Methacrylic Polymers Bearing in the Side-Chain an Optically Active Moiety Linked to the *trans*-4-Azobenzene Chromophore: Chiroptical Properties of Poly[(*S*)-(+)-N-methyl-(2-methacryloyloxypropanoyl)-4-aminoazobenzene]

Luigi Angiolini, Loris Giorgini, Elisabetta Salatelli*

Dipartimento di Chimica Industriale e dei Materiali, University of Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy
E-mail: angiolin@ms.fci.unibo.it

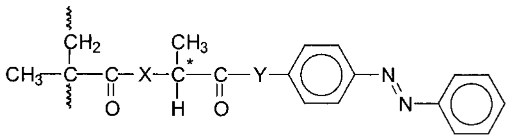
Summary: The synthesis by radical homopolymerization of a novel optically active methacrylic polymer containing a side-chain chiral moiety linked to a photochromic chromophore has been carried out starting from the related monomer *trans*-(*S*)-(+)-N-methyl-(2-methacryloyloxypropanoyl)-4-aminoazobenzene. The chiroptical properties in solution of the polymer have been investigated by circular dichroism and compared with those of the corresponding low molecular weight model compound, *trans*-(*S*)-(+)-N-methyl-(2-pivaloyloxypropanoyl)-4-aminoazobenzene. The optical activity displayed by the polymer is discussed in terms of extent of chiral conformations assumed by the macromolecules as a consequence of dipole-dipole interactions between the azoaromatic chromophores.

Keywords: azo polymers; circular dichroism; conformational analysis; optically active methacrylic polymers; photochromic polymers

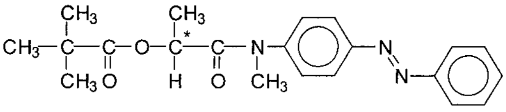
Introduction

The presence of a chiral moiety of one prevailing configuration interposed between the (meth)acrylic backbone and the azoaromatic chromophore gives the possibility to have at disposal optically active polymers with hydrocarbon main chain and side-chain photochromic groups. Due to the chirality of the pendant groups, the photochromic chromophores located along the macromolecular chain undergo an asymmetric perturbation of their electronic transitions which can be revealed by circular dichroism (CD). If the chromophores are disposed according to a mutual chiral geometry of one prevailing handedness, the electrostatic interactions which are involved may produce exciton splitting of the related dichroic bands, thus allowing to observe by CD the presence of dissymmetric conformations assumed by the macromolecules, at least for sections.[1,2]

DOI: 10.1002/masy.200451417



Poly(MLO) X = O Y = O
Poly(MLA) X = O Y = NH
Poly(MAA) X = NH Y = NH
Poly(MLM) X = O Y = NCH_3



PLM

Previous research[3,4] on optically active methacrylic polymers bearing in the side chain the chiral moiety of L-lactic acid or L-alanine, indicated a strong dependence of optical activity, as measured by CD, on the chemical structure of the asymmetric group. In particular, when the optically active residue was L-lactic acid linked through an estereal bond to the azoaromatic moiety, such as in poly(MLO), an exciton couplet of weak intensity ($\Delta\varepsilon = -1.52$ and $+0.08$ $l \cdot mol^{-1} \cdot cm^{-1}$ at 336 and 290 nm, respectively)[4] could be observed in the CD spectral region related to the π-π^* azoaromatic transitions, thus suggesting the presence in solution of dissymmetric conformations of one prevailing helicity assumed by chain sections of the macromolecules. A much enhanced evidence of conformational dissymmetry was however noticed in the polymeric derivative having the L-lactic acid residue linked to the azobenzene group through a secondary amide bond, as in poly(MLA): in this case a strong CD exciton couplet ($\Delta\varepsilon = +5.49$ and -5.15 $l \cdot mol^{-1} \cdot cm^{-1}$ at 362 and 325 nm, respectively)[3]was observed in the chromophore absorption region, indicative of the presence to a much higher extent of dissymmetric conformations of the macromolecules. By contrast, with poly(MAA), bearing the L-alanine moiety linked to the azobenzene group through a secondary amide bond, no appreciable dichroic bands at all were observed.[3] This behaviour was attributed to the existence of hydrogen bonding by the secondary amide groups stabilizing in poly(MLA), or disfavouring in poly(MAA), the presence of chiral conformations of the macromolecules.

To confirm this hypothesis, we have envisaged the synthesis of a further polymeric derivative, unable to produce hydrogen bonds, poly[(*S*)-(+)-N-methyl-(2-methacryloyloxypropanoyl)-4-aminoazobenzene] [poly(MLM)], containing the L-lactic acid residue linked to the azobenzene group by a tertiary amide bond, in order to verify to what extent the contribution of this interaction can affect the prevailing conformation of the macromolecules. Poly(MLM) has been prepared by radical homopolymerization of the corresponding monomer MLM. In order to evaluate the effect on optical activity produced by the presence of the macromolecular chain, we have also synthesized and investigated the reference compound (*S*)-(+)-N-methyl-(2-pivaloyloxypropanoyl)-4-aminoazobenzene (PLM), as the structural model of the repeating unit of the polymer.

Experimental part

Trans-(S)-(+)-N-methyl-(2-methacryloyloxypropanoyl)-4-aminoazobenzene (MLM)

The monomer was synthesized starting from O-methacryloyl-L-lactic acid[5], prepared according to a more convenient method,[6] followed by condensation with ethyl chloroformiate and subsequent reaction with *trans*-N-methyl-4-aminoazobenzene.[7]

Trans-(S)-(+)-N-methyl-(2-pivaloyloxypropanoyl)-4-aminoazobenzene (PLM)

Model compound PLM was obtained by following the same procedure described above for MLM, starting from O-pivaloyl-L-lactic acid,[3] $[\alpha]_D^{25} = +235.7$ (c = 0.31, $CHCl_3$).

Poly[(S)-(+)-N-methyl-(2-methacryloyloxypropanoyl)-4-aminoazobenzene] [poly(MLM)]

The homopolymerization of MLM was carried out in THF at 60°C for 72 hours using 2,2'-azobisisobutyronitrile (AIBN) as free radical initiator, $[\alpha]_D^{25} = +277.0$ (c = 0.30, $CHCl_3$).

Measurements

The number average molecular weight ($\overline{M}_n$) and polydispersity ($\overline{M}_w/\overline{M}_n$) of the polymer were determined in THF solution by SEC using a HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5μ MXL column and a UV-Vis detector Linear Instruments model UVIS-200, working at 254 nm. Calibration curves were obtained by using several monodisperse polystyrene standards. UV absorption spectra were recorded at 25°C on a Perkin Elmer Lambda 19 spectrophotometer on $CHCl_3$ solutions by using cell path lengths of 1 and 0.1 cm for the 550-400 and 400-250 nm spectral regions, respectively. Azobenzene chromophore concentrations of about $5 \cdot 10^{-4}$ mol $\cdot$ l^{-1} were used. Optical activity measurements were accomplished at 25°C on $CHCl_3$ solutions with a Perkin Elmer 341 digital polarimeter, using a cell path length of 1 dm. Specific rotation values at the sodium D line are expressed as deg $\cdot$ $dm^{-1} \cdot g^{-1} \cdot dm^3$. CD spectra were recorded at 25°C on a Jasco 810 A dichrograph, using the same path lengths, solutions and concentrations as for UV measurements. $\Delta\varepsilon$ values, expressed as $l \cdot mol^{-1} \cdot cm^{-1}$, were calculated by the following equation: $\Delta\varepsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in deg $\cdot$ $cm^2 \cdot dmol^{-1}$ refers to one azobenzene chromophore.

Results and discussion

The chemical structure of monomer MLM and model PLM, prepared in accordance with a procedure previously reported for analogous derivatives,[3] starting from methacryloyl- or pivaloyl-L-lactic acid, respectively, was confirmed by IR and ^{1}H-NMR. The monomer was then submitted to radical homopolymerization in THF solution by adopting the usual procedure employing AIBN as thermal initiator. The polymeric product, purified by repeated dissolution and reprecipitation with methanol, displayed the expected IR and ^{1}H-NMR spectra showing the disappearance of the bands related to the methacrylic double bond, present in the monomer. The number average molecular weight $\overline{M}_n$ of poly(MLM) resulted 4900 g/mol, with polydispersity $\overline{M}_w/\overline{M}_n$ of 1.4, both these values being very close to those previously found for poly(MLA) (3800 g/mol and 1.4, respectively).[3]

The UV-vis spectra in chloroform solution of PLM and poly(MLM) (Fig. 1), exhibit in the region 250-500 nm two absorption bands with maxima centered around 440 and 330 nm, related to the n-π* and π-π* electronic transitions, respectively, of the azoaromatic chromophore in the *trans* configuration.[8] No particular difference between absorption wavelength and intensity is displayed by model and polymer as far as the former band is concerned, whereas a slight hypochromic effect can be noticed in the latter on passing from PLM to poly(MLM) (Table 1).

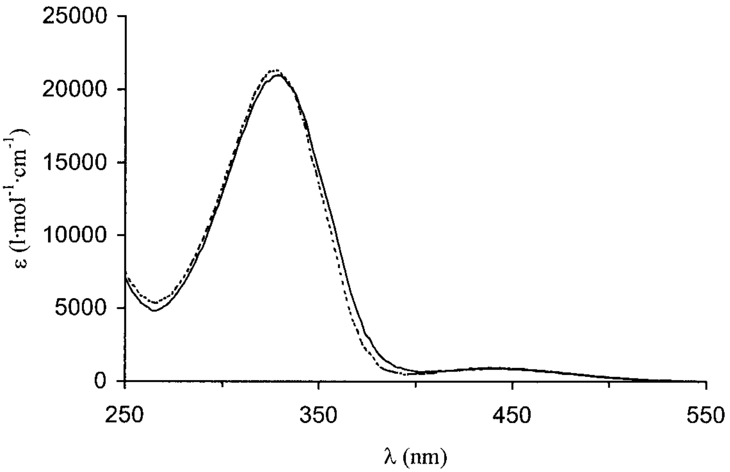


Figure 1. UV-vis spectra in chloroform solution of PLM (---) and poly(MLM) (—).

The presence of hypochromism in polymeric derivatives bearing side chain aromatic chromophores with respect to the related monomeric compounds has been frequently observed[3,9-11] and attributed to the occurrence of electrostatic dipole-dipole interactions between the neighbouring aromatic moieties.[12,13] In the present case the observed effect is very small and indicates that these interactions are present in poly(MLM)only to a low extent.

Table 1. UV-vis spectra in chloroform of poly(MLM) and PLM.

Sample	n-π* transition		π-π* transition	
	λ_{max}	ε_{max}	λ_{max}	$\varepsilon_{max}\cdot 10^{-3}$
	nm	$l\cdot mol^{-1}\cdot cm^{-1}$	nm	$l\cdot mol^{-1}\cdot cm^{-1}$
poly(MLM)	440	900	329	20.9
PLM	444	910	328	21.2

The CD spectrum of PLM in chloroform solution (Fig. 2) displays two positive dichroic absorptions with maxima at 430 and 325 nm (Table 2), strictly related to the UV-vis absorption maxima connected with the n-π* and π-π* electronic transitions, respectively.

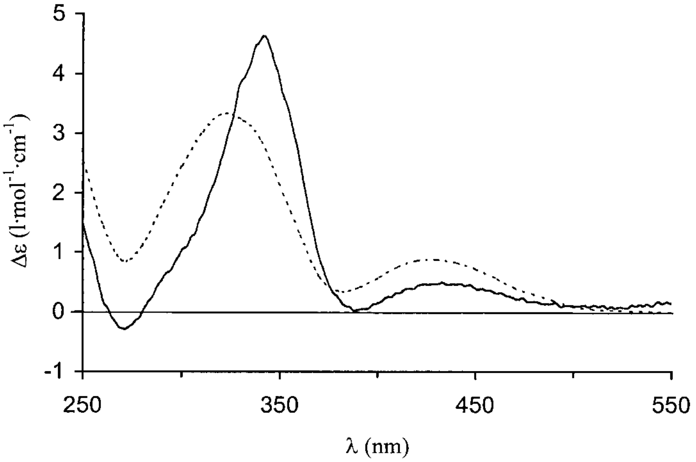


Figure 2. CD spectra in chloroform solution of PLM (---) and poly(MLM) (—).

By contrast, the CD spectrum of poly(MLM) exhibits in the spectral region related to the π-π* electronic transition a strong positive band with maximum at 342 nm and a much less intense negative band at 271 nm, with a crossover point at about 281 nm (Table 2). A further positive dichroic band at 434 nm, connected with the n-π* transition is also present in the CD spectrum of poly(MLM). The presence of two dichroic bands of opposite sign and different intensity in the π-π* region suggests that this is the result of two spectral contributions given by azoaromatic chromophores experiencing different conformational arrangements: the main one giving rise to a positive band with the maximum centered in correspondence with the UV-vis absorption, and related to isolated chromophores, in a similar manner as the model compound, the lesser one being attributable to an exciton splitting of low amplitude providing two bands of opposite sign, with a crossover point at the same wavelength as the UV-vis maximum. This latter contribution, absent in PLM, could be due to the presence of electrostatic interactions between chromophores disposed according to a chiral geometry with a prevailing helicity sense along the macromolecular chain.

Table 2. CD spectra in chloroform of poly(MLM) and PLM.

Sample	n-π* transition		π-π* transition				
	λ_1 [a]	$\Delta\varepsilon_1$	λ_2 [a]	$\Delta\varepsilon_2$	λ_c [b]	λ_3 [a]	$\Delta\varepsilon_3$
	nm	$\mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$	nm	$\mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$	nm	nm	$\mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$
poly(MLM)	434	+ 0.48	342	+ 4.63	281	271	– 0.29
PLM	430	+ 0.88	325	+ 3.25	–	–	–

[a] Dichroic maximum wavelength.

[b] Crossover point.

The contribution by conformational dissymmetry to the overall optical activity of poly(MLM) appears therefore of limited extent, as suggested also by the specific optical rotatory power at the sodium D line of PLM and poly(MLM), the $[\alpha]_D^{25}$ value observed for the polymer (+277.0°) as compared to the model (+235.7°) being not so relevantly larger to suggest the presence of an important amount of chain sections possessing conformational chirality.

Conclusions

The chiroptical properties of poly(MLM) indicate that, differently from the low molecular weight structural model PLM, which does not display any particular conformational order, the macromolecules assume in chloroform solution dissymmetric conformations of one prevailing handedness. However, the amount of ordered structures in poly(MLM) is rather low, similar to that shown by poly(MLO), which also lacks of secondary amide groups potentially able to give hydrogen bonds. It therefore appears that the remarkable optical activity displayed by poly(MLA) is mainly attributable to the presence of the aromatic secondary amide moiety, which gives the possibility of hydrogen bonds favouring the assumption of chiral conformations by the macromolecules. By contrast, the presence in poly(MAA) of the aliphatic secondary amide group in addition to the aromatic one, contributes in a predominant manner to the stabilization of macromolecular structures lacking of significant chirality.

Acknowledgements

The financial support by MURST (fondi ex-40%) and Consorzio INSTM is acknowledged.

[1] L. Angiolini, D. Caretti, C. Carlini, in: "*The Polymeric Materials Encyclopedia*", J. C. Salamone, Ed., CRC Press Inc., Boca Raton 1996, Vol. 7, p.5116.
[2] A. Altomare, R. Solaro, L. Angiolini, D. Caretti, C. Carlini, *Polymer* **1995**, *36*, 3819.
[3] L. Angiolini, D. Caretti, C. Carlini, E. Salatelli, *Macromol. Chem. Phys.* **1995**, *196*, 2737.
[4] L. Angiolini, D. Caretti, L. Giorgini, E. Salatelli, A. Altomare, C. Carlini, R. Solaro, *Polymer* **1998**, *39*, 6621.
[5] US 3067180 (1962), Int. Latex Corp., invs.: V. A. Miller, R. R. Brown, E. B. Gienger Jr.; *Chem. Abstr.* **1963**, *58*, 10381f.
[6] L. Angiolini, D. Caretti, C. Carlini, L. Giorgini, E. Salatelli, *Macromol. Chem. Phys.* **1999**, *200*, 390.
[7] J. A. Miller, C. Miller, *J. Exp. Med.* **1948**, *87*, 139.
[8] H. H. Jaffè, M. Orchin, "*Theory and Applications of Ultraviolet Spectroscopy*", Wiley, New York 1962.
[9] E. Chiellini, R. Solaro, G. Galli, A. Ledwith, *Macromolecules* **1980**, *13*, 1654.
[10] R. N. Majumdar, C. Carlini, *Makromol. Chem.* **1980**, *181*, 201.
[11] C. Carlini, F. Gurzoni, *Polymer* **1983**, *24*, 101.
[12] I. Tinoco Jr., *J. Am. Chem. Soc.* **1960**, *82*, 4785.
[13] K. Okamoto, A. Itaya, S. Kusabayashi, *Chem. Lett.* **1974**, 1167.