

Optically Active Polymers Containing Side Chain Azobenzene Chromophores: Chiroptical Properties and Photochromic Behaviour of 4-Methacryloylazobenzene/(-)-Menthyl Methacrylate Copolymers

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ABSTRACT: Copolymers of *trans*-4-methacryloylazobenzene (MAB) with (-)-menthyl methacrylate (MtMA) have been prepared by using AIBN as free radical initiator. The resulting polymer samples are characterized by a substantially random distribution of monomeric co-units, as evaluated from reactivity ratios. Kinetics of photoinduced *trans* to *cis* and thermally induced *cis* to *trans* back-isomerization of azobenzene side chains have been examined and the relevant kinetic parameters evaluated. Dependence of chiroptical properties on both copolymer composition and extent of *cis/trans* isomerization has been investigated. The circular dichroism induced on azobenzene chromophores has been shown to arise mainly from isolated MAB units, as the chiral perturbation is not appreciably transmitted along MAB sequences. The results have been discussed in terms of tertiary structure reversible variations connected to photoinduced change of local conformation.

KEY WORDS (-)-Menthyl Methacrylate / 4-Methacryloylazobenzene /
Photochromic Polymers / *cis-trans* Isomerization / Chiral Polymers /
Chiroptical Properties / Circular Dichroism /

In previous papers¹⁻³ it has been reported that copolymers of optically active (-)-menthyl acrylate (MtA) with photochromic monomers, such as 4-acryloylazobenzene (AAB), 4-acryloxystilbene (AS), and 4-vinylstilbene (VS), show dichroic bands in the absorption region of the aromatic groups.

The ellipticity of these bands were found to be dependent on the content of photochromic groups and *trans* to *cis* photoisomerization extent.^{1,4-6} In the case of stilbene containing polymers the variation of dichroic properties induced by light irradiation suggested some local conformational change, whereas the re-

sults for AAB/MtA copolymers appeared less evident. As these last copolymers, prepared by radical initiation, are mainly non stereoregular with a substantial tendency to alternating structure ($r_{AAB} \cdot r_{MtA} = 0.45$), it appeared interesting to investigate the influence of main chain stereoregularity and monomer sequence distribution on photophysical and chiroptical properties.

For both purposes 4-methacryloylazobenzene/(-)-menthyl methacrylate copolymers appeared the most convenient. In fact it is well known that in the copolymerization with aromatic monomers, methacrylic esters ex-

hibit fairly higher reactivity ratios than the corresponding acrylic derivatives.⁷⁻¹⁰ In addition, depending on polymerization conditions, methacrylic polymers can be rather easily prepared with stereoregularity degree ranging from mainly syndiotactic to prevailing isotactic.^{11,12} In this paper the preparation is described of copolymers of 4-methacryloxyazobenzene with (-)-menthyl methacrylate copolymers by free radical polymerization, as well as their chiroptical and photochromic behaviour. The stereoregular copolymers of the same monomers and their properties will be reported in a future paper.

EXPERIMENTAL

Monomers

trans-4-Methacryloxyazobenzene (MAB) was synthesized by reacting commercial (Fluka) *trans*-4-hydroxyazobenzene with methacryloyl chloride and triethylamine (molar ratio 1 : 1.5 : 2) in anhydrous diethyl ether at room temperature for 6 h. The reaction mixture was extracted with chloroform and the extracts were washed with dilute HCl, 5% NaHCO₃, and water, in that order, and dried over anhydrous Na₂SO₄. After removal of the solvents the crude product was recrystallized from ethanol/hexane 1 : 1 to give pure MAB (96% yield) as bright yellow lamellae having mp 116°C. ¹H NMR (CDCl₃): δ = 7.95, 7.50 and 7.28 (3m, 9H, aromatic protons), 6.38 and 5.78 (2m, 2H, olefinic protons) and 2.07 ppm (m, 3H, methyl protons). IR (KBr pellet): $\bar{\nu}$ = 3100—3000 (ν_{CH} aromatic), 3000—2900 (ν_{CH} aliphatic), 1782 ($\nu_{\text{C=O}}$), 1637 ($\nu_{\text{C=C}}$ olefinic), 1580, 1490, and 1480 ($\nu_{\text{C=C}}$ aromatic), 1380 ($\delta_{\text{s}}\text{CH}_3$), 1195 ($\nu_{\text{as}}\text{C-O-C}$), 1120 ($\nu_{\text{s}}\text{C-O-C}$), 890 ($\delta_{\text{CH}_2} =$), 815 (δ_{CH} 1,4-disubstituted phenyl), 765 and 685 cm⁻¹ (δ_{CH} monosubstituted phenyl).

(-)-Methyl methacrylate (MtMA) having bp 95°C/2 mm and $[\alpha]_{\text{D}}^{25} = -91.8$ (neat), was prepared in 89% yield starting from (-)-menthol and following the above procedure.

trans-4-(2-Methylpropanoyl)azobenzene (IAB) was synthesized as previously reported.¹

Commercial 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol.

Polymerization Experiments

Free radical copolymerization experiments were performed in benzene at 60°C in vials sealed under high vacuum using AIBN as initiator. After a suitable period of time, polymerization was interrupted by pouring the reaction mixture into a large excess of methanol. The coagulated polymer was purified by repeated precipitation in methanol. Finally, the polymeric product was filtered and dried under vacuum at room temperature.

Physicochemical Measurements

200-MHz ¹H NMR spectra were recorded in CDCl₃ solution with a Varian Gemini-200 spectrometer using TMS as the internal standard. IR examinations were carried out with a Perkin-Elmer 1330 spectrophotometer. UV and CD measurements in the range 500—250 nm were performed in CHCl₃ solution by a JASCO Uvidec 510 spectrophotometer and a JASCO J500A dichrograph. Optical rotatory measurements were performed on polymer solution in CHCl₃ at 25°C with a Perkin-Elmer 141 spectropolarimeter. Melting point determinations were carried out on a hot-plate Kofler microscope with a 3°C min⁻¹ heating rate. Average molecular weights of polymer samples were determined in THF solution by GPC measurements on a Perkin-Elmer Model 2/2 HPLC, equipped with two Shodex columns A 802/S and 803/S connected in series. Poly(styrene) standards were used for calibration. Irradiations of samples in chloroform solution were carried out at room temperature with a halogen lamp (150 W) filtered with a 348 nm interference filter. Thermal *cis* to *trans* isomerization experiments were carried out in chloroform distilled over calcium hydride just prior the use and followed by UV at constant temperature.

Table I. Copolymerization of 4-methacryloylazobenzene (MAB) with (–)-methyl methacrylate (MtMA) in benzene at 60°C with AIBN as initiator^a

Run	Feed MAB	Time h	Conv. ^b %	MAB ^c mol%	Polymer		
	mol%				$[\alpha]_D^{25}$ ^d	\bar{M}_n ^e	\bar{M}_w/\bar{M}_n
MA1	100	40	61.3	100	—	51000	2.1
MA2	85	5	21.1	88.6	–10.1	76000	2.0
MA3	70	5	20.8	74.9	–25.0	88000	1.9
MA4	50	6	12.7	55.4	–42.2	98000	1.7
MA5	30	5	14.2	38.1	–61.5	96000	1.7
MA6	15	2	3.9	19.0	–83.5	104000	1.7
MA7	5	4	22.1	7.1	–89.0	113000	1.6
MA8	0	40	80.0	0	–94.2	108000	1.7

^a Benzene 25 ml, comonomer mixture 3 g, AIBN 0.03 g.

^b Evaluated as (weight of polymer/total weight of starting comonomers) × 100.

^c Evaluated by ¹H NMR.

^d In chloroform.

^e Determined by GPC.

RESULTS AND DISCUSSION

Synthesis and Characterization of Copolymers

Optically active copolymers of (–)-methyl methacrylate with 4-methacryloylazobenzene [poly(MtMA-*co*-MAB)s] were prepared by polymerization in benzene at 60°C in the presence of AIBN as radical initiator; starting molar ratios MAB/MtMA in the range 6–0.05 were used (Table I). Copolymerization runs were interrupted at low conversion in order to determine the comonomer reactivity ratios and to dispose of copolymer samples having substantially homogeneous composition and distribution of monomeric units. The copolymerization diagram (Figure 1) indicates that MAB is slightly more reactive than MtMA. The reactivity ratios calculated by least-square evaluation of the Kelen-Tudos parameters¹³ are $r_{\text{MAB}} = 1.27$ and $r_{\text{MtMA}} = 0.7$. The product of these reactivity ratios is quite close to unit ($r_{\text{MtMA}} \cdot r_{\text{MAB}} = 0.89$) and therefore the copolymer samples are characterized by a substantially random distribution of monomeric units.¹⁴ However a better insight into the chemical structure of different copolymer

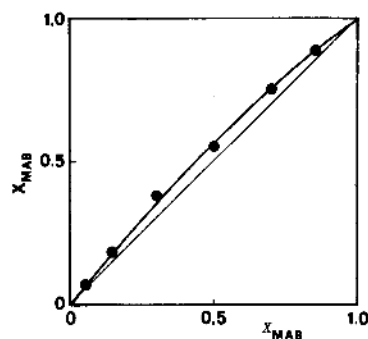


Figure 1. Copolymerization diagram for the MtMA/MAB system: X_{MAB} and X_{MAB} are the MAB molar fractions in the feed mixture and in the copolymerization products, respectively.

samples can be obtained from the average sequence lengths (\bar{l}) and percent molar fractions of units [$X(n)$] inserted in blocks on n units (Table II) as evaluated from the copolymerization data.^{15,16}

Fairly high molecular weights ($5\text{--}11 \times 10^4$) are observed in all cases. The dependence of both molecular weight (\bar{M}_n) and degree of dispersion (\bar{M}_w/\bar{M}_n) on the composition of the copolymerization mixture seems to indicate a higher tendency of MAB, as compared with

Table II. Mean sequence lengths (\bar{l}_{MAB} and \bar{l}_{MtMA}) and percent molar fractions [$X_{\text{MAB}}(n)$ and $X_{\text{MtMA}}(n)$] of units from MAB and MtMA in sequence lengths of n units for poly(MtMA-co-MAB)s^a

Sample	MAB mol%	\bar{l}_{MAB}	\bar{l}_{MtMA}	$X_{\text{MAB}}(n)$						$X_{\text{MtMA}}(n)$					
				$n=1$	2	3	4	5	>5	$n=1$	2	3	4	5	>5
MA2	88.6	10.9	1.1	0.8	1.5	2.1	2.5	2.9	90.2	84.2	13.9	1.7	0.2	0.0	0.0
MA3	74.9	4.8	1.2	4.4	6.9	8.2	8.6	8.5	63.4	65.6	24.9	7.1	1.8	0.4	0.2
MA4	55.4	2.6	1.6	15.1	18.4	16.9	13.8	10.6	25.2	40.9	29.5	15.9	7.7	3.5	2.5
MA5	38.1	1.8	2.1	31.5	27.6	18.2	10.6	5.8	6.3	21.9	23.3	18.6	13.2	8.8	14.2
MA6	19.0	1.3	4.0	59.4	27.3	9.4	2.9	0.8	0.2	6.3	9.4	10.6	10.6	9.9	52.2
MA7	7.1	1.1	10.2	83.1	14.7	2.0	0.2	0.0	0.0	1.0	1.7	2.4	2.8	3.2	88.9

^a Evaluated according to ref 15 and 16.

MtMA, to promote chain transfer and/or termination during the polymerization process.

IR spectra of poly(MtMA-co-MAB)s show the same bands as the corresponding homopolymers mixtures, indicating that both counts are present in the macromolecules. On the other hand solubility and chiroptical properties (see below) rule out the formation of homopolymer mixtures.

In the region of aromatic protons the ¹H NMR spectrum of IAB is characterized by three sets of signals centered at 7.22, 7.46, and 7.93 ppm. Correspondingly the spectra of copolymer samples display three broad bands centered at 7.21, 7.36, and 7.80 ppm. Two small bands are also observed at about 6.95 and 6.75 ppm, whose relative intensity decreases with decreasing the MAB content. As a consequence these two higher field signals have been attributed to partially overlapping MAB chromophores, in close analogy to what already reported for several copolymers of vinylaromatic monomers.¹⁷ However the small relative intensity of these bands, even in the MAB homopolymer (about 0.4H), suggests that the extent of interaction between side chain azobenzene groups should be rather limited, at least in the NMR time scale.

Reversible *trans-cis* Isomerization

By irradiation at 348 nm the investigated polymer samples and the low molecular weight

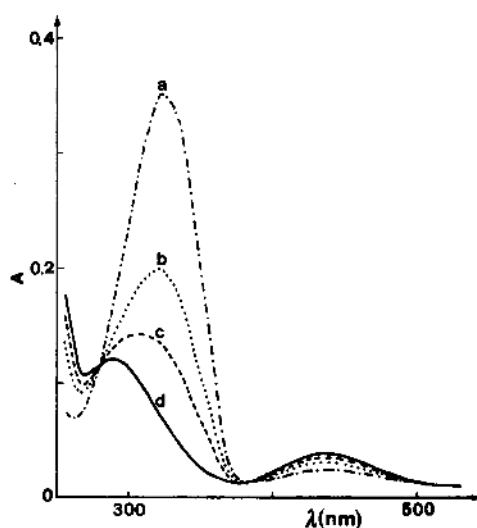


Figure 2. Variation of the UV absorption spectrum in chloroform solution of a MtMA/MAB copolymer sample containing 7.1% mol of MAB units with irradiation time at 348 nm. Curves a to d correspond to 0, 30, 60, and 300 s of irradiation time, respectively.

structural analog IAB undergo *trans* to *cis* photoisomerization until a photostationary state is eventually reached (Figure 2). In all cases a plot of A_t , where A_t is equal to $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$, and A_0 , A_t , and A_∞ are the absorbances at 320 nm at time 0, t and ∞ , respectively, vs. the irradiation time fits a first-order kinetics.⁴ Photoisomerization rates and the ratio A_∞/A_0 of polymer samples are of the same order of magnitude as those observed

Table III. UV absorption properties and photochromism of high and low molecular weight *trans*-azobenzene derivatives

Sample	MAB mol%	UV ^a		Photoisomerization ^b	
		λ_{\max}	ϵ_{\max}	rate constant $\times 10^2$	A_{∞}/A_0
		nm	$\text{mol} \cdot \text{l}^{-1} \cdot \text{cm}^{-1}$	s^{-1}	
MA1	100	321.5	18800	2.1	0.25
MA2	88.6	322.0	18900	2.2	0.26
MA3	74.9	322.0	18000	2.2	0.25
MA4	55.4	322.5	21000	2.2	0.25
MA5	38.1	322.6	21500	2.4	0.26
MA6	19.0	323.5	23000	2.4	0.25
MA7	7.1	324.0	23800	2.7	0.23
IAB	—	324.0	22800	2.3	0.25

^a In chloroform solution at room temperature.

^b Under irradiation at 348 nm in chloroform solution at room temperature.

for IAB (Table III). This indicates that the macromolecular structure has little influence on the photoisomerization process, analogously to what observed for several azobenzene containing polymers.^{4,5,18}

When kept in the dark copolymer samples mainly containing *cis*-azobenzene moieties undergo thermal *cis* to *trans* back-isomerization. The isomerization rates heavily depend on the purity of the chloroform used as solvent. In fact the addition of a small amount of HCl gives rise to an increase of two order of magnitude whereas the presence of 0.75% of ethanol as stabilizer gives rise to both an increase of the rate and a departure from first order kinetics (Figure 3).

The linear dependence of A_t on time is also in this case in accordance with a first order kinetics. The evaluated isomerization rates are almost independent of the copolymer composition and close to that of IAB (Table IV). An Arrhenius plot of the reaction rates in the range 25–55°C gives straight lines (Figure 4) and allows one to evaluate a pre-exponential factor C of about $2.5 \times 10^7 \text{ s}^{-1}$ and an activation energy ΔE^* of about 17 kcal mol^{-1} for the investigated samples (Table IV).

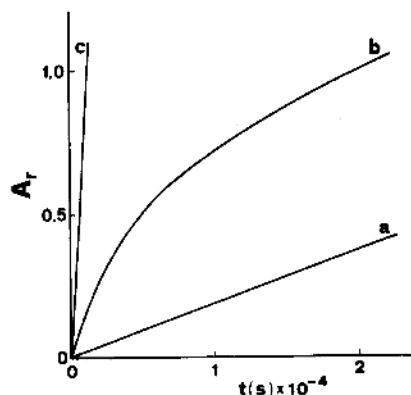


Figure 3. Kinetic plot of thermal *cis*–*trans* isomerization in chloroform solution at 35°C of poly(MtMA-*co*-MAB) samples containing 7.1% mol of MAB units: a) solvent purified over CaH_2 ; b) solvent containing 0.75% of ethanol; c) solvent containing 1% of concentrated HCl.

Chiroptical Properties

The UV spectrum of all the investigated samples is characterized, in the 550–250 nm region, by two absorption bands centered at about 440 and 322 nm (Figure 2) and attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions of azobenzene chromophore, respectively.¹⁹

As compared with the low molecular weight

Table IV. Thermal isomerization of polymers containing MAB structural units and their low molecular weight model compound IAB

Sample	MAB mol%	Isomerization rate constant $\times 10^5$ (s^{-1})				ΔE^{*a} kcal mol $^{-1}$	ln C a
		25°C	35°C	45°C	55°C		
		MA1	100	0.83	2.3		
MA2	88.6	0.85	2.1	4.3	12	16.7	17
MA3	74.9	0.90	2.1	4.3	13	16.8	17
MA4	55.4	0.86	2.0	4.3	13	17.2	17
MA5	38.1	0.84	2.0	4.3	13	17.3	18
MA6	19.0	0.80	2.0	4.3	13	17.6	18
MA7	7.1	0.77	1.9	4.4	13	18.1	19
IAB	—	0.76	2.2	3.6	9	15.5	15

^a Evaluated from the relation $\ln k = \ln C - \Delta E^*/RT$.

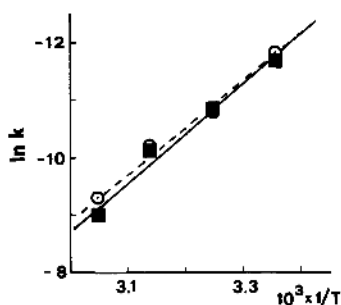


Figure 4. Arrhenius plot of *cis* to *trans* thermal isomerization rates of (—■—) poly(MtMA-*co*-MAB)s and (—○—) IAB.

model compound IAB, polymer samples exhibit progressive hypochromic and hypsochromic effects with increasing content of MAB units (Table III). A similar trend has already been observed in several polymers containing aromatic chromophores^{17,20} and has been attributed to electronic interactions between neighbouring chromophores.^{21,22}

All copolymer samples are characterized by a negative optical rotation at sodium D line, as observed for poly(MtMA) (Table I). A plot of specific rotation $[\alpha]_D^{25}$ vs. the content of MtMA units exhibits a linear trend thus excluding any contribution of the MAB units to optical rotation at 589 nm. A similar behavior has

already been observed in other optically active copolymers of (–)-menthyl acrylate and methacrylate with unsaturated aromatic monomers.^{2,7,23,24} This finding does not exclude an asymmetric perturbation of the azobenzene moiety and indeed CD spectra show in the 550–250 nm region one broad, negative dichroic band centered at about 450 nm (Figure 5). No dichroic absorption is detectable in the correspondence of the $\pi \rightarrow \pi^*$ electronic transition. The absolute value of the ellipticity monotonously increases with the increasing content of MtMA units (Table V) even if no linear dependence on both chemical composition and mean sequence lengths of monomeric units can be detected. On the contrary a plot of $\Delta\epsilon$ vs. the molar fraction of isolated MAB units (Figure 6) fits a straight line, thus suggesting that the observed CD mainly arises from isolated MAB units, *i.e.*, the induced chiral perturbation is not appreciably transmitted along MAB sequences. A similar behaviour has been already reported for copolymers of (–)-menthyl acrylate with 4-hydroxybenzophenone acrylate and has been attributed to the relative conformational mobility of the side chain aromatic chromophore.²⁰

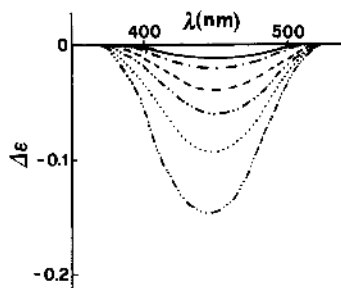


Figure 5. CD spectra of all *trans* poly(MtMA-*co*-MAB)s containing, respectively, (· · ·) 7.1%, (---) 19.0%, (- · - ·) 38.1%, (----) 55.4%, (- - - -) 74.9%, and (—) 88.6% of MAB units.

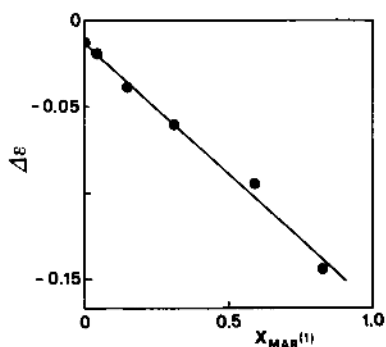


Figure 6. Differential molar dichroic absorption coefficient at 450 nm (D_2) of all *trans* poly(MtMA-*co*-MAB)s in chloroform solution vs. molar fraction of isolated MAB units [$X_{\text{MAB}}(1)$].

The CD spectra of analogous copolymers of (–)-menthyl acrylate with 4-acryloxyazobenzene display two dichroic bands centered at about 300 and 435 nm.¹ The former band has been shown to arise mainly from *trans*-azobenzene containing units inserted in blocks and to a minor extent from isolated ones. As in poly(MtMA-*co*-MAB)s blocks of MAB units are not appreciably chirally perturbed, the contribution to the dichroic absorption at about 300 nm by interacting *trans*-azobenzene chromophores should be absent. As a consequence the anisotropy factor ($\Delta\epsilon/\epsilon$) too small to give rise to measurable CD.

Spectra of copolymer samples containing MAB units mainly in the *cis* form exhibit a broad positive dichroic band and a less intense

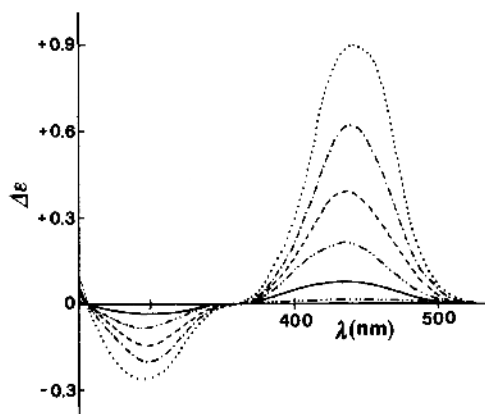


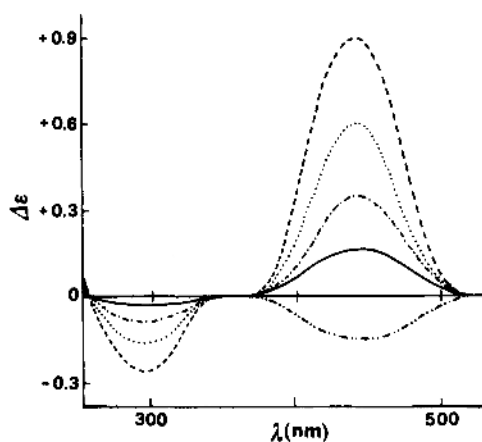
Figure 7. CD spectra at the photostationary state of poly(MtMA-*co*-MAB)s containing, respectively, (· · ·) 7.1%, (---) 19.0%, (- · - ·) 38.1%, (----) 55.4%, (- - - -) 74.9%, and (—) 88.6% of MAB units.

negative one in the correspondence of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions, respectively (Figure 7). Their relative intensity monotonically increases with the increasing content of chiral units (Table V). The positive CD band at 430 nm must be attributed to *cis* MAB units, whereas the dichroic band at 300 nm can be tentatively assigned to residual *trans*-azobenzene chromophores, in close analogy to what reported for the corresponding acrylic copolymers.¹ The appearance of this new band may arise from an increase of the anisotropy factor due to the much lower UV absorption at 300 nm of *cis*-azobenzene moieties (Figure 2).

In the case of the sample containing 7.1% of MAB units, CD spectra have been taken at different *cis/trans* ratios (Figure 8). The 430 nm dichroic band turns from negative to positive and then steadily increases with increasing the *cis* content (Table VI). Correspondingly the negative CD band at 300 nm becomes detectable, its absolute value increasing with the *cis/trans* ratio. The low content of MAB units and the relatively low degree of main chain stereoregularity should rule out the presence of long range cooperative effects. However, the rather sharp variation of the dichroic absorption observed for a relatively small extent of

Table V. Circular dichroism between 500 and 250 nm of side chain *trans*-azobenzene chromophores in poly(MtMA-*co*-MAB)s in all *trans* configuration and at the photostationary state

Sample	MAB mol%	All <i>trans</i> samples ^a		At the photostationary state ^{a,b}			
		λ_{\max}	$\Delta\epsilon_{\max}^c$	λ_{\max}	$\Delta\epsilon_{\max}^c$	λ_{\max}	$\Delta\epsilon_{\max}^c$
		nm	nm	nm	nm	nm	nm
MA2	88.6	450	-0.013	430	+0.02	—	0
MA3	74.9	450	-0.019	430	+0.08	300	-0.04
MA4	55.4	450	-0.040	435	+0.21	295	-0.08
MA5	38.1	450	-0.061	435	+0.39	300	-0.15
MA6	19.6	450	-0.095	435	+0.62	300	-0.20
MA7	7.1	445	-0.145	435	+0.90	295	-0.26

^a In chloroform solution at room temperature.^b Under irradiation at 348 nm.^c Expressed in $\text{l}\cdot\text{d}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and referred to one MAB monomeric unit.**Figure 8.** CD spectra at different *cis/trans* contents of a sample of poly(MtMA-*co*-MAB) containing 7.1% of MAB units: (----) 100%, (—) 91%, (-·-·) 67%, (·-·-·) 47%, and (- - - -) 14% of MAB units in the *trans* form.

isomerization seems to indicate the occurrence of a main chain conformational change of at least short chain section which should involve the modification of the whole macromolecule tertiary structure.

CONCLUSION

Copolymerization of MAB and MtMA by free radical initiation gives rise to copolymer

Table VI. Circular dichroism of the $n\rightarrow\pi^*$ electronic transition of side chain azobenzene chromophores in a sample of poly(MtMA-*co*-MAB) containing 7.1% MAB units at different content of *trans*-MAB units

<i>trans</i> -MAB units ^a	$\Delta\epsilon^b$
%	
100	-0.15
91	+0.17
67	+0.35
47	+0.60
27	+0.83
14	+0.90

^a Evaluated by assuming that at the photostationary state half of the absorbance at 320 nm is attributable to residual *trans*-MAB units.^b Expressed in $\text{l}\cdot\text{d}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and referred to one MAB monomeric unit.

samples having a substantially random distribution of monomeric units. Both *trans* to *cis* photoisomerization and *cis* to *trans* thermal isomerization of poly(MtMA-*co*-MAB)s in all cases follow the first order kinetics and are independent of both polymer chemical composition and macromolecular structure. This result can be attributed either to the relative distance from main chain and rotational freedom of the side-chain azobenzene chromo-

phores or to an isomerization mechanism occurring through a linear transition state without involving large molecular motions.²⁵

The CD spectra of copolymer samples in all *trans* configuration exhibit only a dichroic band connected with the $n \rightarrow \pi^*$ electronic transition, whereas at the photostationary state CD bands are present in the spectral region of both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The observed dependence of the ellipticity of the 430 nm band on the extent of photoisomerization could be attributed to the occurrence of a photoinduced tertiary structure variation.

The monotonic dependence of ellipticity on copolymer chemical composition and comparison with the CD data reported for the corresponding acrylic copolymers¹ suggest that only isolated MAB units are responsible of the observed CD features, the chiral perturbation induced by MtMA units being not transmitted along MAB sequences. The different CD behaviour observed in acrylic and methacrylic polymers may be attributed to variations of either distribution of monomeric units or main chain tacticity. However, an influence of the methyl substituent in the main chain on the conformational arrangement of macromolecules in solution cannot be ruled out. Synthesis of stereoregular copolymer samples in due course can better clarify this point.

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