroism spectra were recorded on a Jasco-715 spectropolarimeter. Optical activities were measured with a Perkin-Elmer 241 polarimeter (at the sodium D line) on solutions of polymers in DMF. The average molecular weights and polydispersity indices of the polymers were estimated by gel permeation chromatography (polystyrene standard calibration), in THF, on a Waters liquid chromatograph equipped with a R410 differential refractometer. Films for birefringence measurements were prepared by spin-coating solutions of polymers in dichloroethane onto clean glass microscope slides and subsequently dried in an oven at 130 °C for 1 h to remove the THF. Films (of absorbance of about 0.9) for UV−vis and circular dichroism spectra were obtained by spin-coating of polymers onto fused quartz slides from solutions in dichloroethane. Films thickness were determined with a Dektak profilometer. Linear birefringence was induced using a linearly polarized 488 nm laser beam (100 mW/cm^2) and measured using a diode laser beam at 670 nm.

Results and Discussion

Copolymer Synthesis and Characterization. The chiral monomer (*S*)-(−)-NPPMMA was obtained by reaction of *N*-nitrophenyl-(*S*)-prolinol with methacryloyl chloride with triethylamine as a base.[15] The polymerization of (*S*)-(−)-NPPMMA and its copolymerization with DR1M and MEA were carried out in toluene at 60 °C, using 5% w/w AIBN as radical initiator. Yields higher than 70% were obtained for reaction times of 2 days. The results of the polymerization are summarized in Table 1. Nitrobenzene is a well-known chain transfer agent; thus, when this group is present, the molecular weights of the resulting polymers and copolymers in Table 1 are lower, as expected. Copolymer composition was obtained from ^{1}H NMR spectra. Both copolymers **3** and **4** contained about 50 mol % chiral structural units ((*S*)-NPPMMA). They were obtained by using equal molar amounts of azo monomers and chiral monomer.

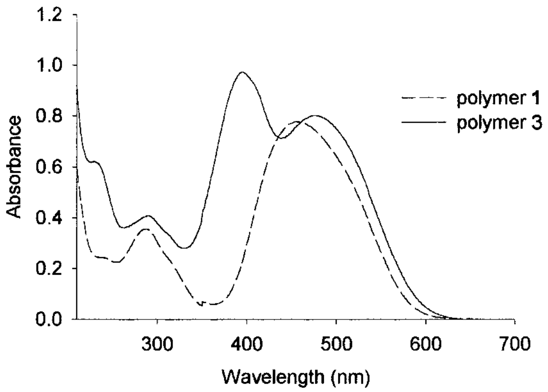

Figure 2. UV−vis spectra of films of pDR1M (**1**) and of copolymer **3** (DR1M-*co*-NPPMMA).

Homopolymer **5** was reported previously[15] and was used for nonlinear optics. For comparison, the two azo homopolymers PDR1M (**1**) and PMEA (**2**) were synthesized as well. The monomers DR1M[16] and MEA[13] were synthesized by slight modification of known procedures. The glass transition temperatures for polymers are listed in Table 1. Polymer **5** (poly((*S*)-NPPMMA) has a relatively high T_g (150 °C) when compared with the polymers **1**−**4**. The copolymers show glass transition temperatures between the homopolymers. They (**3** and **4**) are quite soluble in DMF and dichloroethane but did not dissolve completely in THF. Polymer **5** is insoluble in THF, so that the molecular weight could not be measured by GPC in THF.

The UV−vis spectra of films of polymers **3** and **4** prepared on quartz slides are presented in Figures 2 and 3b, respectively. For comparison, the electronic spectra of the azo polymers **1** and **2**, respectively, are shown in the same figures. The absorption bands for the azo and NPP structural units are listed in Table 2. The λ_{max} for the DR1 structural unit shifts from 456 nm in homopolymer **1** to 476 nm in copolymer **3**. This red shift of 20 nm is comparable to the red shift observed previously in poly{4′-[[[2-(methacryloyloxy)ethyl]ethyl]amino]-4-nitroazobenzene-*co*-[[4-nitrophenyl-4′-[2-methacryloyloxy)ethyl] benzoate]} (poly(DR1M-*co*-BEM))[17] of similar concentration of DR1M structural units. This red shift can be assigned to dipolar interactions between the two polar structural units (NPPMMA and DR1M) of the copolymer, as in the case of poly(DR1M-*co*-BEM). The shift is smaller for the MEA structural unit (10 nm only). This can be explained by the lower dipole moment of the MEA chromophore when compared to the DR1M chromophore. A similar effect of the azo dipole on the NPPMMA unit exists but is less pronounced. There is a red shift of 6 nm of the absorption band of the NPP, from 388 nm in polymer **5** to 394 nm in copolymer **3**. The dipolar interaction between polar different structural units is expected to play a role in the behavior in photoinduced birefringence for the copolymers **3** and **4**, when compared with the homopolymers **1** and **2**.

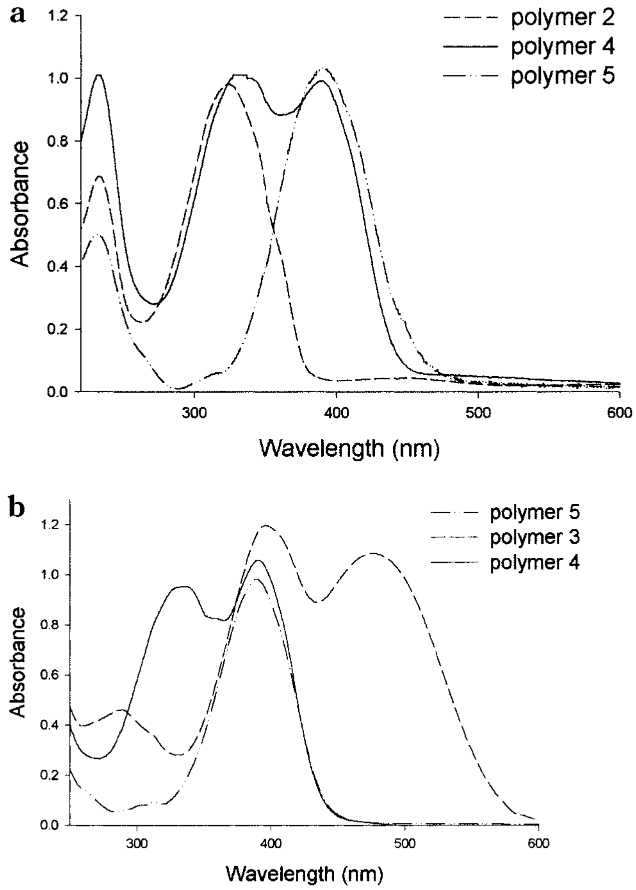

Figure 3. (a) UV–vis spectra of copolymer **3** (DR1M-*co*-NPPMMA), copolymer **4** (MEA-*co*-NPPMMA), and homopolymer **5** (pNPPMMA) in dichloroethane solutions. (b) UV–vis spectra of films of pMEA (**2**), copolymer **4** (MEA-*co*-NPPMMA), and homopolymer **5** (pNPPMMA).

Table 2. λ_{max} in Films of Polymers 1–5

polymer	azo unit group	λ_{max}	comonomer unit group	λ_{max}
1	DR1	456		
2	MEA	324		
3	DR1	476	NPP	394
4	MEA	334	NPP	390
5			NPP	388

For comparison purposes, electronic spectra were also recorded for solutions of polymers in dichloroethane. They are shown in Figure 3a. The λ_{max} values were very close to those obtained in polymer films. Since the *p*-nitroaniline group is strongly polar, it acts as a polar "solvent" when associating with the azobenzene groups. Its polarity is higher than that of the solvent (dichloroethane, spectra in Figure 3a), thus there are no other absorbance shifts in solution. Film thickness and solvent concentrations were adjusted to an approximate optical density of 1. Extinction coefficients were not determined quantitatively.

Photoinduced Birefringence. A linearly polarized writing laser beam (488 nm, 70 mW/cm^2) was used to induce birefringence in all polymer films for 300 s. The writing beam was then turned off for 300 s. When the beam is turned off, there is some loss of photoorientation until a stable birefringence value is obtained (conserved birefringence). Birefringence was then erased by irradiation with circularly polarized light for 100 s. The birefringence was measured using a diode laser probe beam at 670 nm. The experimental setup was previously described.[18] The results are listed in Table 3. For both copolymers the levels of photoinduced birefringence are higher than what is expected given the content of azo chromophore (about 50%) in the copolymer. For example, if the birefringence were due only to the alignment of the DR1M group, the expected maximum of birefringence for the copolymer **3** would be about 0.054. Experimentally, an excess of photoinduced birefringence (0.02) is measured. It is known that, in copolymers containing DR1M structural units and polar comonomer groups, the polar, optically inactive groups are aligned by the movement of the azo chromophore during the irradiation with linearly polarized light.[12] In the case presented here, about 25% of the induced birefringence is due to the alignment of the NPPMMA structural unit. Since NPP has a $\lambda_{max} = 394$ nm while DR1 has a $\lambda_{max} = 476$ nm, we estimate using the Kramers–Kronig relation that it takes twice as many NPPMMA as DR1 to produce the same birefringence change. From this we conclude that one NPP group is reoriented for every reoriented DR1 group. A different behavior is observed for copolymer **4**, containing the MEA azo chromophore. In this case, about 26% of the birefringence is induced by the NPP group. Since MEA has a $\lambda_{max} = 334$ nm, it now takes about 0.6 NPP groups to produce the same change in birefringence as would be produced by MEA. We estimate here that for every MEA group about 0.15 NPP groups are reoriented when birefringence is induced. This difference in cooperative motion is probably due to the low polarity of MEA. Furthermore, we note that—due to a low absorption coefficient—the level of induced birefringence for the P-MEA (**2**) and the copolymer P-MEA-*co*-NPPMMA (**4**) is about 1 order of magnitude lower than that of DR1M-containing polymers. A kinetic model for the phenomenon explains the difference of behavior for the types of chromophores.[19] The cooperative motion between NPP and the DR1 groups was investigated in more detail by polarized UV–vis spectroscopy.

Polarized UV–vis Spectroscopy. For polarized UV–vis spectroscopy, a surface of about 1 cm^2 of a spin-coated film of copolymer **3** was irradiated with linearly polarized light (488 nm, 100 mW/cm^2) for 30 min. Before irradiation the polymer film showed no angular dependence of the absorbance of the DR1 chromophore. After irradiation, birefringence is induced in film. The induced linear dichroism is due to the preferential reorientation of the azobenzene groups (through trans–cis–trans photoisomerization cycles) to a direction perpendicular to the direction of the electric field of the incident linearly polarized light, where they are not affected by the incident light anymore. When the direction of polarization of the probe beam (475 nm) was parallel

Table 3. Photoinduced Birefringence in Polymers 1–4

polymer	azo content wt fract	max birefringence	birefringence induced by NPPMMA value	%	stable birefringence	conserved birefringence (%)
1	1	0.093	0	0	0.071	77
2	1	0.010	0	0	0.006	66
3	0.58	0.071	0.018	25	0.053	74
4	0.52	0.007	0.002	26	0.005	78

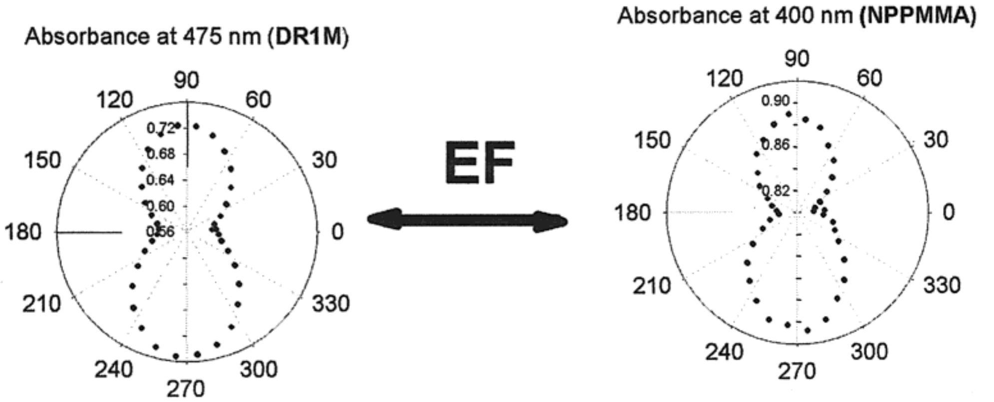

Figure 4. Polarized absorption spectra of copolymer **3** after irradiation with linearly polarized light. The thick arrow shows the direction of the laser polarization.

to the direction of the polarization of the pump beam, the absorbance of the DR1 chromophore reached a minimum. When the direction of the polarization of the probe beam was perpendicular to the polarization direction of the pump beam, a maximum was reached for the absorbance at 475 nm. For angles between 0° and 90° intermediate values for the absorbance were obtained. The angular dependence of the absorbance of the DR1 chromophore, recorded at a wavelength of 475 nm, is shown in Figure 4a. The figure confirms that the preferential orientation of the azobenzene groups is perpendicular to the electric field vector of the pump beam. More interestingly, Figure 4b shows a similar angular dependence for the absorbance of the optically inactive structural unit NPP. Linear dichroism was also induced, and an excess of NPP chromophores are oriented perpendicularly to the polarization direction of the pump beam, exactly as was found for the DR1 chromophores. This means that the optically inactive NPP groups undergo reorientation together with the azobenzene groups. This is another example of cooperative motion in amorphous polymers. The actual numbers shown in Figure 4 may be overestimated, since there is some overlapping between the absorbance wavelength of the NPPMMA unit and of the DR1 group.

Optical Activity and Circular Dichroism. The specific optical rotation measured for a solution of (*S*)-NPPMMA in DMF ($c = 0.5$) is -50.8. At the same concentration, the specific optical rotation of the homopolymer **5** obtained from this chiral monomer is only half of the value measured for the monomer (-24). This suggests that there might be some kind of associations between these chiral structural units in the polymer **5** that do not exist in the monomer, at least in relatively diluted solutions. They are probably responsible for a chirality of the opposite sign to the central chirality present in the NPP group. An increase or a decrease of the optical rotation of the polymer when compared to that of the monomer was previously reported in the literature. It is generally believed that this is due to an additional chirality, helical chirality, of at least some segments of the polymer backbone.[6]

A more detailed investigation of the chiroptical properties was done by circular dichroism spectroscopy (CD). The CD spectra of the (*S*)-NPPMMA (monomer) and of the polymer **5** in dichloroethane at the same concentration are shown in Figure 5. They exhibit a negative CD band at about 310 nm, probably due to a $\pi \rightarrow \pi^*$ transition of high energy, in close correspondence with the UV absorption. A second CD band appears at about 380 nm, related to the $\pi \rightarrow \pi^*$ overlapped with the $n \rightarrow \pi^*$ electronic transition of the chromophore. The monomer showed a single weak positive CD band, while polymer **5** was characterized by the presence of a positive split CD Cotton effect in this region. This could be assigned to the presence of cooperative dipolar interactions between the neighboring side chain chiral chromophores disposed along the polymer backbone. For the monomer solution, because of the high dilution, the occurrence of dipolar interactions is much lower. The relative symmetry of this couplet suggests that the $n \rightarrow \pi^*$ band is very weak when compared to the $\pi \rightarrow \pi^*$ band.

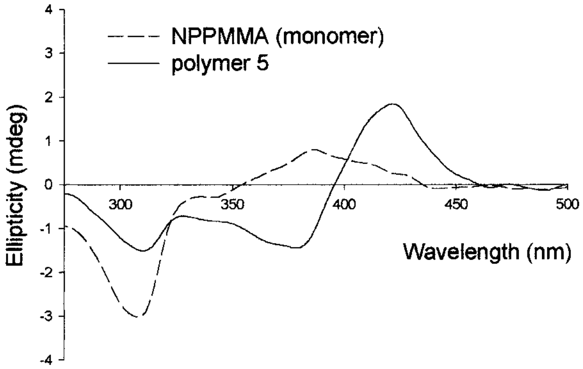

Figure 5. Circular dichroism spectra of the chiral monomer (NPPMMA) and of the homopolymer **5** (pNPPMMA).

For applications like reversible optical storage it is necessary to use solid-state devices. To date, the only successful approach to switching of chiroptical properties in solid-state devices is to use liquid crystals containing photoactive groups. These include cholesteric liquid crystals or smectic azobenzene-containing polymer liquid crystals[10,11] or even prealigned amorphous polymers.[23] The macroscopic switching effect is due to the cooperative effect known to exist in liquid crystals. In amorphous copolymers **3** and **4**, we showed that cooperative motion exists for photoinduced linear dichroism; thus, we decided to investigate whether cooperative motion can be effective for changing the circular dichroism of films of these amorphous copolymers with light.

The CD spectra for the polymers **3** and **4** films are almost identical in shape with the spectrum recorded for the chiral homopolymer **5** (Figure 6). The absence of CD bands due to the azo chromophores in both copolymers **3** and **4** is particularly striking. Some asymmetric perturbation of the azobenzene chromophores induced by the chiral (*S*)-NPPMMA structural

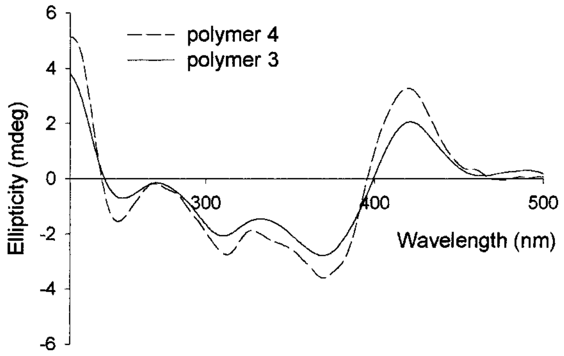

Figure 6. Circular dichroism spectra of the unirradiated films of the two copolymers: **3** (DR1M-*co*-NPPMMA) and **4** (MEA-*co*-NPPMMA).

units could have been present, because dipolar interaction between the two types of chromophores was noticed in the UV−vis spectra. Nevertheless, these CD spectra are taken in the solid state, and chiral perturbation of the azobenzene chromophore in copolymers containing a chiral comonomer structural unit (menthyl derivatives) was reported previously by Carlini and coworkers[20−22] only in solution. For those copolymers, the value of ellipticity increases with the increase of the content of the chiral menthyl structural unit. The lack of chiral perturbation of the azo structural units by the chiral (*S*)-NPP unit is probably due to a relative lack of motion in the copolymer film or to the relatively low content of chiral structural units (about 50%). Another possibility is the linear and smaller shape of the NPP unit, so that the steric hindrance induced by this chiral group is not large enough to affect the azobenzene group. To clarify this point, it will be necessary to synthesize copolymers containing higher amounts of chiral structural units.

The attempt to photoinduce additional chirality in the films by irradiation with circularly polarized light was based on an earlier report in the literature.[23] There, an amorphous azobenzene-based polymer was prealigned with linearly polarized light, and then a supramolecular helical structure was photoinduced with circularly polarized light. Films of copolymer **3** were first aligned with linearly polarized light. However, when these aligned samples were irradiated with circularly polarized light, the only effect was the erasure of the induced linear dichroism, and the CD spectra after irradiation (not shown) with circularly polarized light are identical to the unirradiated sample. No helical suprastructure was obtained in our samples by this irradiating sequence. Irradiation of copolymer **3** film only with circularly polarized light also produced no change of the CD spectrum. Thus, for the amorphous copolymers in this paper, the cooperative motion between azobenzene and the polar chiral groups does not produce changes in the chiroptical properties upon irradiation with circularly polarized light. The spacer length of the chiral monomer may play a role to the cooperative motion and transfer of chirality processes. The length of the NPP monomer is small when compared with the DR1 azobenzene group. The use of larger chiral groups (longer spacers) may result in both transfer of chirality and in photoinduced chirality in these copolymer films. Further investigations are in progress.

Conclusions

Two copolymers containing equal amounts of azobenzene chromophore and a chiral group, poly(DR1M-*co*-(*S*)-NPPMMA) and poly(MEA-*co*-(*S*)-NPPMMA), were synthesized by free radical copolymerization of the monomers. Dipolar interactions between the azobenzene groups and polar "optically inert" comonomer units are observed by UV−vis spectroscopy. Cooperative motion of the two polar structural units was obtained when photoinducing birefringence. About 25% of the birefringence is due to the alignment of the NPP groups by the azobenzene chromophores. Further evidence for cooperative motion was obtained by polarized UV−vis spectroscopy on poly(DR1M-*co*-(*S*)-NPPMMA). Chiroptical properties of these copolymers were determined by measurement of optical rotation and circular dichroism. The CD spectra on films show the absence of chiral perturbation of the azobenzene groups by the chirality of the NPP groups in the solid state. No supramolecular helicity could be photoinduced in films of these copolymers, even after prealignment by linearly polarized light; therefore, the chiral comonomer has no influence on the azobenzene comonomer. Copolymers containing higher amounts of chiral side chains will have to be synthesized, to test whether they have any influence.

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