Photomodulation of the Chiroptical Properties of New Chiral Methacrylic Polymers with Side Chain Azobenzene Moieties

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Abstract: We have investigated the photoinduced optical properties of a new class of chiral methacrylic polymers characterised by the presence in the side chain of an optically active pyrrolidinyl ring linked to a *trans*-azoaromatic system. The homopolymers are enantiomerically pure and their strong optical activity indicates that the macromolecules assume, both in solution and in solid thin films, highly homogeneous conformations with a prevailing chirality. As expected, the studied polymers exhibit reversible linear dichroism and birefringence when irradiated with linearly polarised light. By irradiating with circularly polarised light, we have discovered that it is possible to photomodulate the chiroptical properties of the polymer films. After irradiation with L-polarised light, the CD spectra of the films show a net inversion of their relative sign. The effect is reversible and the original shape of the CD spectra can be restored by pumping with R-polarised radiation. This unexpected new phenomenon can be explained in terms of the ability of the L-polarised radiation to invert the prevailing helicity of the polymeric chains. The observed effect seems to open new possibilities for the use of azobenzene-containing materials as chiroptical switches.

Keywords: azo compounds • circular dichroism • conformation analysis • molecular devices • photochromism

Introduction

Azobenzene-containing polymers are systems that are subject to ongoing studies as a result of their photochromic properties. They have been proposed as materials for serial and parallel holographic optical data storage, relief gratings, and, due to the relatively high second-order hyperpolarizability of the azo dye, also for second-order nonlinear optical applications.[1] It is now well accepted that their photochromic behaviour is related to continuously photoinduced *trans*–*cis*–*trans* isomerisation cycles of the azobenzene chromophores. By irradiating with linearly polarised (LP) pump radiation of the appropriate frequency, it is possible to create a net excess of azobenzene chromophores oriented perpendicular to the direction of the electric field, thus inducing in the material linear dichroism and birefringence that are reversibly erasable by irradiating with depolarised or circularly polarised pump radiation. Recently, the fascinating possibility of inducing circular birefringence (optical activity) in nonchiral azobenzene-containing polymers by using circularly polarised (CP) pump radiation has also been reported. The phenomenon was observed for the first time by Nikolova and co-workers in films of liquid-crystalline cyanoazobenzene polyesters (**P6a12** and **P6a4**).[2, 3] Upon illumination with CP light at 488 nm, the films are imparted with an unusually strong optical activity, which has been monitored by using a probe beam at 632.8 nm: right circularly polarised (CP-R) pump radiation induces right-hand rotation of the probe beam polarisation, the reverse being observed with left circularly polarised (CP-L) pump light. In a first report,[2] the authors suggested that the observed effect may be initiated by a transfer of angular momentum from the circularly polarised light to the azobenzene chromophores. Being attached to the polymer backbone, the mesogenic azo groups cannot freely rotate and the transfer of angular momentum leads to a new ordering of the chromophores inducing chirality of the whole structure with a screw sense that depends on the handedness of the exciting circularly polarised radiation. The authors further suggested that the observed phenomena are related to the presence of liquid-crystalline (LC) ordering (smectic-A phase) in the polymer films prior to irradiation. Analogous results have been found for an amorphous cyanoazobenzene

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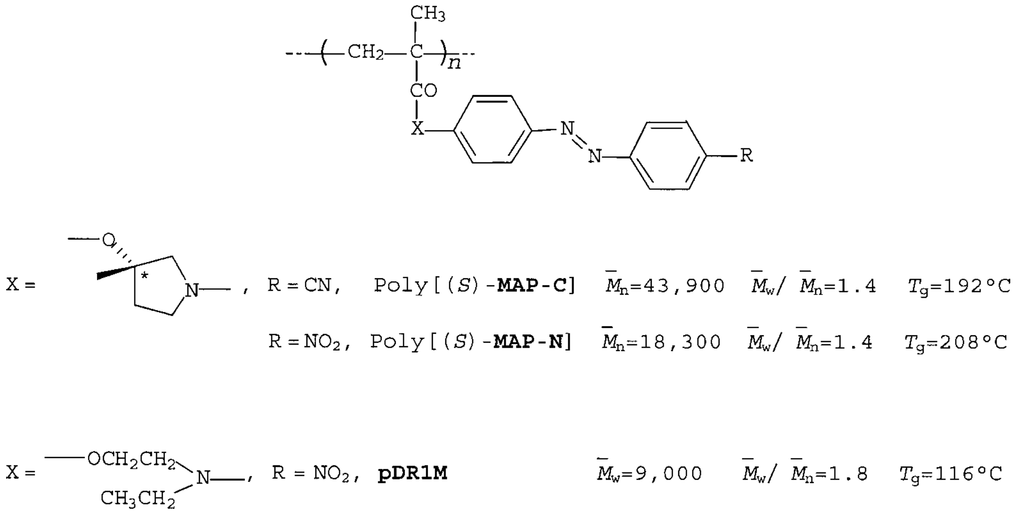

Scheme 1. Chemical structures and principal properties of the studied polymers.

methylmethacrylate copolymer previously ordered by illumination with linearly polarised light.[4] In further work, Nikolova et al. discovered a self-induced rotation of the azimuth of elliptically polarised (EP) light on passing through films of photobirefringent azopolymers.[5] They explained the experimental results by analysis of the propagation of the elliptically polarised radiation in a photobirefringent medium. The EP light propagating through the sample was found to induce an optical axis that gradually rotates along the propagation direction, thus inducing a chiral orientation of the azobenzene chromophores with the same sense of rotation as that of the input light electric vector. The whole film assumes a chiral structure similar to that found in cholesteric liquid crystals with large pitch.

The control of chirality with CP light in films of a new liquid-crystalline nitroazobenzene methyl-methacrylate polymer (**p4MAN**) has also been achieved by Natansohn and coworkers.[6] The films were annealed at 135 °C to produce a liquid-crystalline smectic-A phase that was maintained at room temperature. The authors found that, by irradiation with CP light at 514 nm, the initially achiral films became chiral and showed strong circular dichroism (CD) bands in the UV/visible region. The CD spectra of two different films, one irradiated with CP-R and the other with CP-L light, exhibited opposite signs and were virtually mirror images of each other. In contrast, the amorphous films (not annealed) did not show any induced circular anisotropy, thus pointing out the essential role of the LC arrangement. The authors suggested that the original circular polarisation of the incoming light is made elliptical by the first layers of the smectic domains of the film. On the basis of the model proposed by Nikolova et al.,[5] the EP radiation that propagates into the film produces a progressive rotation of the optical axis of each LC domain, resulting in a helical supramolecular arrangement of the smectic domains. The sense of the helical structure is congruent with the sense of rotation of the electric vector of the pump radiation. The material can support repeated cycles of irradiation and represents the first example of a reversible chiroptical switching between enantiomeric suprastructures, where the chirality is induced only by irradiation with CP light.

Herein, we report an assessment of the chiroptical properties of a new class of optically active methacrylic polymers bearing in the side chain a *trans*-azoaromatic system linked to the macromolecular main chain through a cyclic chiral bridge. In particular, we have considered two homopolymers, poly[(*S*)-**MAP-N**][7] and poly[(*S*)-**MAP-C**][8] (Scheme 1), obtained by radical polymerisation of the corresponding enantiomerically pure optically active monomers (*S*)-3-methacryloxy-1-(4′-nitro-4-azobenzene)pyrrolidine [(*S*)-**MAP-N**] and (*S*)-3-methacryloxy-1-(4′-cyano-4-azobenzene)pyrrolidine [(*S*)-**MAP-C**], respectively. These derivatives do not display LC behaviour and are characterised by enhanced thermal properties with respect to the previously reported analogous methacrylic polymer **pDR1M**, in which the azoaromatic dye 4′-[(2-hydroxyethyl)ethylamino]-4-nitroazobenzene (Disperse Red 1) is linked to the side chain through an ester bond, and which shows interesting optical storage properties.[9, 10]

Results and Discussion

UV properties: The experiments were carried out on amorphous thin films of thickness 100–350 nm, obtained by spin coating. Figure 1 shows the UV/visible spectra of amorphous thin films of poly[(*S*)-**MAP-C**] (120 nm thick, full line) and poly[(*S*)-**MAP-N**] (140 nm thick, dashed line) on fused silica, normalised for thickness.

The two spectra are quite similar and are characterised by a strong absorption band in the visible region, centred at 428 and 440 nm for poly[(*S*)-**MAP-C**] and poly[(*S*)-**MAP-N**], respectively. These bands are related to the combined contributions of the $n \rightarrow \pi^*$, first $\pi \rightarrow \pi^*$, and intramolecular charge-transfer electronic transitions of the azobenzene chromophores. The absorption bands located between 250 and 350 nm are related to the $\pi \rightarrow \pi^*$ electronic transitions of the individual aromatic rings. The absorption edge observed between 200 and 250 nm pertains to electronic transitions stemming from the methacrylate ester groups and the polymer backbone. In going from poly[(*S*)-**MAP-C**] to poly[(*S*)-**MAP-N**], the positions of the absorption maxima

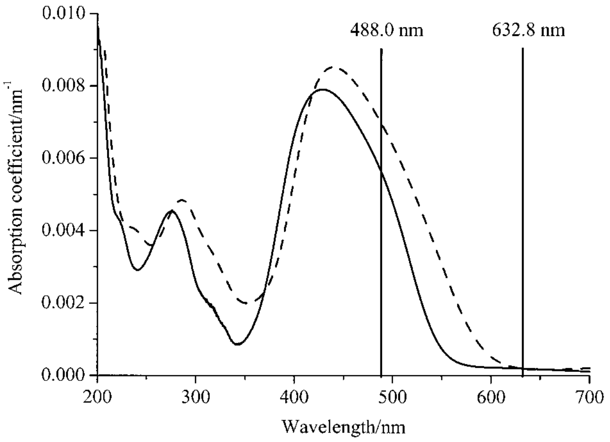

Figure 1. Absorption spectra of amorphous thin films on fused silica of poly[(*S*)-**MAP-C**] (120 nm thick, full line) and poly[(*S*)-**MAP-N**] (140 nm thick, dashed line).

connected with the azobenzene system shift to lower energy. This bathochromic effect is related to the increased electron-withdrawing ability of the nitro group with respect to the cyano group, which improves the degree of conjugation in the chromophore and, as a consequence, reduces the electronic transition energies in the system.

In Table 1, the wavelengths of the absorption maxima of the polymers in the solid state are compared with those of solutions of the polymers in dimethylacetamide (DMA) and with those of the monomeric model compounds, (*S*)-3-pivaloyloxy-1-(4′-cyano-4-azobenzene)pyrrolidine [(*S*)-**PAP-C**][8] and (*S*)-3-pivaloyloxy-1-(4′-nitro-4-azobenzene)pyrrolidine [(*S*)-**PAP-N**].[7] While the positions of the UV bands do not change on going from the model compounds to the polymers in solution and in the solid state, the absorption in the visible region is quite sensitive to chromophore aggregation. Indeed, remarkable blue shifts are observed on comparing the solution spectra of the polymers with those of the model compounds (11 and 19 nm for poly[(*S*)-**MAP-C**] and poly[(*S*)-**MAP-N**], respectively). These shifts become even more pronounced for the polymers in the solid state (30 and 51 nm, respectively). In solution, the origin of the blue shift has been attributed to an intramolecular parallel arrangement of the chromophore electric dipoles (H-type aggregation) imposed by the structural constraints of the macromolecules.[8] The increase in the magnitude of the blue shift on going from the solution to the solid state suggests an increase in the parallel aggregation of chromophores, which, in the latter case, could also involve interchain dipolar interactions. In contrast to the spectra in solution, the two absorption bands of the solid films are characterised by a strong asymmetry, with a broadening of the long-wavelength side. This can be related to the less ordered dipolar interchain interactions that the chromophores experience in the solid phase compared to those in solution, where the dominant dipolar interactions are intramolecular.

Table 1. Maximum wavelength positions of the UV/Vis absorption bands of polymers and model compounds.

Compound	First band λ_{max} [nm]	Second band λ_{max} [nm]
(*S*)-**PAP-C**/DMA solution	458	277
poly[(*S*)-**MAP-C**]/DMA solution	447	277
poly[(*S*)-**MAP-C**]/film	428	276
(*S*)-**PAP-N**/DMA solution	491	287
poly[(*S*)-**MAP-N**]/DMA solution	472	287
poly[(*S*)-**MAP-N**]/film	440	286

Chiroptical properties: The CD spectra of the studied polymers, both in solution and as films, are characterised by two intense dichroic signals of opposite sign and similar intensity. These signals, which are related to the electronic transitions of the azobenzene chromophores in the visible range, are absent in the spectra of the corresponding monomeric model compounds representative of the repeat unit of the polymer. In dilute solution, such behaviour is typical of exciton splitting determined by cooperative interactions between side chain azobenzene chromophores arranged in a mutual chiral geometry of one prevailing handedness.[7, 8, 11] The presence of a rigid chiral moiety of one prevailing absolute configuration, interposed between the main chain of the polymer and the azoaromatic chromophore, favours the adoption of a chiral conformation of one prevailing helical handedness, at least within chain segments of the macromolecules in solution.

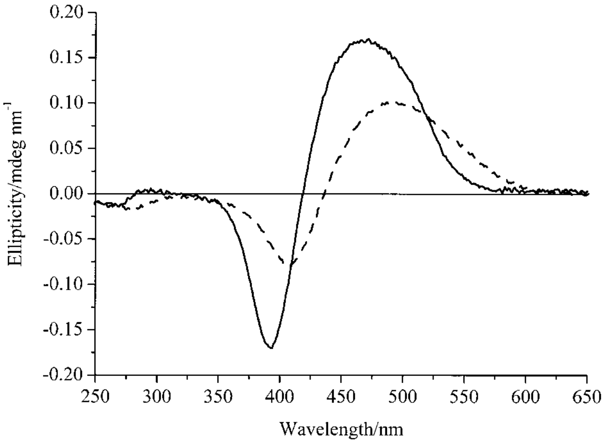

Figure 2. CD spectra of native thin films on fused silica of poly[(*S*)-**MAP-C**] (120 nm thick, full line) and poly[(*S*)-**MAP-N**] (140 nm thick, dashed line).

The CD spectra of native thin films of poly[(*S*)-**MAP-C**] (120 nm thick, full line) and of poly[(*S*)-**MAP-N**] (140 nm thick, dashed line), as depicted in Figure 2, are quite similar to those reported for the polymers in solution.[7, 8] In correspondence with the first strong absorption band in the visible region, they show two intense dichroic signals of opposite sign, with the crossover point[12] close to the position of the maximum absorption. Positions and intensities of the two components of the visible CD couplet, expressed both as ellipticity normalised for the thickness and in molar units, are reported in Table 2, along with those of the polymers and

Table 2. CD spectra in the visible region of polymers and model compounds.

Compound	λ_1[a]	θ_{d1}[b]	$\Delta\varepsilon_1$[c]	λ_0[d]	λ_2[a]	θ_{d2}[b]	$\Delta\varepsilon_2$[c]
(*S*)-**PAP-C**/DMA solution	460		+0.6	–	–	–	–
poly[(*S*)-**MAP-C**]/DMA solution	491		+10.2	447	421		–7.4
poly[(*S*)-**MAP-C**]/film	469	+0.16	+16	419	393	–0.18	–18
(*S*)-**PAP-N**/DMA solution	495		–0.7	–	–	–	–
poly[(*S*)-**MAP-N**]/DMA solution	515		+8.5	465	428		–6.0
poly[(*S*)-**MAP-N**]/film	490	+0.10	+11	436	408	–0.10	–10

[a] Wavelength (in nm) of maximum dichroic absorption. [b] Ellipticity (θ_d) normalized for the thickness expressed in mdegree nm^{-1}. [c] $\Delta\varepsilon$ expressed in L mol^{-1} cm^{-1} and calculated for one repeating unit in the polymer. A mass density of 1 g cm^{-3} has been assumed for the polymer films. [d] Wavelength (in nm) of the crossover of dichroic bands.

model compounds in DMA solution (in molar units). The relative intensities of the CD signals of the films resemble those measured for the polymers in solution and, similar to what was seen in the absorption spectra, a blue shift of the CD bands is seen on going from the solution to the solid state. The close resemblance between the CD spectra of the native polymer films and those of the polymers in solution indicates that the chromophores are also organised according to a chiral order in the solid state. This suggests that the macromolecules maintain chiral conformations of one prevailing helical handedness in the solid amorphous state, at least for chain segments.

As shown in Figure 2, the couplets are asymmetric and the crossover points (Table 2) do not strictly coincide with the maxima of the visible absorption bands (Table 1). This was also found for the spectra in solution[7, 8] and was interpreted as originating from the overlapping of the exciton splitting CD band with a positive CD band having its maximum corresponding to the maximum of the visible absorbance. These positive signals could be attributed to non-interacting chromophores located in conformationally less-ordered segments of the macromolecules, or to a visible absorption band originating from electronic transitions insensitive to the chiral geometry of the macromolecules.

Photomodulation of linear birefringence: On account of the optical properties of poly[(*S*)-**MAP-C**] and poly[(*S*)-**MAP-N**] films, we investigated the possibility of controlling them by using both linearly and circularly polarised radiation at 488 nm, that is, in resonance with the electronic transitions in the visible region. Photoinduced linear dichroism and birefringence were assessed by pumping with LP radiation ($I \approx 100$ mW cm^{-2}) and using probe radiation of $\lambda = 632.8$ nm, at which wavelength the polymers have negligible absorption, the intensity of the probe beam being kept below 1 mW cm^{-2}. After irradiation, the polymers show a photoinduced linear birefringence ($|\delta n|$ of 0.121 for poly[(*S*)-**MAP-C**] and 0.218 for poly[(*S*)-**MAP-N**]), which, after removal of the pump, relaxes to stable values of 0.116 and 0.211, respectively. These values are larger than those obtained under the same experimental conditions for similar achiral systems such as **pDR1M**.[9] For **pDR1M**, we measured a saturated linear birefringence of 0.10 under illumination, and of 0.08 after removal of the pump (a saturated linear birefringence of 0.103 under illumination was reported by Natansohn[10]). It therefore appears that the present homopolymers are characterised by an enhanced photoinduced linear birefringence and an improved conformational stability with respect to **pDR1M**. This behaviour can be related to the values of T_g, which increase in the order **pDR1M** ($T_g = 116\,°C$),[10] poly[(*S*)-**MAP-C**] ($T_g = 192\,°C$),[8] and poly[(*S*)-**MAP-N**] ($T_g = 208\,°C$).[7]

Photomodulation of chiroptical properties: It is well known that the photoinduced linear ordering in azobenzene-containing materials can be reversibly erased by using circularly polarised pump radiation. This is also the case for the investigated polymers; thus, we have indeed verified that by pumping with CP light at 488 nm the photoinduced linear dichroism and birefringence can be reduced to negligible values. However, by monitoring the CD spectra of the irradiated films, we discovered a surprising effect of the CP-L pump radiation. As shown in Figure 3, after a cycle of ordering and erasing with LP and CP-L light at 488 nm, respectively, the CD spectrum of a thin film of poly[(*S*)-**MAP-C**] displays a net inversion of sign, which is particularly evident for the visible excitonic doublet. The two spectra actually appear as mirror images of each other. The observed effect is reversible, and the original shape of the CD spectrum can be substantially restored by pumping with CP-R radiation.

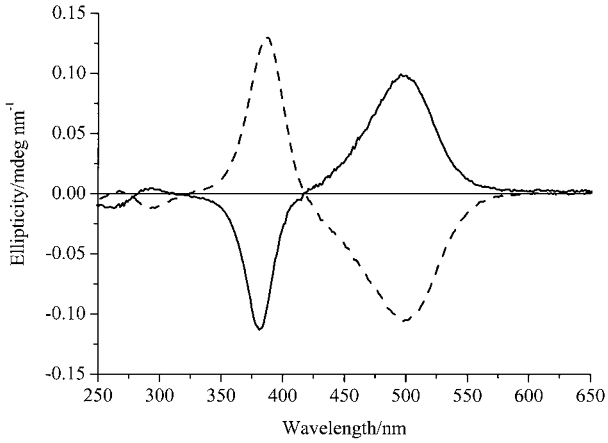

Figure 3. CD spectra of a thin film (340 nm) of poly[(*S*)-**MAP-C**] on fused silica, as prepared (full line) and after a cycle of ordering and erasing (dashed line) with LP and CP-L light at 488 nm ($I \approx 100$ mW cm^{-2}).

Similar results were also obtained for poly[(*S*)-**MAP-N**]. Thus, Figure 4 shows the CD spectrum of the native film (full line) and the spectra obtained after a sequence of pump sessions: film ordered with LP radiation (dashed line), erased with CP-L radiation (dotted line), and finally irradiated with CP-R radiation (dash-dotted line). During the irradiation steps, the degree of ordering was assessed by monitoring the linear birefringence at 632.8 nm. After the writing step with LP light, the CD signal was seen to change slightly: the relative intensity of the visible exciton couplet was reduced, but the shape of the CD spectrum remained essentially the same as that of the native film. The subsequent erasing step with CP-L radiation produced a dramatic change in the CD

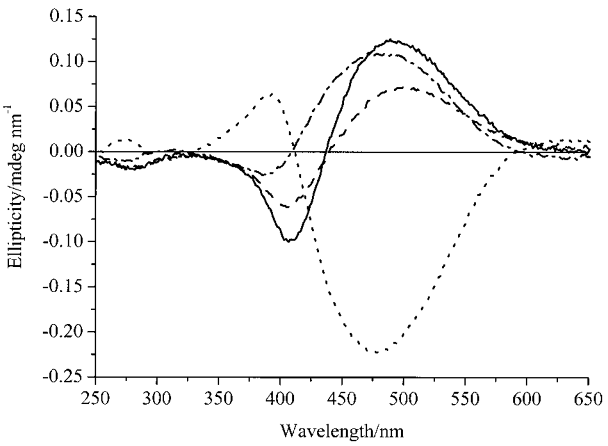

Figure 4. CD spectra of a thin film (130 nm) of poly[(*S*)-**MAP-N**] on fused silica, recorded from the native film (full line) and after each of the following sequential irradiation steps: LP light (dashed line), CP-L light (dotted line), and CP-R light (dotted-dashed line) at 488 nm ($I \approx$ 160 mW cm^{-2}).

spectrum, with the exciton couplet being inverted in sign and becoming strongly asymmetric: the intensity of the negative band became about four times that of the positive one (Figure 4), and the crossover wavelength was shifted to lower values. The final erasing step with CP-R light again inverted the relative sign of the exciton couplet, restoring the original shape of the CD spectrum.

The inversion of the CD signal does not necessarily require a preliminary ordering of the film with LP radiation, the phenomenon also being observed for amorphous films simply upon irradiation with CP light of one given handedness. Figure 5 shows the CD spectra of a film of poly[(*S*)-**MAP-N**] as grown (full line), after an irradiation cycle with CP-L light (dashed line), and after a subsequent pumping step with CP-R light (dotted line). The pump irradiance was set to 160 mW cm^{-2}, and, as in the preceding experiments, during the irradiation cycles we monitored the linear birefringence (negligible in this case). By comparing the three spectra reproduced in Figure 5, it is clear that, here again, the effect of CP-L light is to reverse the CD signals, whereas CP-R radiation is able to restore the original signs of the CD spectrum.

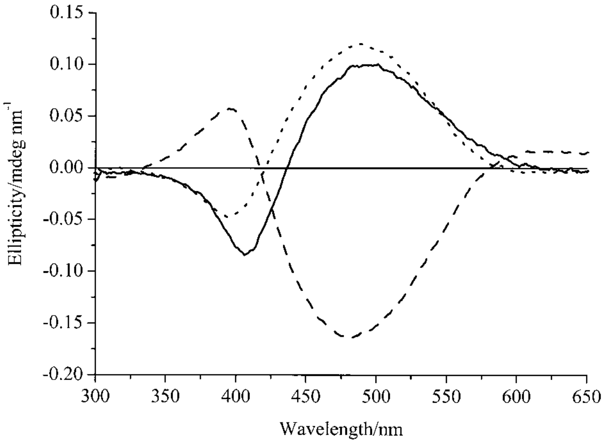

Figure 5. CD spectra of a thin film (150 nm) of poly[(*S*)-**MAP-N**] on glass, recorded from the native film (full line) and after sequential irradiation with CP-L light (dashed line) and CP-R light (dotted line) at 488 nm ($I \approx$ 160 mW cm^{-2}).

From the close similarity between the CD properties of the polymer films and those of the polymers in solution, it is reasonable to assume that the azobenzene chromophores are organised in a helical geometry of one prevailing handedness in the solid state as well, at least within chain segments. This implies that the polymer chains have a predominant helical structure with a well-defined sense, either left- or right-handed. However, the CD data alone do not allow us to establish the absolute sense of the helix, that is, whether it is left or right. The effect of CP-L radiation on the CD signal can be simply interpreted by assuming its ability to invert the prevailing handedness of the polymer structure, or at least to create a statistical net excess of polymer chain sections with inverted helical sense. The observed phenomena appear to be related to the induction of chirality by CP light in achiral azobenzene-containing materials reported by Nikolova and co-workers[2–5] and Natansohn and co-workers,[6] even though the measured ellipticity of our samples, normalised to film thickness, is one order of magnitude lower. In our case, there is an intrinsic chirality of the sample related to the optical activity of the pyrrolidine bridge interposed between the azo chromophores and the polymer backbone, and it is quite reasonable that in the native films the polymer chains should have a predominant helical conformation. The mechanism of the reversible helical inversion induced by CP radiation is not well understood. In any case, for the investigated polymers, it is not related to a preliminary ordering of the azobenzene molecules with LP light, as demonstrated in our experiments. It is known that CP light tends to align the azobenzene side groups along directions close to normal to the film.[3, 13] It is possible that transfer of angular momentum from the CP radiation to the medium, as occurs when a CP photon is absorbed, induces a precession of the chromophores with a sense of rotation congruent with the sense of the CP light. This would mean that CP-L light induces a left-handed organisation of the azobenzene molecules, whereas CP-R light induces a right-handed one. It is reasonable to think of the conformational structure of the polymer chains in the native films as being composed of helical sections of opposite handedness where, due to the chiral interaction of the enantiomeric pyrrolidine moieties, segments of one helicity are thermodynamically favoured with respect to the other, thus confering a prevailing absolute chirality to the polymer. If the net excess of one population over that with the opposite ellipticity is small, it seems reasonable that the chiral interaction with CP light should be able to alter the statistical distribution of the helical sections so as to reverse the absolute chirality of the polymer. It thus follows that the interaction with CP radiation allows the possibility of recognising the absolute handedness of the prevailing chain sections. For the present polymers, the interaction with CP-R light does not substantially affect the CD signals, whereas CP-L light leads to their net inversion, thus allowing the assignment of a prevailing right-handed conformation to the native macromolecules. All the aforementioned CD effects persist for at least one month and are well reproducible. Whatever the mechanism responsible for the inversion of the CD signal by interaction with the CP light, the unusual CD properties of the polymers, together with the phenomena reported by Nikolova and co-workers[2–5] and Natansohn and co-workers,[6] seem to open new possibilities for the use of azobenzene-functionalized materials in the all-optical manipulation of information. In particular, it is possible to foresee applications for materials combining optical storage capabilities, based on the modulation of the linear refractive index, with a capacity for logic functions based on chiroptical switching (Figure 6). Clearly, for technological applications, the switching time would be important. In our basic experiments, the typical irradiation time required to observe the reversal of chirality was around 60 s with a maximum irradiance of 160 mW cm^{-2}, which corresponds to a fluence of about 10 J cm^{-2}. Further investigations of the dynamics of the observed phenomena are in progress.

Conclusion

Beside the linear properties, birefringence and linear dichroism, we have studied the effect of circularly (R and L) polarised light on the chiroptical properties of native chiral films of the title polymers. A marked effect of CP-L pump radiation on the CD spectra of poly[(*S*)-**MAP-C**] and poly[(*S*)-**MAP-N**] films has been observed. Thus, after irradiation, the CD spectra show a net inversion of sign. The effect is reversible and the original shape of the CD spectra can be restored by pumping with CP-R radiation. The phenomenon does not seem to depend on a preliminary ordering of the azobenzene chromophores in the film obtained with linearly polarised pump radiation. In fact, it is observed both for linearly ordered and native amorphous films. The effect, which is analogous to those reported by Nikolova and co-workers[2–5] and by Natansohn and co-workers,[6] may be interpreted as a photoinduced inversion of the prevailing helical handedness of the polymeric macromolecules driven by a transfer of angular momentum from the circularly polarised light to the azobenzene chromophores.

In addition to the optical control of linear birefringence and dichroism, the above mentioned methacrylic polymers, as shown in Figure 6, offer the possibility of producing reversible chiroptical switching between two enantiomeric chiral arrangements of the polymeric film.

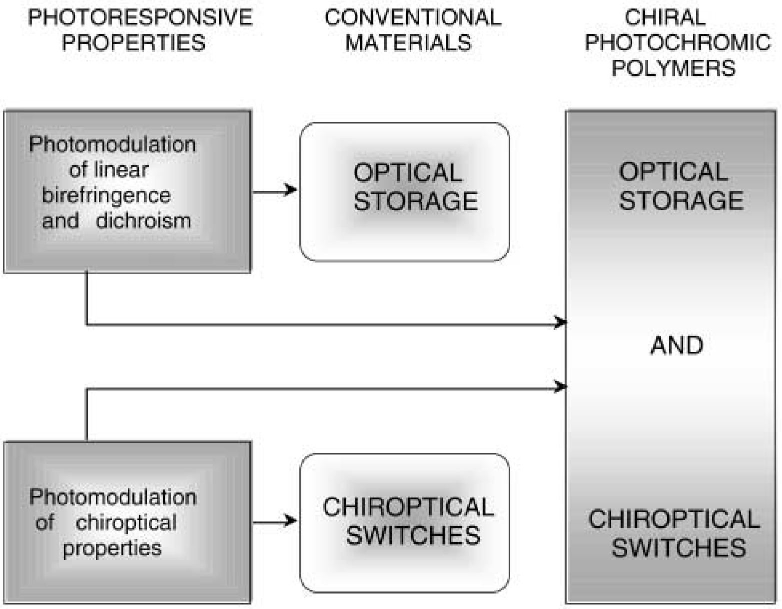

Figure 6. Coupled optical and chiroptical responses in chiral azobenzene side-chain methacrylic polymers for all-optical manipulation of information.

Experimental Section

Structures, molecular weight distributions, and thermal characterisations of the studied azobenzene polymers are shown in Scheme 1. They were synthesised as described previously.[7–9] Amorphous thin films were prepared by spin-coating of a solution of the polymer in 1-methyl-2-pyrrolidinone/tetrahydrofuran (NMP/THF) on fused silica or glass slides. The thickness of the films, measured using a Tencor P-10 profilometer, was in the range 100—350 nm, depending on the conditions of preparation. By inspection with a cross-polarised optical microscope, the native films were seen to be optically isotropic. The photoinduced linear birefringence of the polymer films was measured in situ using a pump and probe set-up by monitoring the transmittance of the samples interposed between two crossed polarisers. The pump radiation, of $\lambda = 488$ nm, was produced by a small-frame Ar$^+$ laser (Spectra Physics model 165), whereas the source of the probe light at $\lambda = 632.8$ nm was a Melles-Griot 1 mW He-Ne laser. A multiple order $\lambda/4$ quartz waveplate for 488 nm was used to circularise the pump radiation. Absorption spectra were measured with a Varian Cary 5 UV/Visible/NIR spectrometer. CD spectra were recorded with a Jasco J-810 spectropolarimeter.

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