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Optically Active Methacrylic Polymers Bearing in the Side Chain the (*S*)-3-Hydroxypyrrolidinyl Group Linked to *trans*-bisazoaromatic Chromophore: Synthesis and Characterization

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Summary: The synthesis by radical homopolymerization of a novel optically active methacrylic polymer containing a side-chain chiral moiety linked to a photochromic bisazoaromatic chromophore has been carried out starting from the related monomer (*S*)-3-methacryloyloxy-1-[4′-phenylazo-(4-azobenzene)]-pyrrolidine [(*S*)-**MPAAP**]. The polymeric derivate has been fully characterized and its spectroscopic properties compared to those of the monomer and of the corresponding homopolymer bearing only one azoaromatic chromophore in the side chain. The optical activity displayed by the bisazo polymer is discussed in terms of extent of chiral conformation assumed by the macromolecules as a consequence of dipole-dipole interactions between the bisazoaromatic chromophores.

Keywords: bisazoaromatic chromophore; circular dichroism; optically active methacrylic polymers; photochromic polymers

Introduction

Photochromic azo-containing polymers are currently intensively studied for their potential use as materials for serial and parallel optical data storage, relief gratings, and for second-order nonlinear optical applications.[1] Their photoresponsive behaviour is related to photoinduced *trans-cis-trans* isomerization cycles of the azobenzene chromophores, by irradiation with light of the appropriate frequency, polarization and intensity.

Previously,[2,3] methacrylic polymers bearing in the side chain the chiral cyclic (*S*)-3-hydroxypyrrolidine moiety interposed between the main chain and the trans-azoaromatic chromophore, substituted or not in the 4′ position by an electron-withdrawing group, have been synthesized and investigated (Fig. 1 poly[(*S*)-**MAP**]). In these materials, the presence of a rigid chiral moiety of one prevailing absolute configuration favours the establishment, at least within chain segments of the macromolecules, of a chiral conformation of one prevailing helical handedness, which can be observed by circular dichroism (CD).

The presence of both the azoaromatic and chiral functionalities allows the polymers to display both the properties typical of dissymmetric systems (optical activity, exciton splitting of dichroic absorptions), as well as the features typical of photochromicmaterials (photorefractivity, photoresponsiveness, NLO properties).[4–6]

In this context, it appeared of interest to investigate analogue polymeric materials containing in the side chain a more rigid conjugated system such as the bisazoaromatic chromophore, which is expected

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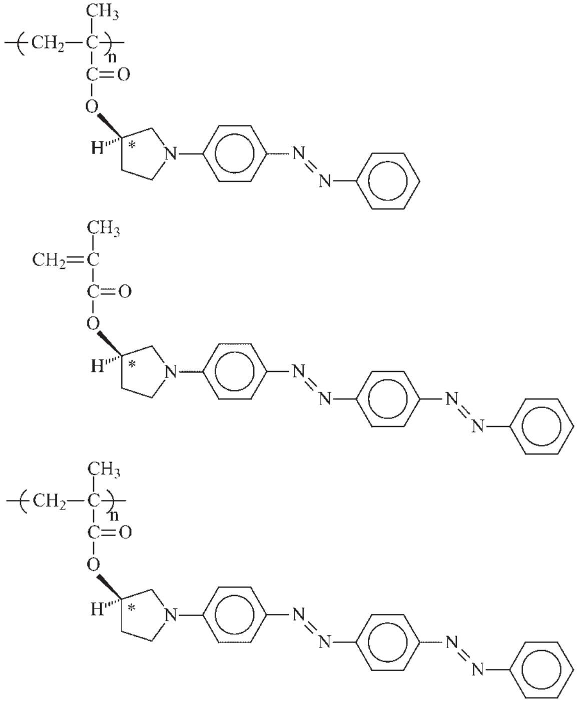


poly[(*S*)-**MAP**]

(*S*)-**MPAAP**

poly[(*S*)-**MPAAP**]

Figure 1.
Structure of poly[(S)-**MAP**], (S)-**MPAAP** and poly[(S)-**MPAAP**].

to have larger NLO and photoresponsive properties as compared with the previously investigated polymers with only one azoaromatic group in the side chain.[7–9]

In the present paper, we report synthesis and characterization of the optically active monomer (*S*)-3-methacryloyloxy-1-[4′-(phenylazo)-4-azobenzene] pyrrolidine [(*S*)-**MPAAP**] and its radical polymerization to give the corresponding homopolymer poly{(*S*)-3-methacryloyloxy-1-[4′-phenylazo-(4-azobenzene)]-pyrrolidine} {poly[(*S*)-**MPAAP**]}. The structures of these two novel compounds are shown in Figure 1.

Monomer and homopolymer have been fully characterized and their spectroscopical properties compared to those of the related derivate poly[(*S*)-**MAP**] bearing only one azoaromatic chromophore in the side chain [2] (Figure 1).

Experimental Section

*(S)-3-Hydroxy-1-[4′-phenylazo-(4-azobenzene)]-pyrrolidine [(S)-**HPAAP**].*

The intermediate was obtained by coupling of the diazonium salt of 4-amino-4′-azobenzene[10] with (*S*)-(−)-3-hydroxy-1-phenyl pyrrolidine [(*S*)-**HPP**].[2] Yield 40.5%, m.p. 150–152 °C.

UV-VIS (in $CHCl_3$): $\varepsilon_{max} = 19900$ (332 nm) and 36000 (474 nm) L mol^{-1} cm^{-1}.

*(S)-3-Methacryloyloxy-1-[4′-phenylazo-(4-azobenzene)]-pyrrolidine [(S)-**MPAAP**].*

The monomer was synthetized by reaction of (*S*)-**HPAAP** with methacryloyl chloride in anhydrous THF in the presence of triethylamine and a catalytic amount of dimethylaminopyridine (DMAP). Yield 65.0%, m.p. 158–160 °C.

*Poly{(S)-3-methacryloyloxy-1-[4′-phenylazo-(4-azobenzene)]-pyrrolidine} {poly[(S)-**MPAAP**]}.*

The homopolymerization of (*S*)-**MPAAP** was carried out in glass vials in DMF at 60 °C for 72 hours using 2,2′-azobisisobutyronitrile (AIBN) as free radical thermal initiator.

Measurements

Number average molecular weight ($\overline{M}_n$) and polydispersity ($\overline{M}_w/\overline{M}_n$) of poly[(*S*)-**MPAAP**] were determined in THF solution by SEC using a HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5 μ 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 L^{-1} were used. 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 mol^{-1} cm^{-1}, were calculated by the following equation: $\Delta\varepsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in deg cm^2 $dmol^{-1}$ refers to one azobenzene chromophore. The glass transition temperature values were determined by differential scanning calorimetry (DSC) on a TA Instrument DSC 2920 Modulated apparatus at a heating rate of 10 °C/min under nitrogen atmosphere on samples of 5–9 mgr.

The initial thermal decomposition temperature (T_d) was determined on the polymeric samples with a Perkin-Elmer TGA-7 thermogravimetric analyzer by heating the samples in air at a rate of 20 °C/min. Checking of the liquid crystalline behaviour was carried out with a Zeiss Axioscope2 polarising microscope through crossed polarizers fitted with a Linkam THMS 600 hot stage.

Melting points (uncorrected) were determined in glass capillaries on a Büchi 510 apparatus at a heating rate of 1 °C/min.

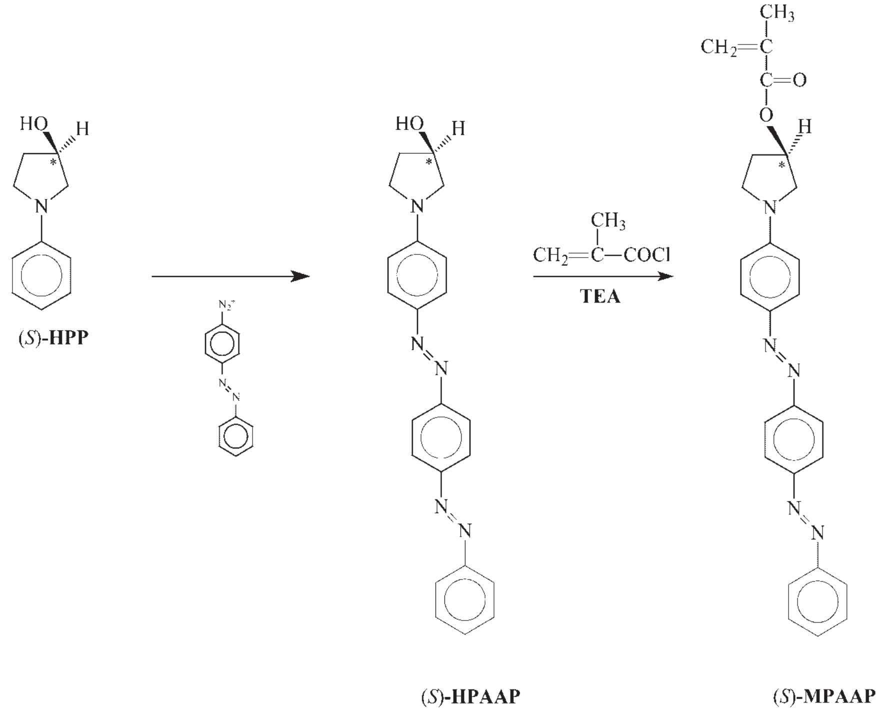
Results and Discussion

The synthesis of monomer (*S*)-**MPAAP** (Scheme 1) was carried out starting from (*S*)-**HPP** by coupling with the diazonium salt deriving from 4-amino-4′-azobenzene to give the novel azoderivate (*S*)-**HPAAP**, which was finally submitted to esterification with methacryloyl chloride.

The structures of the products were confirmed by ^{1}H-NMR and FT-IR. The optical activity at the sodium D-line of (*S*)-**MPAAP** as well of the precursor (*S*)-**HPAAP** could not be measured with accuracy because of the strong absorption of the azoaromatic chromophore at that wavelength. However, previous data[2] concerning the optical purity of the 4′-unsubstituted methacryloyl derivatives bearing in side-chain one azoaromatic group prepared through a similar synthetic pathway indicate that an enantiomeric excess of at least 90% was present in those compounds, thus excluding the possibility of racemization at the asymmetric center in the course of the synthesis.

Polymerization of monomer, carried out in DMF solution under radical conditions by using AIBN as a thermal initiator, produced the desired poly[(*S*)-**MPAAP**]. The solid polymeric product was repeatedly dissolved in DMF, reprecipitated again in methanol, and submitted to a final purification from monomeric and oligomeric impurities by exhaustive Soxhlet extraction with methanol followed by acetone.

The occurrence of polymerisation involving the methacrylic double bond was confirmed by FT-IR, showing the disappearance of the band at 1634 cm^{-1}, related to the stretching vibration of the double bond in the monomer, and the shift of the ester carbonyl stretching frequency from 1709 cm^{-1} in the monomer to higher frequency (1729 cm^{-1}) in the polymer, due to the reduced electron delocalization



Scheme 1.
Synthetic route to monomer (*S*)-**MPAAP**.

determined by the reaction of the methacrylic double bond. In accordance with these data, the resonances at 5.60 and 6.10 ppm, related to the methacrylic CH_2 protons of monomer (*S*)-**MPAAP** were absent in the ^1H NMR spectra of the polymer, and the methacrylic methyl resonance was shifted from 1.95 ppm to higher field.

As reported in Table 1, poly[(*S*)-**MPAAP**] was obtained in poorer yield and with lower number average molecular weight, as determined by SEC, as compared to the related poly[(*S*)-**MAP**],[2] probably due to the stiffness and steric hindrance of the bisazoaromatic group disfavouring the radical propagation in the polymerisation process.

Thermal stability of poly[(*S*)-**MPAAP**], which is one of the most important properties for the applicability of these materials in optoelectronics field, was measured as

Table 1.
Characterization data of polymeric derivative compared whit poly[(S)-**MAP**].

Sample	Yield[a)]	$\overline{M}_n$[b)]	$\overline{M}_w/\overline{M}_n$[b)]	T_g[c)]	T_d[d)]
	%	g/mol		°C	°C
Poly[(S)-**MPAAP**]	14	27.300	1.3	191	283
Poly[(S)-**MAP**][e)]	69	31.500	1.6	169	314

[a)] Calculated as (g polymer/g monomer) · 100.
[b)] Determined by SEC in THF solution at 25 °C.
[c)] Glass transition temperature determined by DSC at 10 °C/min heating rate under nitrogen flow.
[d)] Initial decomposition temperature as determined by TGA at 20 °C/min heating rate under air flow.
[e)] Ref [2].

the onset decomposition temperature (T_d) (Table 1) by thermogravimetric analysis (TGA) in the air. The high value ($T_d = 283\,^{\circ}C$) observed, indicative of appreciable thermal stability of the polymer under the adopted conditions, is due to the remarkable presence of strong dipolar interactions in the solid state among the bisazoaromatic chromophores located in the side chain. Observation of a thin film of poly[(*S*)-**MPAAP**] with a polarising microscope did not reveal any liquid crystalline behaviour.

Poly[(*S*)-**MPAAP**] exhibits by differential scanning calorimetry (DSC) measurements in the 25–250 °C temperature range, only a second order thermal transition attributed to glass transition. No endothermic crystalline melting peaks, in accordance with the substantially amorphous character of the macromolecules in the solid state, are evidenced.

It is worth observing that poly[(*S*)-**MPAAP**] exhibits a considerably higher T_g value (191 °C) than poly[(*S*)-**MAP**] ($T_g = 169\,^{\circ}C$), indicative of larger inter- and/or intramolecular polar interactions between the neighbouring side chain aromatic chromophores, due to the increased dipole moment of the bisazoaromatic chromophore, originated by the larger extension of the conjugated system (Table 1 and Figure 2).

T_g values greater than 150 °C are considered very desirable in order to preserve at room temperature the photo- or electrically-originated orientation of the dipoles present in polymethacrylates bearing side-chain conjugated azoaromatic systems, as they allow to obtain a temporal stability as good as that of many crosslinked NLO systems described in the literature.[11]

Both the good thermal stability and the high value of T_g suggest that this polymeric material, may be promisingly used for applications in optoelectronics.

The UV-vis spectrum of poly[(*S*)-**MPAAP**] in $CHCl_3$ solution (Table 2 and Figure 3) exhibits, in the 250–700 nm spectral region, two absorption bands, centred at around 463 and 332 nm. The former one, more intense, is attributed to electronic transitions such as n-π^*, π-π^* and internal charge transfer of the bisazoaromatic chromophore. The latter to the π-π^* electronic transitions of singles aromatic rings.[13]

As expected, a remarkable bathochromic shift of 55 and 74 nm for the first and the second bands, respectively, is observed by comparing poly[(*S*)-**MPAAP**] to poly[(*S*)-**MAP**] (Table 2 and Figure 3). This effect can be attributed to the larger conjugation through the bisazoaromatic system, upon introduction of an additional azoic bond which delocalizes the π electrons and reduces the electronic transition energies.[7]

A significant hypochromism and a blue shift are observed for both the first and the second band when passing from the mono-

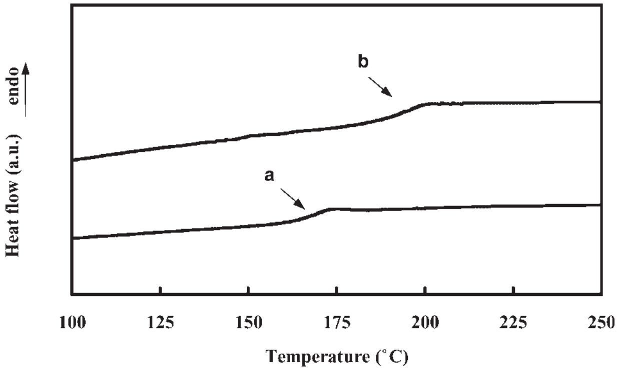


Figure 2.
DSC thermograms of poly[(S)-**MAP**](**a**) and poly[(S)-**MPAAP**] (**b**).

Table 2.
UV-vis spectra in $CHCl_3$ of poly[(*S*)-**MPAAP**], (*S*)-**MPAAP** and poly[(*S*)-**MAP**].

Sample	1st band		2nd band	
	λ_{max}[a]	$\varepsilon_{max}\ 10^{-3}$[b]	λ_{max}[a]	$\varepsilon_{max}\ 10^{-3}$[b]
	nm	L mol^{-1} cm^{-1}	nm	L $mol^{-1}cm^{-1}$
Poly[(*S*)-**MPAAP**]	463	33.4	332	17.0
(*S*)-**MPAAP**	465	34.3	332	15.6
Poly[(*S*)-**MAP**][c]	408	28.3	258	10.5

[a] Wavelength of maximum absorbance.
[b] Calculated for one repeating unit in the polymers.
[c] Ref [2].

mer (*S*)-**MPAAP** to the corresponding polymer poly[(*S*)-**MPAAP**]. Similar behaviour was previously observed in several polymers bearing side-chain azoaromatic chromophores[2,14–16] and attributed to the occurrence of electrostatic dipole-dipole interactions between the neighbouring aromatic chromophores.

This behaviour suggests that the investigated macromolecules are characterized by strong intramolecular polar interactions favoured by the closeness of the side-chain chromophores disposed along the macromolecular chain.

The chiroptical properties of poly[(*S*)-**MPAAP**] and (*S*)-**MPAAP** have been investigated by CD in the spectral region 250–700 nm in order to assess the conformational features of the macromolecular chains.

The CD spectrum of (*S*)-**MPAAP** in chloroform solution (Fig. 3) displays only weak positive and negative dichroic absorptions with maxima at 465 and 330 nm (Table 3), strictly related to the UV-vis 1st and 2nd bands, respectively.

By contrast, the CD spectrum of poly[(*S*)-**MPAAP**] exhibits two intense dichroic bands of opposite sign and comparable intensity, connected to the electronic transitions of the UV-vis first band, with a cross over point around 454 nm, close to the UV-vis maximum absorption. Such a behaviour is typical of an exciton splitting determined by cooperative interactions between side-chain azoaromatic chromophores disposed in a mutual chiral geometry of one prevailing handedness.[17]

A further exciton coupling, of smaller intensity, is also present with a cross over point near to the second UV maximum absorption. Consequently, the much higher optical activity of poly[(*S*)-**MPAAP**] with respect to that one of the corresponding monomer, can be attributed to the presence of dipole-dipole interactions between side-chain bisazoaromatic chromophores favouring a conformational arrangement with a pre-

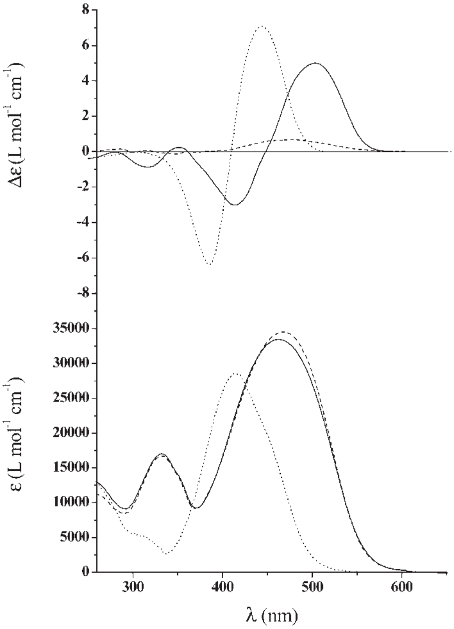


Figure 3.
CD (up) and UV-vis (bottom) spectra in $CHCl_3$ solution of (*S*)-**MPAAP**(---), poly[(*S*)-**MPAAP**] (—) and poly[(*S*)-**MAP**] (····).

Table 3.
CD Spectra in $CHCl_3$ of poly[(*S*)-**MPAAP**], (*S*)-**MPAAP** and poly[(*S*)-**MAP**].

Sample	1st band					2nd band				
	λ_1 [a]	$\Delta\varepsilon_1$	λ_0 [b]	λ_2 [a]	$\Delta\varepsilon_2$	λ_3 [a]	$\Delta\varepsilon_3$	λ_0 [b]	λ_4 [a]	$\Delta\varepsilon_4$
	nm	$Lmol^{-1}cm^{-1}$	nm	nm	$Lmol^{-1}cm^{-1}$	nm	$Lmol^{-1}cm^{-1}$	nm	nm	$Lmol^{-1}cm^{-1}$
Poly[(S)-**MPAAP**]	500	+5.09	450	415	−3.22	350	+0.42	340	318	−0.81
(S)-**MPAAP**	465	+0.73	—	—	—	330	−0.12	—	—	—
Poly[(S)-**MAP**] [c]	445	+7.35	409	387	−6.42	258	−0.32	—	—	—

[a] Dichroic maximum wavelength.
[b] Wavelength at cross over point.
[c] Ref [2].

vailing chirality in the macromolecule, at least for chain sections.

Similar results were previously found also for the analogous poly[(*S*)-**MAP**],[2] having in the side chain only one azoaromatic moiety (Table 3 and Figure 3).

A commonly adopted assessment of the strength of dichroic signals is made in terms of chiral anisotropy coefficient, *g*, defined as the ratio between the CD signal ($\Delta\varepsilon$) and the UV-vis absorption coefficient (ε) measured for the same sample at the same frequency, usually chosen at the maximum of the CD band.[18–20]

In order to compare the chiroptical properties of poly[(*S*)-**MAP**] and poly[(*S*)-**MAAP**] and avoid ambiguities and uncertainties due to the choice of a specific frequency, it has been preferred to determine an integrated *g*-factor, defined as the ratio between the integrated area in absolute value of the CD signal and that of the 1st UV-vis absorption band.

With this approach, poly[(*S*)-**MPAAP**] exhibits in chloroform solution, a chiral anisotropy degree (0.012×10^{-2}) lower than poly[(*S*)-**MAP**] (0.025×10^{-2}).

This result is presumably due to intrinsic structural properties of poly[(*S*)-**MAP**], which with only one azo bond in comparison to the bisazoaromatic chromophore, is sterically less hindered, thus favouring a mutual chiral geometry of one prevailing handedness for longer chain sections.

However, the significant intensity of the dichroic bands of poly[(*S*)-**MAAP**] still makes this materials potentially useful for chiroptical switching applications.

Conclusions

A new homopolymeric methacrylate has been obtained by radical polymerization of monomer (*S*)-**MPAAP**, bearing the optical active (*S*)-3-hydroxy pyrrolidinyl group linked to the bisazoaromatic chromophore.

The pronounced red shift of the maximum absorption wavelength on passing from the polymeric derivative bearing only one azo bond to the bisazoaromatic containing polymer appears of great interest for photoresponsive applications utilizing a laser light of wavelength above 488 nm.

The optical activity of poly[(*S*)-**MAAP**] suggests that the macromolecules assume in solution highly homogeneous conformations with a prevailing chirality, as demonstrated by the presence of a strong exciton couplet in the CD spectra.

This behaviour can be attributed to the combined effects of the strongly dipolar conjugated bisazoaromatic system with the conformational stiffness of pyrrolidine ring, favouring the instauration of chain sections of the macromolecules with a prevailing handedness. The presence of strong polar interactions between chromophores in the solid state also produces relevant thermal properties with a high value of T_g, which can be of interest for nanoscale technological applications such as all-optical manipulation of informations, optoelectronics and chiroptical switches.

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[1] J. A. Delaire, K. Nakatani, *Chem. Rev.* **2000**, *100*, 1817.

[2] L. Angiolini, D. Caretti, L. Giorgini, E. Salatelli, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3257.

[3] L. Angiolini, D. Caretti, L. Giorgini, E. Salatelli, *Polymer* **2001**, *42*, 4005.

[4] L. Angiolini, R. Bozio, L. Giorgini, D. Pedron, G. Turco, A. Daurù, *Chem. Eur. J.* **2002**, *8*, 4241.

[5] L. Angiolini, T. Benelli, L. Giorgini, A. Painelli, F. Terenziani, *Chem. Eur. J.* 2005, in press.

[6] L. Angiolini, T. Benelli, R. Bozio, A. Daurù, L. Giorgini, D. Pedron, E. Salatelli, *Eur. Polym. J.* **2005**, *41*, 2045.

[7] X. Meng, A. Natansohn, P. Rochon, *Polymer* **1997**, *38*, 2677.

[8] J. Wang, L.Z. Zhang, Y. Niu, Z. Liang, Y. Chen, Y. Huang, H. Wang, W. Lin, *Polym. Int.* **2003**, *52*, 1165.

[9] M. Jin, Q. Xing, R. Lu, T.H. Xu, Y.Y. Zhao, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4237.

[10] A.A.R. Sayigh, A. Stuber, H. Ulrich, DE patent 2123623, **1971**.

[11] M.A. Shoondorp, A.J. Shouten, J.B.E. Hulshof, E.P. Shuddle, B.L. Feringa, *Recueil*, **1994**, *113*, 250.

[12] D.R. Robello, P.T. Dao, J.S. Schildkraut, M. Scozzafava, E.J. Urankar, C.S. Willand, *Chem. Mater.* **1995**, *7*, 284.

[13] A. Altomare, F. Ciardelli, M.S. Ghiloni, R. Solaro, N. Tirelli, *Macromol Chem. Phys.* **1997**, *198*, 1739.

[14] E. Chiellini, R. Solaro, G. Galli, A. Ledwith, *Macromolecules* **1980**, *13*, 1654.

[15] RN. Majumdar, C. Carlini, *Makromol Chem.* **1983**, *181*, 201.

[16] Jr. I. Tinoco, *J. Am. Chem. Soc.* **1960**, *82*, 4785.

[17] F. Ciardelli, C. Carlini, R. Solaro, A. Altomare, O. Pieroni, JL. Houben, A. Fissi, *Pure Applied Chem.* **1999**, *15*, 2450.

[18] A. Rodger, B. Nord'en, *Circular Dichroism, and Linear Dichroism*. Oxford: Oxford University Press, **1997**, Chapters 5 and 7.

[19] S.F. Mason, *Molecular Optical Activity and the Chiral Discrimination*. Cambridge: Cambridge University Press, **1982**, Chapter 3.

[20] N. Berova, K. Nakanishi, R.W. Woody, *Circular dichroism, principles and applications*. New York: Wiley-VCH inc., **2000**.