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Photoresponsive properties of optically active (meth)acrylic homopolymers with pendent L-lactic acid or L-alanine residues connected to 4-aminoazobenzene

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The photochromic behaviour and photoisomerization kinetics of optically active homopolymers of *trans*-(*S*)-4-*N*-(2-methacryloyloxypropanoyl)aminoazobenzene and *trans*-(*S*)-4-*N*-(2-acryloyloxypropanoyl)-aminoazobenzene were studied by u.v. spectroscopy under irradiation at 366 nm. The resulting data are compared with those obtained for the corresponding low molecular weight structural models *trans*-(*S*)-4-*N*-(2-pivaloyloxypropanoyl)aminoazobenzene and *trans*-(*S*)-4-*N*-(2-isobutyroyloxypropanoyl)aminoazobenzene. The photoresponsive behaviour of the above polymeric systems was also investigated by circular dichroism measurements at various extents of photoisomerization. The results are discussed in terms of the structural requirements of the macromolecules.

(Keywords: photochromic chiral polymers; azobenzene-containing polymers; circular dichroism)

INTRODUCTION

It is well known that optically active poly(α-amino acid)s bearing side-chain azobenzene moieties exhibit photoresponsive properties[1–6]. Indeed, photoinduced reversible changes in the circular dichroism (c.d.) spectra of the peptide region (190–220 nm) can be readily associated with conformational variations in the macromolecules. The concurrent change in the c.d. bands in the 250–550 nm region connected with the azobenzene chromophores may also give a deeper insight into the arrangement of the side-chain photochromic groups around the polypeptide backbone. However, only a few examples are known regarding optically active polymers with hydrocarbon main chains and side-chain azobenzene chromophores.

Usually, the synthetic approach for the preparation of the above systems is based on the copolymerization of an optically active unsaturated monomer with an achiral comonomer containing the azobenzene chromophore[7–12]. These macromolecules can exist in a dissymmetrical conformation with a prevailing handedness, the achiral co-units being forced to assume a molecular arrangement of the same chirality as that adopted by the optically active co-units[13–15]. However, no dichroic bands strictly related to ordered conformations of the macromolecules exist in these systems. This implies that only c.d. bands associated with the azobenzene chromophore may give indications on the photoinduced conformational variations of the macromolecules.

In these copolymer systems, high conformational dissymmetry is accompanied by a quite large average distance between side-chain azobenzene chromophores, as the number of conformations with a predominant screw sense increases with increasing content of optically active co-units. This situation, reducing dipole–dipole interactions between photochromic groups, implies the lowering or even the disappearance of possible exciton splitting of the related c.d. bands, thus making difficult a close correlation between the chiroptical properties of the azobenzene chromophores and the conformations of the macromolecules.

Indeed, for copolymers of (−)-menthyl acrylate and (−)-menthyl methacrylate (MtMA) with 4-acryloxyazobenzene and 4-methacryloxyazobenzene, respectively[7,8], a significant variation in the c.d. bands associated with the photochromic groups is induced by irradiation with light, although the lack of exciton splitting does not allow correlation of this occurrence with the photoinduced conformational transitions.

In the case of copolymers of MtMA with 4-(2-methacryloyloxyethylenoxy)azobenzene, where a low amplitude couplet connected with the $\pi \rightarrow \pi^*$ electronic transition of the *trans*-azobenzene chromophore is observed[9,10], the disappearance upon irradiation of the

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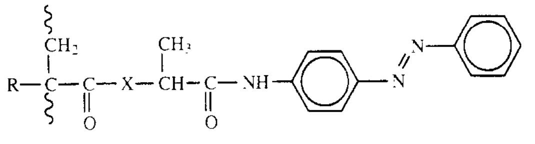
exciton splitting has been associated with the incapability of skewed *cis*-azobenzene moieties to assume mutual arrangements suited to exciton interactions, rather than with light-induced conformational order–disorder transitions of the macromolecules.

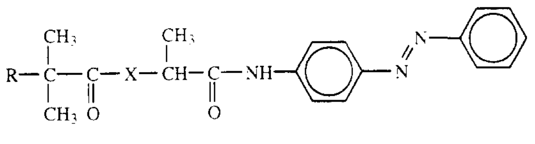
Analogous conclusions have been drawn for copolymers of (−)-menthyl vinyl ether with *N*-(4-azobenzene)maleimide, despite the higher stiffness of the macromolecules, owing to the presence of azobenzene chromophores directly anchored to a cyclic imide in the main chain[11,12].

Very recently, the synthesis of homopolymers of *trans*-(*S*)-4-*N*-(2-methacrylaminopropanoyl)aminoazobenzene (poly(MAA)), *trans*-(*S*)-4-*N*-(2-methacryloyloxypropanoyl)aminoazobenzene (poly(MLA)) and *trans*-(*S*)-4-*N*-(2-acryloyloxypropanoyl)aminoazobenzene (poly(ALA)) was reported[16]. The structures of these polymers were tailored to enhance both the predominant handedness of the macromolecules and the dipole–dipole interactions between side-chain azobenzene chromophores, thus in principle amplifying the exciton coupling and hence making easier the correlation between the chiroptical properties and conformations of the macromolecules.

Poly(MAA), analogously to the corresponding low molecular weight structural model *trans*-(*S*)-4-(2-pivaloylaminopropanoyl)aminoazobenzene (PAA), does not exhibit appreciable dichroic absorptions. On the contrary, poly(MLA) and poly(ALA) each show a strong c.d. couplet in the $\pi \rightarrow \pi^*$ spectral region of the *trans*-azobenzene chromophore. The amplitude of the couplet is one order of magnitude higher than that ever observed in previous copolymer systems, thus suggesting that both polymers are characterized by a high conformational homogeneity with a significantly predominant handedness.



poly(MAA) R = CH_3 X = NH
poly(MLA) R = CH_3 X = O
poly(ALA) R = H X = O



PAA R = CH_3 X = NH
PLA R = CH_3 X = O
ILA R = H X = O

It therefore appears very attractive to investigate the photochromic behaviour of the above polymeric systems in order to elucidate the possible conformational transitions of the macromolecules induced by photoisomerization of the side-chain azobenzene chromophores. Indeed, polymeric materials that undergo photoinduced changes in their secondary structures may be successfully applied to the design of optical data storage devices for optoelectronics.

EXPERIMENTAL

Materials

Poly(MAA), poly(MLA) and poly(ALA) were prepared by free radical homopolymerization of the corresponding monomers in THF solution at 70°C using 2,2′-azobisisobutyronitrile (AIBN) as a thermal initiator[16]. The most relevant properties of these polymers are summarized in *Table 1*. The low molecular weight structural models (*S*)-4-*N*-(2-pivaloylaminopropanoyl)aminoazobenzene (PAA), (*S*)-4-*N*-(2-pivaloyloxypropanoyl)aminoazobenzene (PLA) and (*S*)-4-*N*-(2-isobutyrzolyloxypropanoyl)aminoazobenzene (ILA) were synthesized as described elsewhere[16].

Physicochemical measurements

U.v. spectra of low and high molecular weight samples were recorded at 25°C in chloroform solution on Perkin–Elmer Lambda 19 and Jasco Uvidec 510 spectrophotometers. The spectral regions 550–400 and 400–250 nm were investigated using concentrations of about 1×10^{-3} mol l^{-1} and 5×10^{-4} mol l^{-1} (referred to the azobenzene chromophore) and cell path lengths of 1 cm and 0.1 cm respectively.

C.d. spectra were recorded at 25°C in chloroform solution on a Jasco 500A dichrograph. The same spectral regions, concentrations and cell path lengths were used as for the u.v. measurements.

Table 1 Structural characteristics and u.v. absorptions of the investigated optically active photochromic homopolymers in the all-*trans* configuration and the low molecular weight structural models

			U.v. absorption[a]			
			$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	
Sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	λ_1 (nm)	ϵ_1 (l mol^{-1} cm^{-1})	λ_2 (nm)	ϵ_2 (l mol^{-1} cm^{-1})
Poly(MAA)	6600	2.1	434	1140	347	21 700
Poly(MLA)	3800	1.4	437	1100	344	24 200
Poly(ALA)	2700	2.6	436	840	340	19 700
PAA			438	1250	351	27 400
PLA			435	1200	346	26 900
ILA			439	1240	346	26 900

[a] In chloroform solution

Photoisomerization experiments were carried out at 25°C on polymer solutions in chloroform (absorbance of < 0.3) using the following experimental set-up. The emission from a 150 W high pressure Hg–Xe lamp, filtered by a 366 nm interference filter (Balzer) with a ±5 nm bandwidth, was guided by a 3 mm × 50 cm quartz fibre to the top of a magnetically stirred solution in a 10 mm quartz cell placed within the u.v. spectrophotometer. The isomerization kinetics were monitored by measuring the 355 nm absorbance every 10 s until the photostationary state was reached. About 1000–1500 data points were collected for each photoisomerization experiment.

RESULTS AND DISCUSSION

Photochromic properties

The u.v. absorption spectra of all-*trans*-poly(MAA), all-*trans*-poly(MLA) and all-*trans*-poly(ALA) in chloroform solution are characterized by the presence of two bands centred at about 435 nm and 345 nm, associated respectively with $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions of the azobenzene chromophore[16] (*Table 1*). Analogous behaviour is shown by the corresponding low molecular weight structural models PAA, PLA and ILA, although a hyperchromic effect is observed in these systems as compared to the polymers[16].

As far as the $\pi \rightarrow \pi^*$ band is concerned, the reduced values of the molar extinction coefficients of the polymeric samples can be attributed to the occurrence of dipole–dipole electrostatic interactions between the side-chain azoaromatic groups[16–18].

Irradiation at 366 nm of the polymer samples in chloroform solution promotes the *trans–cis* isomerization of the side-chain azobenzene chromophores. This process gives rise to a shift towards higher frequencies and a decrease in intensity of the $\pi \rightarrow \pi^*$ absorption band. At the same time, the molar extinction coefficient of the $n \rightarrow \pi^*$ absorption band increases (*Figure 1*). Analogous behaviour is observed for the corresponding low molecular weight models.

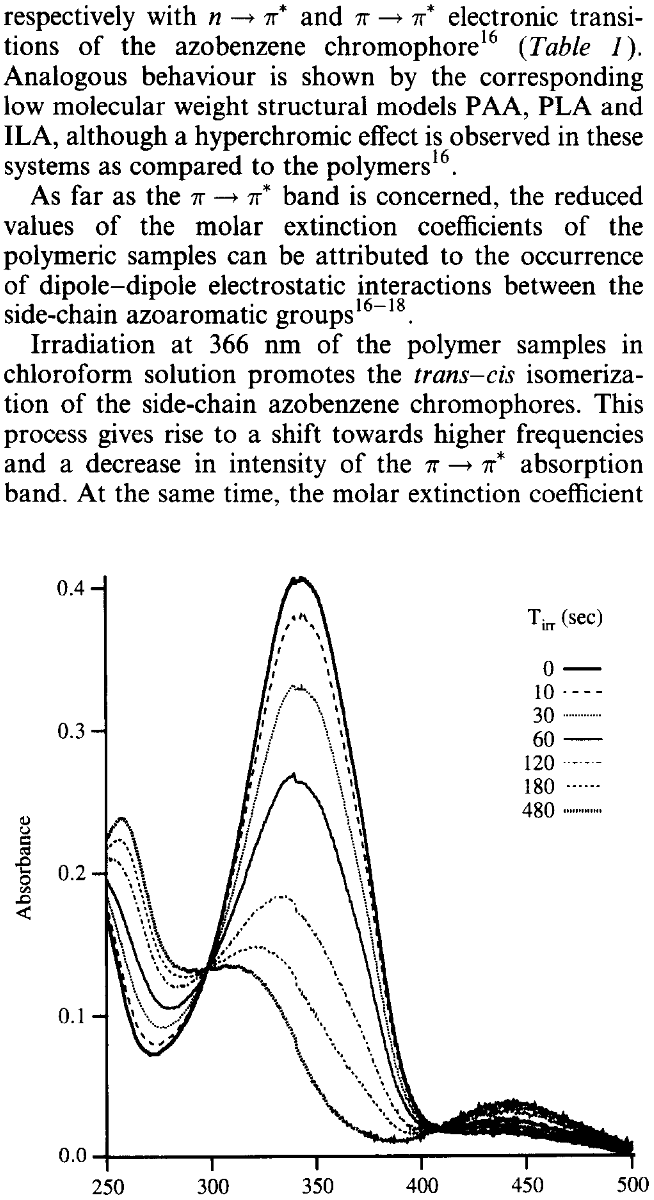


Figure 1 U.v. spectra of poly(MLA) samples for different irradiation times at 366 nm in chloroform solution at 25°C

In all cases two well-defined isosbestic points at about 405 nm and 300 nm are observed (*Figure 1* and *Table 2*), thus substantiating that only two absorbing species, namely *trans*-azobenzene and *cis*-azobenzene, are involved in the process. This rules out the photochemical formation of secondary by-products, as required for a completely reversible process.

A plot of the absorbance at 355 nm *versus* irradiation time exhibits a monoexponential decrease for all samples in accordance with first-order kinetics. Similar behaviour has been reported for several polymeric systems bearing side-chain azobenzene chromophores[7,12,19]. This result clearly indicates homogeneous photochromic behaviour for *trans*-azobenzene chromophores in polymer samples. 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.

The photoisomerization rate constants k_i and the ratios A_∞/A_0, where A_0 and A_∞ represent the initial and photostationary absorbances at 355 nm, were evaluated from the best fit of the experimental data (*Table 2*). Although both the k_i and A_∞/A_0 values are of the same order of magnitude for both low and high molecular weight samples, slightly lower rates and higher A_∞/A_0 ratios, i.e. larger contents of residual *trans*-azobenzene chromophores, were evaluated for the polymers as compared to the corresponding structural models. These results suggest that the macromolecular backbone has a tendency to reduce the photoisomerization rate of side-chain *trans*-azobenzene chromophores, probably owing to steric effects.

Photoresponsive properties

Samples of all-*trans*-poly(MAA) and *trans*-PAA in chloroform solution display very weak negative c.d. bands centred at 430–440 nm, whereas no dichroic bands associated with the $\pi \rightarrow \pi^*$ electronic transition of the photochromic group are detected (*Table 3*). Moreover, no variation in the chiroptical properties is observed upon changing the polarity of the solvent[16]. These results can be interpreted by assuming that all-*trans*-poly(MAA) adopts substantially achiral conformations in

Table 2 Photochromism of low and high molecular weight azobenzene derivatives

Sample	Isosbestic points[a] λ_1 (nm)	λ_2 (nm)	$10^{-3} \times k_i$[b] (s^{-1})	A_∞/A_0[c]
Poly(MAA)	407.5	300.0	11.9	0.095
Poly(MLA)	407.5	298.0	10.2	0.032
Poly(ALA)	406.0	296.5	9.5	0.053
PAA	407.5	299.5	15.7	0.004
PLA	404.5	299.5	12.5	0.005
ILA	405.0	299.0	12.6	0.015

[a] In chloroform solution at 25°C

[b] Photoisomerization rate constant under irradiation at 366 nm in chloroform solution at 25°C

[c] A_0 and A_∞ are the 355 nm absorbances respectively at $t = 0$ and at the photostationary state

Table 3 Chiroptical properties in chloroform solution of the model compounds and the corresponding homopolymers bearing side-chain azobenzene chromophores

	Circular dichroism properties[a]					
	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$			
Sample	λ_1 (nm)	$\Delta\epsilon_1$ (l mol^{-1} cm^{-1})	λ_2 (nm)	$\Delta\epsilon_2$ (l mol^{-1} cm^{-1})	λ_3 (nm)	$\Delta\epsilon_3$ (l mol^{-1} cm^{-1})
trans-PAA	440	−0.01				
trans-Poly(MAA)	430	−0.01				
trans-PLA	438	0.06	345	−0.80		
cis-PLA	436	0.26	311	−0.48		
trans-Poly(MLA)	434	−0.11	362	5.49	325	−5.15
cis-Poly(MLA)	449	0.27	289	−2.37		
trans-ILA	440	0.09	345	−1.35		
cis-ILA	440	0.12	310	−0.36		
trans-Poly(ALA)	436	0.13	363	1.91	318	−0.75
cis-Poly(ALA)	436	−0.36	329	0.61		

[a] The λ and $\Delta\epsilon$ values refer to related c.d. maxima; $\Delta\epsilon$ values refer to the concentration of azobenzene chromophores

solution, probably owing to the presence of two amide groups per repeat unit, which may strongly favour the formation of rather stable inter- and intramolecular hydrogen bonds[16].

Poly(MLA) and poly(ALA) in chloroform solution exhibit (*Table 3*) dichroic bands centred at about 435 nm related to the $n \rightarrow \pi^*$ electronic transition of the azobenzene chromophore in the *trans* configuration and, in contrast to the corresponding models PLA and ILA, strong c.d. couplets in the spectral region of the $\pi \rightarrow \pi^*$ absorption band whose intensities are affected by solvent polarity[16]. This behaviour, particularly relevant for poly(MLA), can be interpreted in terms of a rather high conformational homogeneity and dissymmetry of the macromolecules. However, the two bands of opposite sign in the c.d. couplet have substantially the same ellipticity for poly(MLA), whereas this is not the case for poly(ALA) (*Table 3*), suggesting that in chloroform the latter polymeric system assumes a less ordered chiral conformation.

In this context it was of interest to investigate the photoresponsive properties of the above polymers in order to elucidate possible order–disorder conformational transitions induced by irradiation with light. Therefore, poly(MLA), poly(ALA), PLA and ILA were irradiated at 366 nm and their chiroptical properties studied at different times of exposure, i.e. at variable extents of *trans–cis* photoisomerization.

On irradiation, both PLA and ILA give rise to a modest increase in the $n \rightarrow \pi^*$ c.d. band, whereas the negative $\pi \rightarrow \pi^*$ band progressively shifts towards shorter wavelengths (*Table 3*).

For both polymers the ellipticity of the band connected with the $n \rightarrow \pi^*$ electronic transition changes sign and its absolute value increases with increasing content of *cis*-azobenzene chromophores. However, the rather low intensity of this dichroic band makes it difficult to relate the variation in the c.d. spectrum to the extent of photoisomerization. More information can be obtained from the variation in the c.d. couplets in the $\pi \rightarrow \pi^*$ absorption band. Indeed, a progressive reduction of the exciton splitting is observed for poly(MLA) (*Figure 2*) until the two bands coalesce into a single negative band centred at around 300 nm at the photostationary state (about 11% of residual *trans*-azobenzene groups).

No sharp variation in the c.d. spectrum is observed during the *trans–cis* isomerization of the side-chain azobenzene chromophores and a rather strong dichroic band at about 300 nm is still present at the photostationary state. A light-induced order–disorder conformational transition of poly(MLA) macromolecules can therefore be ruled out. The observed reduction in amplitude of the exciton splitting of the c.d. band on irradiation can be attributed to a decrease in the number of residual *trans*-azobenzene chromophores in suitable chiral arrangements for exciton coupling.

The contribution to the observed c.d. spectrum from

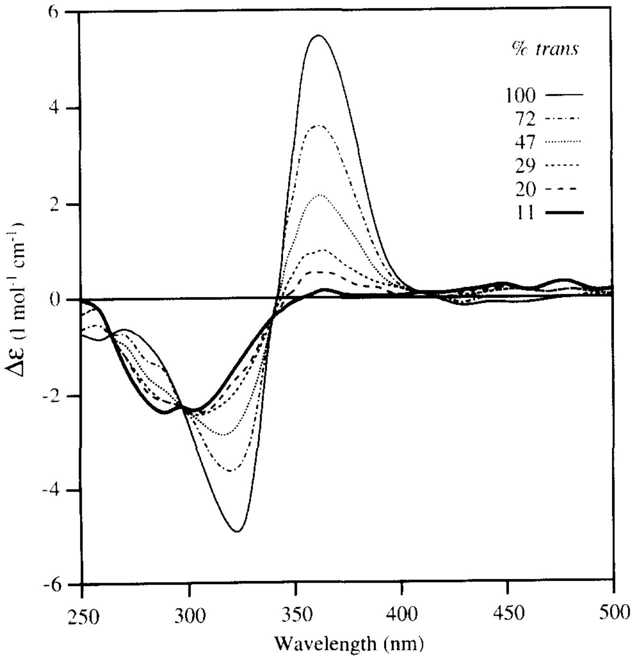


Figure 2 Dependence of c.d. spectrum of poly(MLA) on the extent of *trans–cis* photoisomerization of azobenzene chromophores in chloroform solution at 25°C

isolated *trans*-azobenzene chromophores should be negligible if we take into account the low percentage of *trans*-azobenzene chromophores at the photostationary state and the lower $\Delta\epsilon$ value shown by the model compound *trans*-PLA as compared to the corresponding polymer[16]. Moreover, the presence of several isosbestic points (*Figure 2*) clearly indicates that the observed c.d. spectra originate from only two different species. Therefore, the observed variation in the $\pi \rightarrow \pi^*$ dichroic band under irradiation must be the result of the contributions from chirally perturbed *cis*-azobenzene and coupled *trans*-azobenzene chromophores inserted in polymer segments having a particular chiral conformation. On the other hand, the overall conformational homogeneity and dissymmetry of the macromolecules seem to be little affected by the isomerization process. This is strongly supported by the rather large ellipticity of the $\pi \rightarrow \pi^*$ c.d. band at the photostationary state ($\Delta\epsilon = -2.3$ l mol^{-1} cm^{-1}) as compared to that for *cis*-PLA ($\Delta\epsilon = -0.48$ l mol^{-1} cm^{-1}). This implies a significant chirality of the polymer chains in solution.

Also for poly(ALA) the amplitude of the $\pi \rightarrow \pi^*$ couplet is reduced on increasing the content of *cis*-azobenzene chromophores, until finally a single positive dichroic band is formed (*Figure 3*). However, the absence of definite isosbestic points seems to indicate that the contributions from *trans*-azobenzene and *cis*-azobenzene moieties to the c.d. spectra depend on the relative amounts of the two species. Coupled and uncoupled *trans*-azobenzene and uncoupled *cis*-azobenzene moieties may give rise to different dichroic effects when located in sections of macromolecules with a different extent of prevailing chirality. This may be related to the lower conformational homogeneity of the macromolecules in poly(ALA) as compared to poly(MLA).

Also in this case, the rather large ellipticity of the c.d. band at the photostationary state ($\Delta\epsilon = 0.6$ l mol^{-1} cm^{-1}) confirms that a certain conformational order and prevailing handedness of the macromolecules is retained after photoisomerization of the side-chain azobenzene chromophores. This picture is confirmed by the opposite signs of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ c.d. bands for *cis*-poly(ALA) and *cis*-ILA.

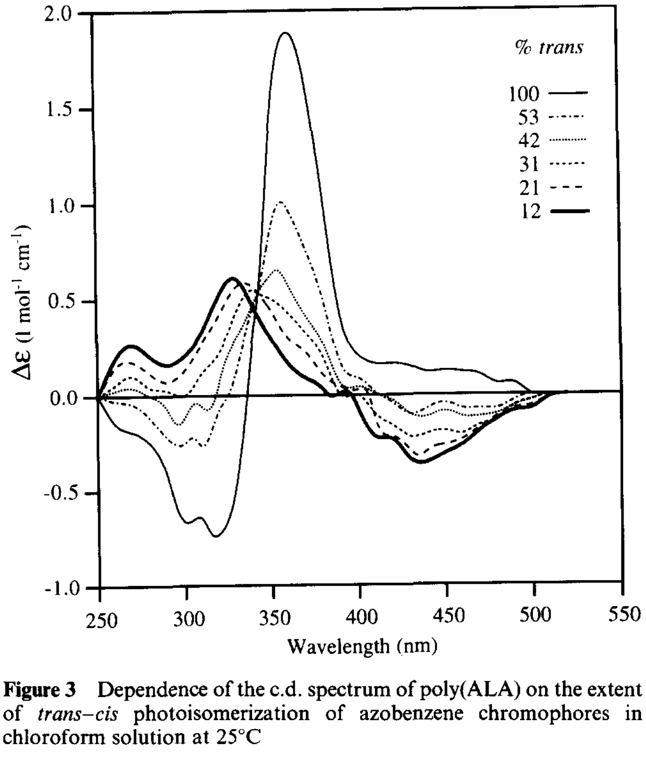


Figure 3 Dependence of the c.d. spectrum of poly(ALA) on the extent of *trans–cis* photoisomerization of azobenzene chromophores in chloroform solution at 25°C

CONCLUSIONS

The photochromic and photoresponsive behaviour of optically active homopolymers containing side-chain azobenzene groups spaced from the main-chain by L-alanine and L-lactic acid residues has been investigated in solution. On the basis of the results obtained, the following final remarks can be made.

The *trans–cis* photoisomerization behaviour of the azobenzene chromophores is not affected by the presence of adjacent azobenzene groups in either the *trans* or the *cis* configuration or by the chemical structure of the polymeric system. However, comparison of the photoisomerization rates of the polymers with those of the corresponding low molecular weight structural models seems to suggest that the macromolecular structure slightly hinders the isomerization process.

On irradiation at 366 nm, remarkable changes are observed in the c.d. spectra of poly(MLA) and poly(ALA). The exciton splitting of the $\pi \rightarrow \pi^*$ dichroic band progressively disappears and eventually a single band is obtained. The residual exciton splitting observed for both poly(ALA) and poly(MLA) at intermediate levels of photoisomerization can be attributed to the presence of azobenzene moieties in the *trans* configuration still close enough to give dipole–dipole interactions. The disappearance of the couplet at the photostationary state can be associated with the incapability of non-planar *cis*-azobenzene chromophores to give exciton coupling. The rather large intensity of the dichroic bands at the photostationary state seems to indicate that a photoinduced order–disorder conformational transition of the macromolecules does not occur. Comparison of the c.d. properties of the polymers on irradiation seems to indicate that the conformational homogeneity of poly(MLA) is greater than that of poly(ALA).

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REFERENCES

1 Pieroni, O., Houben, J. L., Fissi, A., Costantino, P. and Ciardelli, F. *J. Am. Chem. Soc.* 1980, **102**, 5913
2 Ueno, A., Takahashi, K., Anzai, J. and Osa, T. *Bull. Chem. Soc. Jpn* 1980, **53**, 1988
3 Fissi, A., Pieroni, O. and Ciardelli, F. *Biopolymers* 1987, **26**, 1993
4 Fabbri, D., Pieroni, O., Fissi, A. and Ciardelli, F. *Chim. Ind. (Milan)* 1990, **72**, 115
5 Hallensleben, M. L. and Menzel, H. *Br. Polym. J.* 1990, **23**, 199
6 Yamamoto, H., Ikeda, K. and Nishida, A. *Polym. Int.* 1992, **27**, 67
7 Altomare, A., Carlini, C., Ciardelli, F. and Solaro, R. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 1267
8 Altomare, A., Carlini, C., Ciardelli, F. and Solaro, R. *Polym. J.* 1988, **20**, 801

9 Altomare, A. Ciardelli, F., Lima, R. and Solaro, R. *Polym. Adv. Technol.* 1991, **2,** 3

10 Altomare, A., Ciardelli, F., Lima, R. and Solaro, R. *Chirality* 1991, **3,** 292

11 Angiolini, L. and Carlini, C. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29,** 1455

12 Angiolini, L., Caretti, D., Carlini, C., Altomare, A. and Solaro, R. *J. Polym. Sci., Polym. Chem. Edn* 1994, **32,** 2849

13 Ciardelli, F., Carlini, C., Chiellini, E., Salvadori, P., Lardicci, L., Menicagli, R. and Bertucci, C. in 'Preparation and Properties of Stereoregular Polymers' (Eds R. W. Lenz and F. Ciardelli), Reidel, Dordrecht, 1979, p. 353

14 Ciardelli, F., Pieroni, O., Fissi, A., Carlini, C. and Altomare, A. *Br. Polym. J.* 1989, **21,** 97

15 Ciardelli, F., Altomare, A., Solaro, R., Carlini, C. and Angiolini, L. *Indian J. Technol.* 1993, **31,** 278

16 Angiolini, L., Caretti, D., Carlini, C. and Salatelli, E. *Macromol. Chem. Phys.* in press

17 Tinoco Jr, I. *J. Am Chem. Soc.* 1960, **82,** 4785

18 Okamoto, K., Itaya, A. and Kusabayashi, S. *Chem. Lett.* 1974, 1167

19 Ciardelli, F., Pieroni, O., Fissi, A., Altomare, A., Solaro, R. and Tirelli, N. *Polym. Adv. Technol.* 1995, **6,** 32