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Synthesis, chiroptical properties and photoresponsive behaviour of optically active poly[(S)-4-(2-methacryloyloxypropanoyloxy)azobenzene]

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A novel optically active monomer containing a photochromic chromophore, such as *trans*-(S)-4-(2-methacryloyloxypropanoyloxy)azobenzene and its low molecular weight model compound *trans*-(S)-4-(2-pivaloyloxypropanoyloxy)azobenzene were prepared. Free radically initiated homopolymerization of the methacrylic monomer afforded in fairly high yield a rather high molecular weight polymer which was molecularly and structurally characterized. The molecular mobility of the polymer in all *trans* configuration, as well as chiroptical properties, photoisomerization kinetics and photochromic behaviour were investigated and compared with those of the low and high molecular weight related compounds. The polymer photoresponsive properties were evaluated by circular dichroism measurements at various extents of photoisomerization. All the results are discussed in terms of structural requirements of the macromolecules. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

The simplest synthetic route for preparing optically active hydrocarbon main-chain polymers with pendant photochromic moieties is based on the copolymerization of an optically active vinyl or vinylidenic monomer with an achiral comonomer having the appropriate photochromic chromophore[1–8]. Indeed, the resulting copolymer macromolecules are found to exist in a dissymmetric conformation with a prevailing chirality, at least for sections, due to the presence in the side chains of asymmetric centres having one single absolute configuration. In this particular situation the conformational dissymmetry with a prevailing handedness is transmitted to the achiral co-units[9–11], thus inducing a chiral perturbation on the electronic transitions of the photochromic chromophores, readily observable by circular dichroism (CD) measurements.

However, in order to obtain a prevalence of one-handed chirality, a high content of optically active co-units is required and this causes the contemporary increase of the average distance between the photochromic groups along the backbone, thus strongly reducing the possibility of cooperative dipole–dipole interactions between the side-chain chromophores disposed in a fixed mutual geometry of a prevailing chirality (responsible for exciton splitting of the related dichroic bands) and hence lowering the amplitude of their CD bands.

Taking into account that hydrocarbon main-chain polymers do not exhibit any skeletal chromophore CD

band directly connected to the type of conformational order of the macromolecules, as occurs in the case of polypeptides[3,12–14], the unique source of conformational information derives from the CD bands related to the side-chain chromophores. This makes it more difficult to establish a close correlation between chiroptical and conformational properties of the macromolecules.

In order to overcome this drawback, we recently proposed[15] the synthesis of optically active polymers containing in the side chain of each repeating unit both an asymmetric carbon atom of one single absolute configuration and a photochromic group. The resulting polymers are therefore characterized simultaneously by the high prevalence of one-handed conformational dissymmetry and the close proximity of the side-chain photochromic groups. Such structural features are in principle expected to amplify the exciton splitting of the related CD bands and hence to better disclose their correlation with the conformational properties of the macromolecules.

Indeed, very encouraging results were obtained[15] from optically active hydrocarbon main-chain polymers in which the side-chain azobenzene chromophore was connected to the backbone through an L-lactic acid residue, such as in the homopolymers of *trans*-(S)-4-(2-methacryloyloxypropanoylamino)azobenzene and of *trans*-(S)-(2-acryloyloxypropanoylamino)azobenzene [poly(**MLA**) and poly(**ALA**), respectively].

The above polymers, in contrast to the corresponding low molecular weight models **PLA** and **ILA**, in fact display[15] in the $\pi \rightarrow \pi^*$ spectral region of the *trans*-azobenzene moiety
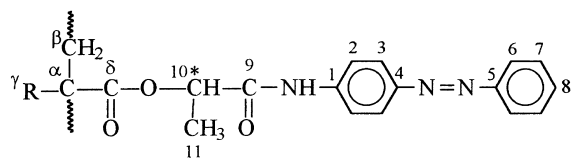
poly(**MLA**) (R = CH₃)

poly(**ALA**) (R = H)
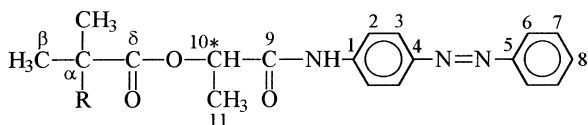
PLA (R = CH₃)

ILA (R = H)

CD couplets whose amplitude is one order of magnitude higher than that previously observed for optically active hydrocarbon main-chain photochromic copolymers, thus suggesting that they possess a rather highly ordered conformational homogeneity with a significant prevalence of one single chirality, despite their low degree of stereoregularity in the main chain.

In principle, however, the conformational dissymmetry of the above polymeric systems could be attributed to hydrogen bonding between carbonyl and amino groups in neighbouring units belonging either to the same or different macromolecules, thus allowing stabilization to a significant extent of one prevailing handedness. To clarify this point, it appeared of great interest to prepare an optically active homopolymer where the side-chain chiral centre of each repeating unit was bound to the backbone and the azobenzene moiety through two ester functions, thus removing the possibility of hydrogen bonding interaction[5]. Therefore, this paper deals with the synthesis and structural characterization of *trans*-poly[(S)-4-(2- methacryloyloxypropanoyloxy)azobenzene] [poly(**MLO**)] as well as the investigation of its photochromic, chiroptical and photoresponsive properties in comparison with those of the above-mentioned chiral azobenzene polymers and of the corresponding low molecular weight model, *trans*-(S)-4-(2-pivaloyloxypropanoyloxy)azobenzene (**PLO**).
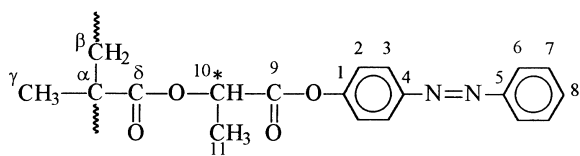
poly(**MLO**)
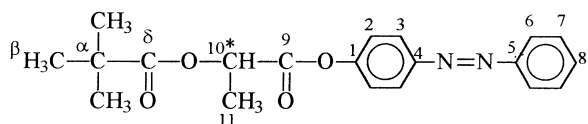
PLO

EXPERIMENTAL

Reagents, monomer and model

(+)-L-lactic acid (Aldrich) was purified (b.p. = 99°C/0.3 mbar) according to the literature[16] in order to remove L-lactide and anhydride impurities, $[\alpha]_D^{25} = +3.7$ ($c = 5$, H₂O) (lit.[17]: $[\alpha]_D^{15} = +3.8$ ($c = 10.5$, H₂O)).

Trans-4-hydroxyazobenzene (**HA**) (Aldrich) was recrystallized from an EtOH/H₂O (1:1, v/v) solution just before use.

Methacryloyl chloride (Aldrich) was distilled under dry nitrogen in the presence of traces of 2,6-di-*tert*.butyl-*p*.cresol as polymerization inhibitor just before use.

Pivaloyl chloride (Aldrich) was distilled under dry nitrogen just before use.

Methacrylic acid (Aldrich) and 4-dimethylaminopyridine (Aldrich) were used as received.

4-Dimethylaminopyridinium 4-toluenesulfonate (**DPTS**) was prepared from 4-dimethylaminopyridine and 4-toluenesulfonic acid (Aldrich) as previously described[18].

Trans - (S)-4-(2-methacryloyloxypropanoyloxy)azobenzene (**MLO**) was prepared (*Scheme 1a*) by esterification of methacryloyl-L-lactic acid (**ML**), $\{[\alpha]_D^{25} = -28.0$ ($c = 1$, EtOH)[19]$\}$ with **HA** in the presence of *N,N*-diisopropylcarbodiimide (**DIPC**) and **DPTS**, as coupling agent and condensation activator, respectively[18], the reaction being described in detail as follows.

A solution of 6.33 mmol of **ML**, 0.05 g of hydroquinone and 6.33 mmol of **HA** in 10 ml of anhydrous CH₂Cl₂, was placed in a 100 mL three-necked round-bottomed vessel, under dry nitrogen, then 6.33 mmol of **DPTS** and 8.22 mmol of **DIPC** were successively added under magnetic stirring and the reaction mixture was kept at room temperature for 72 h. The solid N,N-diisopropylurea thus formed was filtered off and the liquid phase was washed with several portions of aqueous 1M HCl, aqueous 5% Na₂CO₃ and water, in that order. After drying the organic layer on anhydrous Na₂SO₄ and evaporation of the solvent under vacuum the crude product was purified by column chromatography on silica gel (70–230 mesh) by using chloroform as eluent to afford pure **MLO** in a 20% yield.

MLO was also synthesized by one-pot reaction involving equimolar amounts of methacrylic acid, L-lactic acid and **HA** in the presence of **DIPC** and **DPTS** (*Scheme 1b*) as follows.

A solution of 29.2 mmol of L-lactic acid, 29.2 mmol of methacrylic acid and 0.05 g of hydroquinone as polymerization inhibitor, in 100 ml of CH₂Cl₂, was placed in a 250 ml three-necked round-bottomed vessel, under dry nitrogen. Then, 32.2 mmol of **HA**, 29.2 mmol of **DPTS** and 73.7 mmol of **DIPC** were added and the resulting solution was kept at room temperature for 72 h under vigorous stirring. The reaction mixture, after filtration to remove the *N,N*-diisopropylurea thus formed, was treated with several portions of aqueous 1 M HCl, 5% aqueous Na₂CO₃ and water, in that order. The organic layer was dried on anhydrous Na₂SO₄ and the solvent removed under vacuum to dryness. The solid crude product was purified by column chromatography on silica gel by using chloroform as eluent, to give in 15% yield (with respect to L-lactic acid) pure **MLO**.

^{1}H-n.m.r. (CDCl₃): $\delta = 8,0–7,2$ (m; 9H, aromatic protons), 6,3 and 5,7 (2d; 2H, CH₂ =), 5,3 (q; 1H, CH-), 2,0 (s; 3H, CH₃-C =), 1,7 (d; 3H, *CH₃*-CH-) ppm.

FT i.r. (KBr): 3060 (ν_{CH}, aromatic), $\overline{2993}$ (ν_{CH}, aliphatic),

Table 1 Physical characterization of poly(**MLO**), **MLO** and **PLO**

Compound	$[\alpha]_D^{25\,a}$	$[\Phi]_D^{25\,b}$	M_n^c	M_w/M_n^c
MLO	− 19.1	− 64.3	–	–
poly(**MLO**)	− 138	− 464	29 000	1.6
PLO	− 43.6	− 154	–	–

[a] Specific optical rotation [b] Molar optical rotation, calculated as $([\alpha]_D^{25} - M)/100$, where M represents the molecular weight of the compound or of the repeating unit in the case of poly(**MLO**) [c] Determined by SEC

1784 ($\nu_{C=O}$, aromatic ester), 1722 ($\nu_{C=O}$, methacrylic ester), 1636 ($\nu_{C=C}$, methacrylic), 1594 ($\nu_{C=C}$, aromatic), 1453 (δ_{CHas}, CH$_3$), 1381 (δ_{CHs}, CH$_3$), 827 (δ_{CH}, 1,4-disubstituted phenyl ring), 769 and 688 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}. Optical activity data are reported in *Table 1*.

Trans-(S)-4-(2-pivaloyloxypropanoyloxy)azobenzene (**PLO**) was prepared according to a procedure implying the reaction of pivaloyl chloride with L-lactic acid to give[15] pivaloyl-L-lactic acid (**PL**) $\{[\alpha]_D^{25} = -43.4$ (c = 1, EtOH), 78% yield$\}$, its subsequent chlorination by oxalyl chloride to afford pivaloyl L-lactic acid chloride (**PLC**) which was finally reacted with **HA** to give **PLO** (*Scheme 2*), as reported in detail below:

Pivaloyl L-lactic acid chloride (**PLC**) was prepared by adding dropwise, under dry nitrogen, 46.9 mmol of oxalyl chloride to 31.9 mmol of **PL** under vigorous stirring at room temperature. The reaction mixture was allowed to stand for 2 h at room temperature and for a further 2 h at 40°C until the IR band at 1760 cm^{-1}, related to ν_{CO} of the carboxylic group of **PL**, completely disappeared. The excess of oxalyl chloride was removed by addition of anhydrous benzene, followed by distillation to dryness under vacuum. **PLC** was thus obtained as a solid residue and directly submitted to reaction with **HA**.

A **PLC** (6.3 mmol) solution in 10 mL of anhydrous THF was added dropwise at room temperature, under dry nitrogen, to 6.3 mmol of **HA** dissolved in 8 ml of anhydrous THF. Then, 12.7 mmol of triethylamine (**TEA**) were added dropwise to the reaction mixture at room temperature. A precipitate of triethylammonium chloride was immediately observed. The reaction mixture was left at room temperature for 2 days and after filtration was treated with an equal volume of CHCl$_3$, washed with aqueous 1 M HCl, 5% aqueous Na$_2$CO$_3$ and finally with water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under vacuum to dryness. The solid crude product was crystallized from EtOH/H$_2$O (1:1, v/v) and further purified by column chromatography on silica gel, using CHCl$_3$ as eluent to afford pure **PLO** $\{[\alpha]_D^{25} = -43.6$ (c = 0.493, CHCl$_3$)$\}$ in 36% yield with respect to **PL**.

[1]H-n.m.r. (CDCl$_3$): δ = 7,95 (m; 4H, CH-3 and CH-6), 7,50 (m; 3H, CH-7 and CH-8), 7,24 (m; 2H, CH-2), 5,25 (q; J$_{10,11}$ 6,96 Hz, 1H, CH-10), 1,65 (d; 3H, CH$_3$-11) and 1,30 (s; 9H, CH$_3$-β) ppm.

*FT*i.r. (KBr): 3057 (ν_{CH}, aromatic), 2972 (ν_{CH}, aliphatic), 1775 ($\nu_{C=O}$, aromatic ester), 1733 ($\nu_{C=O}$, aliphatic ester), 1593 ($\nu_{C=C}$, aromatic), 1385 and 1367 (δ_{CH}, gem-dimethyl groups in *tert*-butyl moiety), 1191 (ν_{C-O}, aromatic ester), 832 (δ_{CH}, 1,4-disubstituted phenyl rings), 772 and 692 (δ_{CH}, monosubstituted phenyl ring) cm^{-1}. Optical activity data are reported in *Table 1*.

Polymerization of **MLO**

Homopolymerization of **MLO** was carried out in a glass vial using 2,2′-azobisisobutyronitrile (**AIBN**) as free radical initiator and THF as solvent. The reaction components (1 g of monomer and 0.02 g of **AIBN** in 15 ml of THF) were introduced into the vial under nitrogen, submitted to several freeze–thaw cycles and heated at 70°C for 120 h. The polymerization was stopped by pouring the reaction mixture into a large excess of petroleum ether. The coagulated polymer was filtered off, redissolved in CHCl$_3$, precipitated in methanol and finally dried under high vacuum (78% yield). Poly(**MLO**) was characterized by [1]H-n.m.r., *FT*i.r. and SEC. The most relevant data are reported in *Table 1*.

[1]H-n.m.r. (CDCl$_3$): δ = 7,85 (4H, CH-3 and CH-6), 7,45 (3H, CH-7 and CH-8), 7,15 (m; 2H, CH-2), 5,1 (1H, CH-10), 2,20 (2H, CH$_2$-β), 1,6 (3H, CH$_3$-11) and 1,2 (3H, CH$_3$-γ) ppm.

Physicochemical measurements

N.m.r. spectra were recorded at room temperature on 5–10% CDCl$_3$ solutions with a Varian Gemini 200 spectrometer. [1]H-n.m.r. spectra were recorded at 200 MHz, by using the following experimental conditions: 11.968 data points, 3 kHz spectral width, 30° pulse, 2 s acquisition time, 1 transient. 2D COSY spectra were recorded at 200 MHz, by using the following experimental conditions: 1024 data points, 1742 Hz spectral width, 8 transients, 1.7 s delay. A total of 256 spectra were recorded in order to have 1742 Hz spectral width in the second dimension. Final spectra have been symmetrized. ^{13}C-n.m.r. spectra were recorded at 50.3 MHz, under full proton decoupling, by using the following experimental conditions: 23.936 data points, 15 kHz spectral width, 70° pulse, 0.8 s acquisition time, 44,000 transients. No weighing function was applied prior to Fourier transformation. The 2D HETCOR spectra were recorded at 50.3 MHz by using a sweep width of 10 kHz and 2 k data points. A total of 256 spectra were used to provide the equivalent of a 1.6 kHz sweep width in the ^{1}H frequency dimension. [13]C T_1 measurements were performed at 50.3 MHz, by using the $\pi - \tau - \pi/2$ pulse sequence and the following experimental conditions: 23,936 data points, 15 kHz spectral width, 70° pulse, 0.8 s acquisition time, 1024 transients, 6 s delay between sequences, delay between pulses τ = 0.023, 0.047, 0.094, 0.188, 0.375, 0.75, 1.5, 3.0 and 6.0 s.

Number-average molecular weights of the polymers (M_n) were determined by an HPLC Waters Millipore 590 apparatus, equipped with an injector Waters Model U6K, a column Toso Haas G4000HXL and a UV–VIS detector Perkin-Elmer Model LC-95, working at 254 nm. The calibration curve was obtained by using several mono-disperse polystyrene standards.

*FT*i.r. spectra were carried out on a Perkin-Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station. The samples were prepared as KBr pellets or as liquid films interposed between KBr discs.

Optical activity experiments were accomplished at 25°C on a Jasco DIP-360 digital polarimeter, using a cell path length of 1 dm. Specific rotation values at sodium D-line ($[\alpha]_D^{25}$) are expressed as deg dm^{-1} g^{-1} dL.

UV absorption spectra of the samples were recorded at 25°C in CHCl$_3$ solution on a Perkin-Elmer Lambda 19 spectrophotometer. The spectral regions 550–400 and 400–250 nm were investigated by using cell path lengths of 1 and 0.1 cm, respectively. Azobenzene chromophore concentrations of about 1×10^{-3} and 5×10^{-4} mol L^{-1} were used.

CD spectra of the samples were recorded at 25°C in CHCl$_3$ and THF solution on a Jasco 500 A dichrograph. The same spectral regions, cell path lengths and concentrations
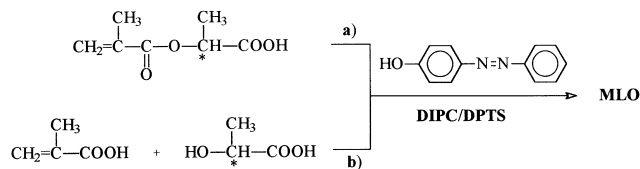
Scheme 1
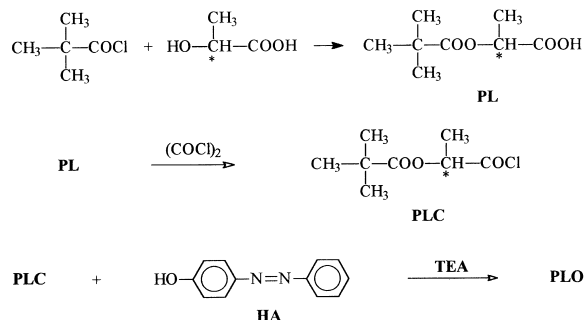
Scheme 2

as for UV measurements were used. $\Delta\varepsilon$ values, expressed in $L\,mol^{-1}\,cm^{-1}$, 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.

Photoisomerization experiments were carried out at 25°C on samples in chloroform solution (absorbance ≈ 0.1 at the irradiation wavelength) using the following experimental set-up: the emission from a 150 W high pressure Hg-Xe lamp, filtered by a 366 or 437 nm interference filter (Balzer) with a $\pm$ 5 nm bandwith, was guided by a 3 mm $\times$ 50 cm quartz fibre on top of a magnetically stirred solution of the sample in a 10 mm quartz cell placed within the UV spectrophotometer. The isomerization kinetics were monitored by measuring the 310 nm absorbance every 10 s until the photostationary state was reached.

RESULTS AND DISCUSSION

Synthesis and structural characterization of low and high molecular weight azobenzene derivatives

Initially, **MLO** synthesis was attempted by following the same procedure as described for obtaining *trans*-(S)-4-(2-methacryloyloxypropanoylamino)azobenzene which involved the preparation of methacryloyl-L-lactic acid (**ML**), its successive transformation by means of ethyl chloroformate into the corresponding anhydride and finally its reaction in situ with *trans*-4-aminoazobenzene[15]. However, when this last reactant was replaced by *trans*-4-hydroxyazobenzene (**HA**), the above synthetic approach failed, the expected monomer being not obtained at all. An alternative synthetic route involving the reaction of methacryloyl-L-lactic acid chloride (**MLC**) with **HA** was then explored, but it equally failed as the reaction of **ML** with either thionyl chloride or oxalyl chloride to give **MLC** did not proceed to an acceptable extent. Therefore, a novel approach, based on the direct reaction of **ML** with **HA** in the presence of *N,N*-diisopropyl-carbodiimide (**DIPC**) and 4-(diphenylamino)pyridinium 4-toluenesulfonate (**DPTS**) as coupling agent and condensation activator, respectively, was developed (*Scheme 1a*), according to what was previously reported for the preparation of high molecular weight polyesters[18]. However, when this method was applied to the synthesis of **MLO**, a mixture of products containing only 20 mol % of the desired monomer was obtained. The products were separated by column chromatography on silica gel and identified by ^{1}H-n.m.r. analysis. The nature of the different components and their relative amounts are reported below.

n = 0		66%
n = 1	(**MLO**)	20%
n = 2		11%
n = 3		3%
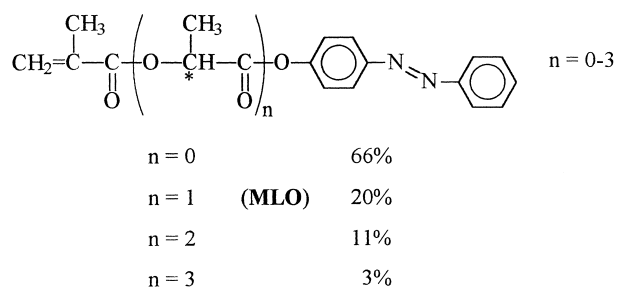
Taking into account that the above procedure afforded the desired monomer in low yield and with poor selectivity, the preparation of **MLO** starting directly from equimolar amounts of methacrylic acid, L-lactic acid and a slight excess of **HA** in the presence of **DIPC** and **DPTS** (*Scheme 1b*) was explored. Indeed, this one-pot reaction gave rise to a mixture of products having substantially the same composition as that previously obtained from **ML**, pure **MLO** being recovered by column chromatography in 15% yield. Nevertheless, this latter reaction was preferred to the previous one, due to the simplicity of the procedure. Considering the successful application of the above method to the synthesis of optically active polyesters starting from chiral hydroxy acid monomers[18] and the very mild conditions adopted (room temperature and non protic apolar solvents), no racemization should occur during the reaction. Hence, the obtained laevorotatory **MLO** (*Table 1*) has been assumed to be as optically pure as the L-lactic acid precursor. Indeed, **MLO** prepared by the last route displays substantially the same specific rotation as that obtained from **ML**, according to *Scheme 1a*, thus supporting the above assumption.

The low molecular weight model **PLO** was prepared in 36 mol % yield by a different synthetic pathway with respect to **MLO** (*Scheme 2*), involving the synthesis of the precursor **PLC**, readily obtained by reacting **PL** with oxalyl chloride (contrary to what occurred for **ML**) followed by reaction with **HA**, in the presence of triethylamine.

PLO is also laevorotatory (*Table 1*). However, its $[\Theta]_D^{25}$ is more than twice that of **MLO**, thus suggesting a higher conformational rigidity of the model, due to the bulkiness of the pivaloyl group.

Assignment of signals present in the ^{1}H-n.m.r. spectrum of **PLO** was performed on the basis of additive group contributions, signal multiplicity and 2D COSY spectrum. In particular, signals at 7.24, 7.50 and 7.95 ppm were attributed to the aromatic protons bonded to C-2, C-7 and C-8, and C-6 and C-3 carbons, respectively, thus ruling out any appreciable contribution of internal charge transfer to the electronic distribution of the azobenzene chromophore[20].

Poly(**MLO**) was prepared by free radical initiation in the presence of a rather large amount (2 wt%) of AIBN, due to the well known low reactivity of unsaturated monomers bearing an azoaromatic group[7,21]. Under these conditions and by using a long polymerization time the polymer was obtained in a fairly high yield (78%). The average molecular weight of poly(**MLO**) was appreciably high and the molecular weight distribution typical of a free radical polymerization process (*Table 1*).
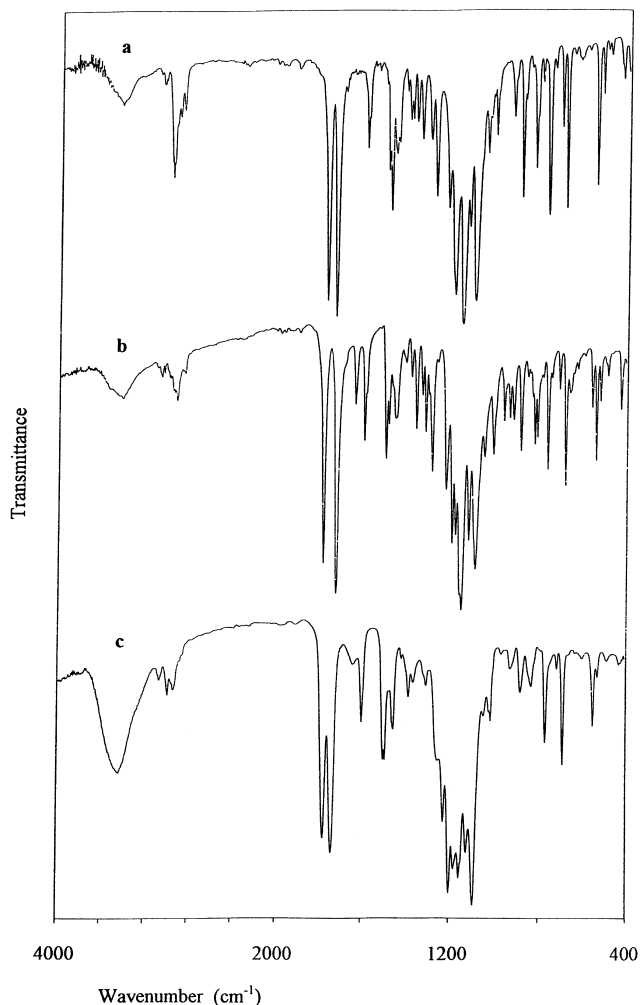
Figure 1   IR spectra of: (a) **PLO**, (b) **MLO** and (c) poly(**MLO**)

Table 2   Assignments of ^{13}C-NMR signals of **PLO**, poly(**MLO**), **ILA** and poly(**MLA**) in CDCl$_3$ solution at 25°C

Attribution	Sample PLOδ (ppm)	poly(MLO)δ (ppm)	ILAδ (ppm)	poly(MLA)δ (ppm)
C$_\alpha$	38.53	45.55 + 45.15	33.88	45.29
C$_\beta$	25.96	55–50	18.84	55–50
C$_\gamma$	–	20–16	–	20–16
C$_\delta$	177.94	178–175	175.85	178–175
C$_1$	152.46	152.39	139.53	139.60
C$_2$	121.91	121.93	119.97	120.35
C$_3$	124.05	124.03	123.91	123.85
C$_4$	150.38	150.30	149.20	149.17
C$_5$	152.20	152.07	152.56	152.40
C$_6$	122.82	122.83	122.70	122.72
C$_7$	129.02	129.00	128.98	128.98
C$_8$	131.50	131.04	130.76	130.86
C$_9$	169.27	168.79	168.84	167.76
C$_{10}$	68.38	69.26	70.52	72.10
C$_{11}$	16.62	16.69	17.57	16.91

The IR analysis of poly(**MLO**) confirmed the expected structure (*Figure 1*). Indeed, the polymer did not show bands at 854 and 1636, related respectively to C–H bending and C=C stretching vibrations of the methacrylic group, contrary to **MLO**, thus confirming that the polymerization process involved only the above unsaturated function. Moreover, the bands present at 1775 and 1736 cm^{-1}, connected with the stretching vibrations of aromatic and

Table 3   Relaxation (T_1) and correlation (τ) times of the ^{13}C-NMR signals of **PLO**, poly(**MLO**), **ILA** and poly(**MLA**) in CDCl$_3$ solution at 25°C^a

Carbon atom	PLO		poly(MLO)		ILA		poly(MLA)	
	T_1	$\tau 10^{11}$	T_1	$\tau 10^{11}$	T_1	$\tau 10^{11}$	T_1	$\tau 10^{11}$
C$_\alpha$	> 14	n.d.	1.12	n.d.	3.54	1.3	1.03	n.d.
C$_\beta$	1.91	0.8	0.08	64	2.13	0.7	0.07	130
C$_\gamma$	–	–	0.07	87	–	–	0.07	87
C$_\delta$	> 27	n.d.	1.50	n.d.	> 29	n.d.	2.04	n.d.
C$_1$	> 38	n.d.	4.12	n.d.	> 18	n.d.	1.71	n.d.
C$_2$	1.88	2.5	0.37	12.9	0.93	5.1	0.19	26.6
C$_3$	1.87	2.5	0.38	12.6	0.93	5.1	0.19	26.6
C$_4$	> 33	n.d.	3.34	n.d.	> 18	n.d.	2.18	n.d.
C$_5$	> 26	n.d.	3.09	n.d.	> 18	n.d.	3.62	n.d.
C$_6$	2.30	2.1	0.68	7.0	1.38	3.4	0.37	13.0
C$_7$	2.22	2.1	0.66	7.2	1.37	3.4	0.36	13.3
C$_8$	0.56	8.5	0.18	28.4	0.41	11.6	0.17	30.4
C$_9$	> 27	n.d.	2.45	n.d.	> 14	n.d.	2.00	n.d.
C$_{10}$	1.37	3.4	0.17	30.4	0.83	5.7	0.20	25.9
C$_{11}$	0.99	1.7	0.29	5.5	0.83	1.9	0.29	5.5

^{a} Correlation times evaluated from T_1 values by assuming that the only relaxation process is dipolar and that only directly bonded hydrogens contribute to the relaxation process. All numerical values are expressed in seconds
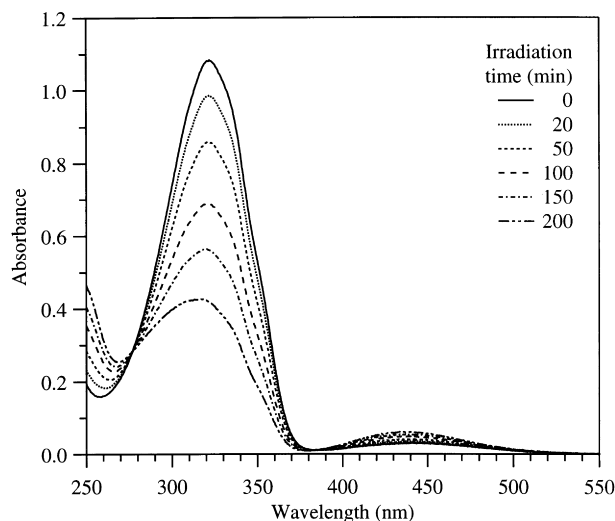

Figure 2   UV spectra of poly(**MLO**) at different irradiation times at 366 nm in chloroform solution at 25°C

aliphatic C=O ester groups in that order, were shifted by 9 and 14 cm^{-1} towards lower and higher frequencies, respectively, as compared with **MLO**. Similar results were previously observed for the C=O ester group stretching vibration in methacrylic and acrylic polymers bearing side-chain azoaromatic moieties[15,21]. Accordingly, the saturated model **PLO** also showed a similar shift of the above bands (9 and 11 cm^{-1}) with respect to **MLO** (*Figure 1*).

The main chain stereoregularity of poly(**MLO**) was analysed by ^{13}C-n.m.r.. Attribution of the signals present in the spectra of the different polymer samples (*Table 2*) was performed on the basis of additive group contributions[22], 2D HETCOR spectrum and multiplicity in non-decoupled spectra. It is however possible that the attributions of the signals of quaternary aromatic carbons, made only from group contributions, are not entirely correct.

^{13}C-n.m.r. signals relevant to $\alpha-\delta$ carbons of poly(**MLO**) appeared as partially overlapping multiplets, thus evidencing their sensitivity to main chain stereochemistry. In

Table 4 UV spectra of poly(**MLO**) and **PLO** in *trans* configuration at 25°C in THF and CHCl$_3$ solution^a

Sample	Solvent	$n \rightarrow \pi^*$ transition		$\pi \rightarrow \pi^*$ transition	
		λ_{max}	ε_{max}	λ_{max}	$\varepsilon_{max} \times 10^{-3}$
Poly(**MLO**)	CHCl$_3$	440	770	320	18.6
	THF	442	690	322	22.2
PLO	CHCl$_3$	441	750	321	21.3
	THF	441	740	323	19.9

^{a} λ_{max} and ε_{max} are expressed in nm and L mol^{-1} cm^{-1}, respectively
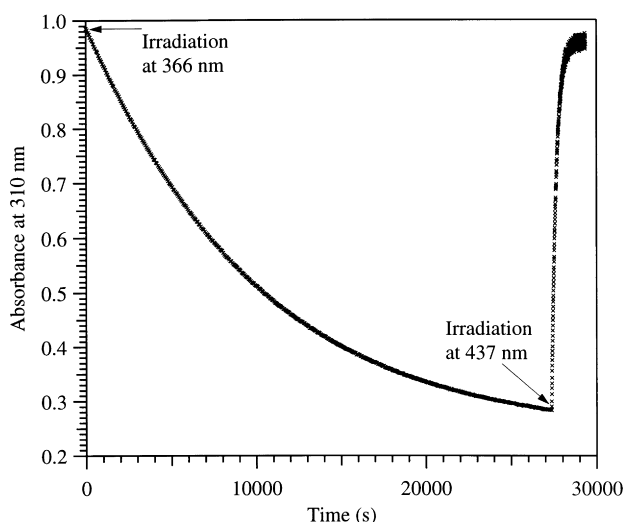
Figure 3 UV absorption at 310 nm of poly(**MLO**) in chloroform solution as a function of irradiation time at 366 and 437 nm

Table 5 Photoisomerization kinetics of poly(**MLO**), **PLO**, poly(**MLA**) and **PLA** in chloroform solution at 25°C

Sample	λ irradiation (nm)	$\bar{\kappa} \times 10^5 (s^{-1})$	A_∞/A_0
trans-**PLO**	366	9.3	0.22
trans-poly(**MLO**)	366	8.1	0.26
cis-**PLO**	437	33.0	–
cis-poly(**MLO**)	437	30.1	–
trans-**PLA**	366	7.9	0.51
trans-poly(**MLA**)	366	5.8	0.45

particular, the relative intensities of the components of the C-δ signal at 175–178 ppm allowed to assign a 70% content of syndiotactic dyads to the polymer sample, by assuming Bernoullian statistics[23]. Similar results were obtained from the ^{13}C-n.m.r. spectrum of poly(**MLA**) performed for comparison.

To gain some information on the molecular mobility of the azobenzene chromophores, ^{13}C-n.m.r. relaxation times (T_1) of poly(**MLO**) and, for comparison, **PLO** were measured at 50.3 MHz, in chloroform solution at room temperature (*Table 3*). Correlation times (τ) of methyne and methylene carbons were evaluated from the corresponding T_1 values, under the rather crude assumption that the only relaxation mechanism is dipolar and that only directly bonded hydrogen atoms contribute to the relaxation process[22]. The consistently small values of methyl groups were attributed to their fast internal rotation[24].

Correlation times of **PLO** carbon atoms, not taking into account quaternary ones, resulted included between 2.5 and 8.5 × 10^{-11} s, thus evidencing an appreciable mobility of the molecule with some deviation from an isotropic overall

tumbling model with a single correlation time. In particular, the rather large τ of C8 (8.5 × 10^{-11} s) is in agreement with the cylindrical symmetry of the molecule. However, the reported correlation times are almost one order of magnitude lower than those of typical low molecular weight compounds, in accordance with the rather extended and stiff structure of **PLO**.

T_1 values of the carbons of poly(**MLO**) resulted much lower than those of **PLO** model compound, as expected from the reduced mobility of macromolecular systems. In addition, the correlation times decreased in going from the polymer main chain to the farthest phenyl ring, due to the backbone stiffness.

Comparison of the relaxation times of **PLO** and poly(**MLO**), respectively, with those of **ILA** and poly-(**MLA**), the corresponding structurally analogous compounds containing an amide bond instead of an ester bond between the azobenzene group and the lactate residue, showed evidence of an appreciably lower mobility of the latter derivatives (*Table 3*), as expected from the reduced rotational freedom of the amide bond.

UV absorption and photochromic properties

The UV absorption spectra in THF and CHCl$_3$ solution of poly(**MLO**) (*Figure 2*) and **PLO** in *trans* configuration showed in the 250–550 nm region two bands centered around 320 and 440 nm, related respectively to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of the azobenzene chromophore[25]. A more detailed examination of the UV spectra in CHCl$_3$ solution indicated (*Table 4*) a hypochromic effect of poly(**MLO**) with respect to the **PLO** model as far as the $\pi \rightarrow \pi^*$ absorption band is concerned. This may be addressed to the occurrence of electrostatic dipole–dipole interactions between the neighbouring aromatic moieties[26,27], as previously observed in several polymeric systems bearing side-chain aromatic[28,29] and azoaromatic[15,21] chromophores. However, an opposite behaviour was observed in THF solution for poly(**MLO**) against **PLO**, thus suggesting that the ethereal solvent owing to its high electron-donor character and/or to the higher polarity (dielectric constants at 25°C for THF and CHCl$_3$ are 7.4 and 4.64, respectively[30]), may affect the above dipolar interactions and hence influence also the conformational arrangement of the macromolecules.

On irradiation of poly(**MLO**) and **PLO** solutions in the correspondence of the first $\pi \rightarrow \pi^*$ electronic transition, azobenzene chromophores underwent a *trans* to *cis* photoisomerization process. Correspondingly, shape, intensity and position of the UV absorption bands were modified (*Figure 2*). Indeed the UV spectra recorded at different irradiation times were characterized by the presence of two isosbestic points at about 277 and 384 nm, thus confirming that only two absorbing species, namely *cis* and *trans* isomers of the azobenzene group, were present in solution.

Photoisomerization kinetics were investigated at 25°C on chloroform solutions having absorbance lower than 0.1 at the irradiation wavelength. Experiments were performed by irradiation at 366 nm while monitoring the 310 nm absorbance until a photostationary state was reached, as reported for poly(**MLO**) in *Figure 3*.

Kinetic data were fitted to equation: $\ln[(A_0 - A_\infty)/(A_t - A_\infty)] = \kappa_{exp}t$, where A_0, A_t and A_∞ are the 310 nm absorbance at time 0, t and ∞, respectively[31].

In all cases experimental and calculated data were in very good agreement. Taking into account that the measured photoisomerization rate constant linearly depends on the

Table 6 CD spectra of poly(**MLO**) and **PLO** at 25°C, as compared with poly(**MLA**) and **PLA**

Sample	Solvent	λ_1^a	$\Delta\varepsilon_1^b$	λ_2^a	$\Delta\varepsilon_2^b$	λ_3^a	$\Delta\varepsilon_3^b$
trans-poly(**MLO**)	CHCl₃	440	−0.18	336	−1.52	290	+0.08
	THF	440	−0.19	335	−2.79	294	+0.24
trans-**PLO**	CHCl₃	430	−0.06	321	−0.19	–	–
trans-poly(**MLA**)[c]	CHCl₃	434	−0.11	362	+5.49	325	−5.15
	THF	435	−0.12	358	+0.38	325	−0.93
trans-**PLA**[c]	CHCl₃	438	+0.06	345	−0.80	–	–
	THF	435	+0.06	351	−0.38	–	–
cis-poly(**MLO**)	CHCl₃	430	−0.80	–	–	280	+0.70
cis-**PLO**	CHCl₃	430	−0.13	–	–	280	+0.12
cis-poly(**MLA**)[d]	CHCl₃	449	+0.27	–	–	289	−2.37
cis-**PLA**[d]	CHCl₃	436	+0.26	–	–	311	−0.48

[a] Expressed in nm
[b] Expressed in L mol⁻¹ cm⁻¹
[c] Refs 15 and 32
[d] Ref. 32
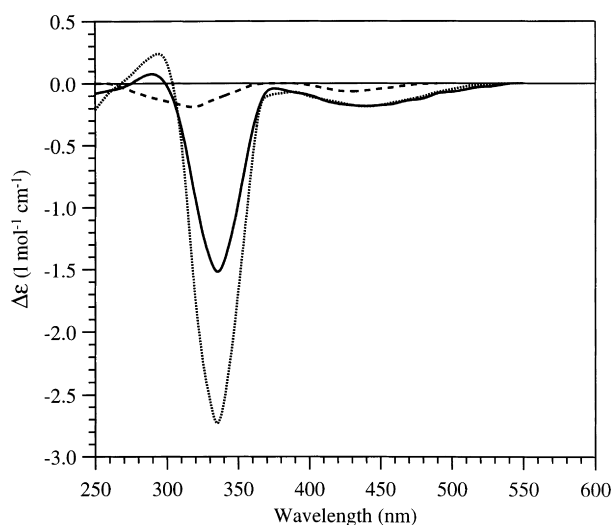
Figure 4 CD spectra at 25°C of poly(**MLO**) in THF (.....) and in CHCl₃ (———) as well as of **PLO** in CHCl₃ (- - -) all in the *trans* configuration

light intensity at the irradiation wavelength (I_λ) [according to the equation, $\kappa_{exp} = 2.303 I_\lambda (\varepsilon_{cis}\Phi_{cis} + \varepsilon_{trans}\Phi_{trans})$[31]], the experimental values of the kinetic constants (κ_{exp}) were corrected (κ_c) for the variation of I_λ, as measured by a photodiode, normalizing the data at a light intensity of 40 ($\kappa_c = \kappa_{exp} 40/I_\lambda$), and averaged over 4–5 experiments ($\bar{\kappa}$). The recorded $\bar{\kappa}$ and A_∞/A_0 values (*Table 5*) did not show a large dependence on the nature of the investigated samples, analogously to what was observed for other azobenzene-containing polymers[5]. It is however possible to observe a small decrease in $\bar{\kappa}$ (from 9.3 to 8.1 × 10⁻⁵ s⁻¹) and a slight increase in A_∞/A_0 average values (from 0.22 to 0.26) in going from the low molecular weight model **PLO** to the macromolecular system poly(**MLO**). An analogous behaviour was obtained for **PLA** and poly(**MLA**) (*Table 5*). However, it is worth noting that the values of the *trans* → *cis* photoisomerization rate for **PLA** and poly(**MLA**), here obtained for comparison, appear about 2 orders of magnitude lower than those previously reported[32], due to the much lower irradiation intensity of the lamp and to the fact that no normalization on the light intensity was adopted at that time.

When irradiated at 437 nm, the 310 nm absorbance of *cis*-isomerized samples steadily increased up to the starting value before irradiation, thus confirming the reversibility of the photoisomerization process (*Figure 3*). In this case also, the process obeyed first-order kinetics. This result clearly indicates homogeneous photochromic behaviour for *trans* and *cis* azobenzene chromophores in the polymer sample. Accordingly, the photoisomerization rate constants do not depend on the extent of isomerization, i.e. the presence of adjacent azobenzene moieties in either the *trans* or the *cis* configuration does not affect the photoisomerization kinetics. *Cis* to *trans* photoisomerization rate constants, as measured at 25°C on chloroform solution of poly(**MLO**) and **PLO** were respectively 3.0 and 3.3 × 10⁻⁴ s⁻¹. The much higher rate constant value for the *cis* to *trans* isomerization reaction with respect to the reverse process has to be attributed to the different irradiation intensity of the lamp at the two wavelengths as well as to the different molar absorption extinction coefficients and quantum yields of photoisomerization of *cis* and *trans* isomers at the above wavelengths. Comparison of rate constants reported in *Table 5* suggests that in all cases the photoisomerization of the polymeric compounds is slightly slower than that of the low molecular weight model compounds, thus indicating that the macromolecular backbone has the tendency to depress the isomerization process, probably owing to steric hindrance. However, these effects appear to be appreciably smaller than those expected on the basis of the different mobility of high and low molecular weight compounds (*Table 3*).

Indeed, the photoisomerization process has been proposed[33−38] to occur by in-plane translation of the benzene ring further from the main chain rather than by rotation around the N=N bond. The absence of a pronounced influence of the azobenzene mobility on the recorded photoisomerization rates seems to be in agreement with this proposal.

Chiroptical and photoresponsive properties

All low and high molecular weight compounds in the *trans* configuration are optically active in chloroform solution at the sodium D-line (*Table 1*). Indeed, poly(**MLO**) displays a molar rotatory power which is one order of magnitude higher than that of **MLO** and three times larger than that of **PLO**, thus suggesting that the macromolecules are characterized by a higher conformational rigidity.

The CD spectra of poly(**MLO**) and its model **PLO** in the *trans* configuration, both in THF and CHCl₃ solution,
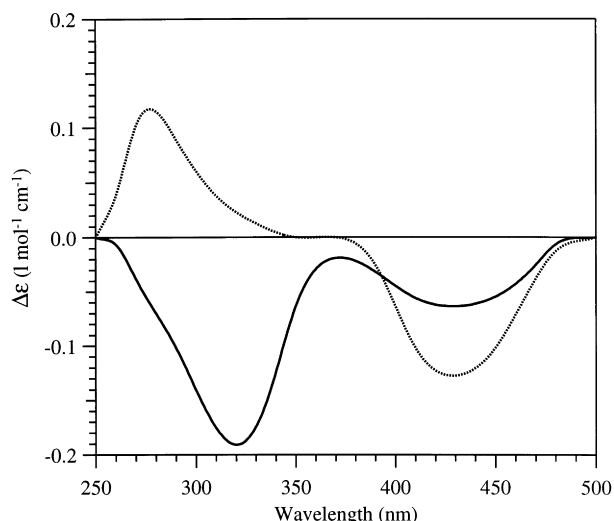
Figure 5 CD spectra in chloroform solution at 25°C of **PLO** in *trans*-configuration (———) and at the photostationary state (90% of *cis*) (.....)
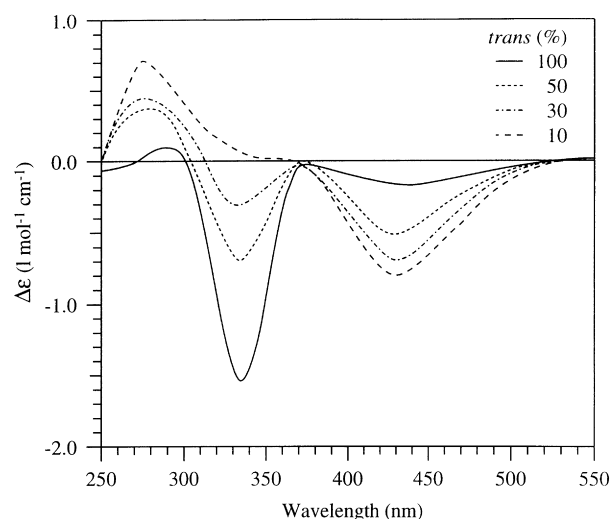
Figure 6 Dependence of CD spectra at 25°C of poly(**MLO**) on the extent of *trans* → *cis* photoisomerization of azobenzene chromophores in chloroform solution

exhibited (*Table 6* and *Figure 4*) a weak and broad negative band, in close correspondence with the UV absorption, related to the $n \rightarrow \pi^*$ electronic transition of the azobenzene chromophore. By contrast, in the $\pi \rightarrow \pi^*$ spectral region **PLO** showed a single CD band centered around 320 nm, whereas poly(**MLO**) was characterized by the presence of two CD bands of opposite sign, located at about 335 and 290 nm, shifted with respect to the corresponding UV absorption maximum (around 320 nm), and with a crossover point around 300 nm. It is worth noting that the ellipticity value of the negative band at 335 nm is about one order of magnitude higher than that of the positive band around 290 nm. The large asymmetry of this couplet could be ascribed to the superposition of an exciton splitting CD band, caused by cooperative interactions between side-chain coupled *trans*-azobenzene chromophores disposed along the backbone in a mutual chiral geometry with a prevailing handedness, with a negative CD band due to uncoupled *trans*-azobenzene chromophores present in less ordered conformational sections of the macromolecules. This behaviour suggests that the macromolecules in

poly(**MLO**) are characterized by a lower conformational homogeneity as compared with that previously observed[15,32] for poly(**MLA**) (*Table 6*), where the presence of one amido group per repeating unit probably favours the establishment of intramolecular hydrogen bonds which cannot occur in poly(**MLO**). The enhancement of the couplet amplitude in poly(**MLO**) when CHCl$_3$ is replaced by THF, in contrast to what occurred for poly(**MLA**)[15], (*Table 6*) seems to confirm the above picture. However, it cannot be completely ruled out that two independent CD bands of opposite sign are present in the $\pi \rightarrow \pi^*$ spectral region of the *trans*-azobenzene chromophore, as the corresponding UV absorption band shows (*Figure 2*) the presence of shoulders on both sides.

The investigation of CD spectra of poly(**MLO**) in all *trans*-configuration at variable temperature below 0°C, looking for increases in the amplitude of the postulated bisignated couplet, could be useful for clarifying this point.

The CD spectra, recorded in chloroform solution at 25°C on all *trans*-**PLO** and at the photostationary state after irradiation at 366 nm (residual *trans* content ~10%), exhibited a two-fold increase of the 430 nm dichroic band, whereas the 320 nm band changed from negative to positive and moved to about 280 nm *Figure 5*).

An analogous four-fold increase in the intensity of the 440 nm dichroic band was observed in the CD spectra of poly(**MLO**) on decreasing the content of *trans*-azobenzene chromophores from 100 to about 10% (*Figure 6*). Moreover, the negative 335 nm band vanished, whereas the positive small band at about 290 nm increased its intensity of about one order of magnitude and shifted to 280 nm.

The absence of definite isosbestic points in CD spectra of poly(**MLO**) on irradiation (*Figure 6*) seems to indicate that the contributions from *trans*- and *cis*-azobenzene moieties depends on the relative amount of the two species. Coupled and uncoupled *trans*-azobenzene and uncoupled *cis*-azobenzene chromophores may give rise to different dichroic effects when located in sections of macromolecules characterized by a different extent of prevailing chirality. This may be related to the lower conformational homogeneity of poly(**MLO**) macromolecules, as compared with poly(**MLA**). However, the rather high ellipticity of CD bands at the photostationary state in poly(**MLO**) with respect to **PLO** suggests that a certain conformational order and prevailing handedness of the macromolecules is retained after photoisomerization of the side-chain azobenzene moieties.

CONCLUSIONS

A novel optically active methacrylic homopolymer [poly-(**MLO**)], with pendant L-lactic acid residue connected through ester functionalities to both main chain and *trans*-azobenzene moieties, has been prepared and fully characterized.

[13]C-n.m.r. analysis indicates a certain degree of stereoregularity of syndiotactic type (about 70%). Moreover, ^{13}C-n.m.r. relaxation and correlation times of poly(**MLO**), as compared with the low molecular weight **PLO**, suggests a reduced mobility of the macromolecules and a certain stiffness of the backbone. However, poly(**MLO**) appears less conformationally rigid than poly(**MLA**), the corresponding homopolymer where the ester group connecting the L-lactate residue with the *trans*-azobenzene chromophore is replaced by an amide group.

CD properties of *trans*-poly(**MLO**) in solution indicate that the macromolecules exist in a conformational arrangement

with a prevailing chirality, but with a lower homogeneity with respect to poly(**MLA**), the presence of amido groups in this last system favouring the establishment of inter- and intramolecular hydrogen bonds.

As far as the photochromic and photoresponsive behaviour of poly(**MLO**) is concerned, the following final remarks can be made.

The *trans → cis* photoisomerization of azobenzene moieties follows a first-order kinetics, thus suggesting that the above process is not affected by the presence of adjacent azobenzene chromophores along the macromolecules in either the *trans* or the *cis* configuration. However, the comparison of photoisomerization rate constants of poly-(**MLO**) and **PLO** suggests that the macromolecular structure slightly hinders the isomerization process.

On irradiation at 366 nm, remarkable changes are observed in the CD spectrum of poly(**MLO**), the dichroic couplet in the $\pi \rightarrow \pi^*$ spectral region becoming a single band at the photostationary state. The disappearance of the couplet at the photostationary state may be very likely associated with the incapability of non-planar *cis*-azobenzene chromophores to provide exciton coupling. However, the rather high intensity of the dichroic bands in poly(**PLO**) with respect to **PLO** seems to rule out a photoinduced order–disorder conformational transition of the macro-molecules.

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