

Methacrylic polymers bearing side-chain permanent dipole azobenzene chromophores spaced from the main chain by chiral moieties

Part 2¹: Copolymers with methyl methacrylate

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Abstract: Optically active photochromic copolymers, deriving from methyl methacrylate (MMA) and the methacrylic ester of (*S*)-3-hydroxypyrrolidine linked through the nitrogen atom to the highly conjugated photochromic 4'-(β -cyano- β -(methylsulfonyl)vinyl)-4-azobenzene moiety, have been prepared and characterized with the aim to evaluate the effect on their chiro-optical and thermal properties exerted by the insertion of inactive MMA groups along the main chain. The results indicate that these properties are still remarkable at a content of photochromic units as low as 26 mol-%.

Introduction

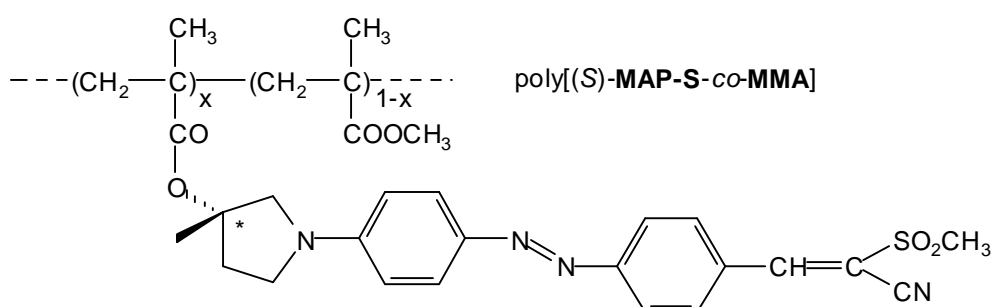
In previous studies [1,2] we reported on synthesis and characterization of optically active photochromic homopolymeric derivatives bearing in their side chain both a chiral group of one single configuration and the *trans*-azoaromatic moiety with a strongly conjugated electron donor-acceptor system. This functional combination allows the polymers to display both the properties typical of dissymmetric systems (optical activity, absorption of circularly polarized light in the UV-Vis spectral regions), as well as the features typical of photochromic materials (photorefractivity, photo-responsiveness, NLO properties) [3,4]. Thus, these materials are considered of potential interest for technological applications, such as optical storage, waveguides, chiro-optical switches, etc. [5-8] Indeed, investigations on the photoinduced birefringence of the above mentioned optically active photochromic polymers have recently allowed us to obtain promising results for their potential application in optical information storage [9,10].

In the present paper we report on the evaluation of the effects induced on the properties of the material by progressively separating along the polymer backbone the photochromic optically active repeating units. This has been achieved through radical copolymerization of the monomer (*S*)-3-methacryloyloxy-1-[4'-(β -cyano- β -(methylsulfonyl)vinyl)-4-azobenzene]pyrrolidine [(*S*)-**MAP-S**] [11] with different

¹ Part 1: ref. [11]

amounts of an inactive co-monomer such as methyl methacrylate (**MMA**), so as to obtain the corresponding copolymers, poly[(*S*)-**MAP-S-co-MMA**]s, depicted below.

The thermal, physicochemical and dichroic features of the resulting copolymeric products have been investigated and compared with those displayed by the homopolymer, poly[(*S*)-**MAP-S**], and by the low molecular weight model compound (*S*)-3-pivaloyloxy-1-[4'-(β-cyano-β-(methylsulfonyl)vinyl-4-azobenzene)]pyrrolidine [(*S*)-**PAP-S**] [11], representative of the repeating unit of the polymeric derivatives, thus allowing us to obtain conclusions about the induction of chirality and the interactions between chromophores present in the copolymeric systems.



Results and discussion

Monomer [(*S*)-**MAP-S**], having optical purity higher than 95%, was submitted to copolymerization with **MMA** under radical conditions in dry *N,N*-dimethylformamide (DMF) solution at 60° C for 72 h. After product purification, the occurred polymerization was proved by IR spectroscopy, by checking the disappearance in the spectra of the absorption at 1631 cm⁻¹, related to the methacrylic double bond, and the contemporary appearance of the band at 1728 - 1731 cm⁻¹, related to the carbonyl stretching vibration of the α,β saturated methacrylic ester group, shifted to higher frequency by ca. 10 cm⁻¹ with respect to the corresponding band of the monomers. Accordingly, in the ¹H NMR spectra of polymeric derivatives (Fig. 1) the resonances of the vinylidenic protons of monomeric methacrylate were absent.

The molar composition of copolymers was also assessed by ¹H NMR by comparing the integrated singlet of the methylsulfonyl protons of (*S*)-**MAP-S** co-units, located at 3.40 ppm, with that connected to the methyl ester group of **MMA** co-units at 3.75 ppm, after subtraction of the contribution given to the integral by the overlapped resonance of the methylene protons in α position to nitrogen in the pyrrolidine ring of (*S*)-**MAP-S**. As reported in Tab. 1, the composition of copolymers roughly reflects the feed composition, with an appreciably higher reactivity of **MMA** with respect to (*S*)-**MAP-S** for copolymerizations involving a larger content of (*S*)-**MAP-S**.

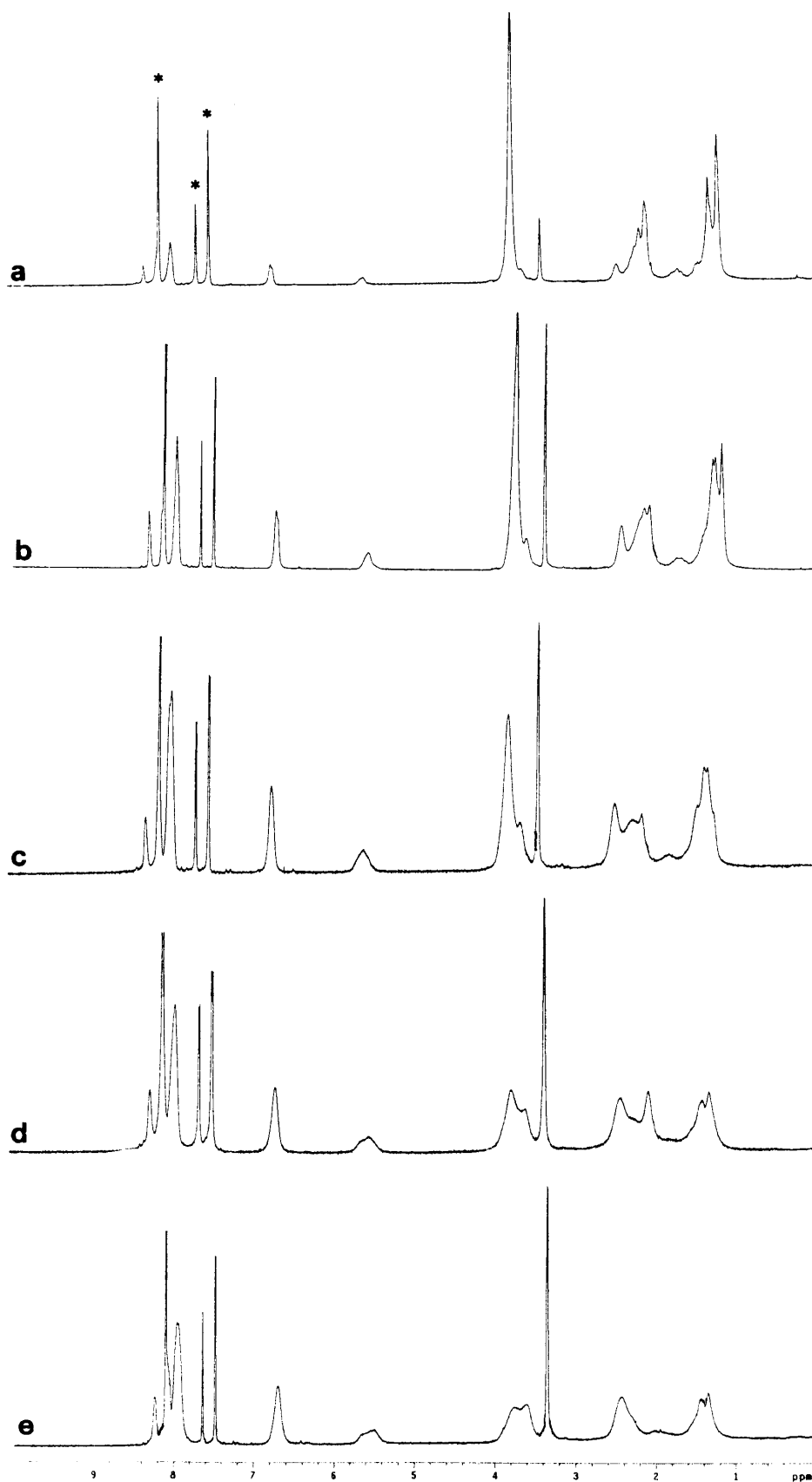


Fig. 1. ^1H NMR spectra in nitrobenzene- d_5 at 80°C of poly[(*S*)-MAP-S-co-MMA]s at 12 mol-% (a); 26 mol-% (b); 46 mol-% (c); 67 mol-% (d) content of (*S*)-MAP-S co-units and of poly[(*S*)-MAP-S] (e). Starred signals refer to solvent resonances

Tab. 1. Characterization data of polymeric derivatives

Feed in mol-%		Yield ^{a)} in %	\bar{M}_n in g/mol ^{b)}	\bar{M}_w / \bar{M}_n	(S)-MAP-S content ^{c)} in mol-%	T_d ^{d)} in °C	T_g ^{e)} in °C
(S)-MAP-S	MMA						
100 ^{f)}	0	66	37600	1.4	100	297	196
75	25	47	35200	1.5	67	297	198
50	50	55	30500	1.9	46	297	184
25	75	64	28600	1.8	26	298	167
10	90	53	25900	1.6	12	308	148

^{a)} Calculated as (g polymer/g monomers) · 100. ^{b)} Determined by GPC in tetrahydrofuran at 25° C. ^{c)} Determined by ¹H NMR. ^{d)} Initial decomposition temperature determined by TGA in air at 20° C/min heating rate. ^{e)} Glass transition temperature determined by DSC under nitrogen at 10° C/min heating rate. ^{f)} Ref. [11]

The copolymerization diagram (Fig. 2) clearly indicates the presence of a well defined azeotropic point, thus suggesting that the reactivity ratios of the monomers are both lower than one. Indeed, an approximate evaluation of the reactivity ratios performed by using the modified Kelen-Tüdös method [12,13] gives $r_{\text{MAP-S}} = 0.51$ and $r_{\text{MMA}} = 0.72$, with a $r_{\text{MAP-S}} \cdot r_{\text{MMA}}$ product of 0.37, indicative of a certain tendency to an alternating distribution of the co-units along the polymer chain.

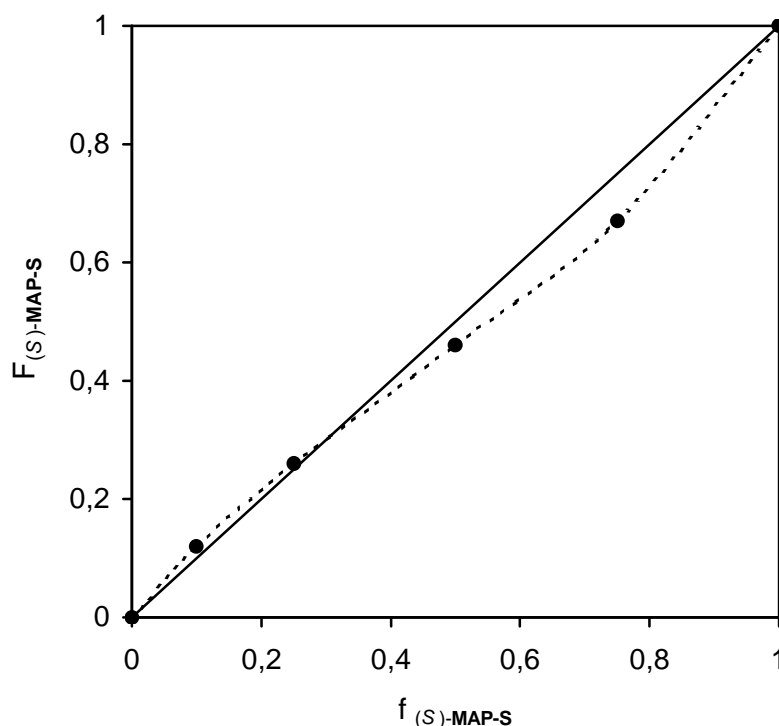


Fig. 2. Copolymerization diagram: mole fraction of (S)-MAP-S co-units in poly[(S)-MAP-S-co-MMA]s (F) as a function of the mole fraction of (S)-MAP-S in the feed (f)

The thermal stability of all polymeric derivatives, as determined by thermogravimetric analysis (TGA), resulted very high, with decomposition temperatures close to 300° C, indicative of a remarkable presence of strong dipolar interactions in the solid state between the chromophores located in the macromolecular side chains and characterized by a high charge delocalization. It can be noted that even the sample containing the smallest amount of azoaromatic co-units (12 mol-%) displays a much higher T_d value than reported for poly(**MMA**) (260° C) [14]. Only second order transitions originated by glass transitions were observed in the material by differential scanning calorimetry (DSC) measurements (Fig. 3), thus suggesting that the macromolecules are substantially amorphous in the solid state.

The T_g values appear quite high, even for the sample poorest in (**S**)-**MAP-S** moieties, laying in the range 150-200° C, that can be of interest for applications in opto-electronics. **PDR1M**, the methacrylic polymer bearing in the side chain the azo-dye Disperse Red 1, namely 4'-[(2-hydroxyethyl)ethylamino]-4-nitroazobenzene, for instance, deeply investigated as polymeric material for optical storage, exhibits an appreciably lower T_g value (129° C) [15]. It is evident that for this type of applications high values of T_g may be well promising to achieve enhanced temporal stability at room temperature of the photo- or electrically-oriented dipoles in the bulk.

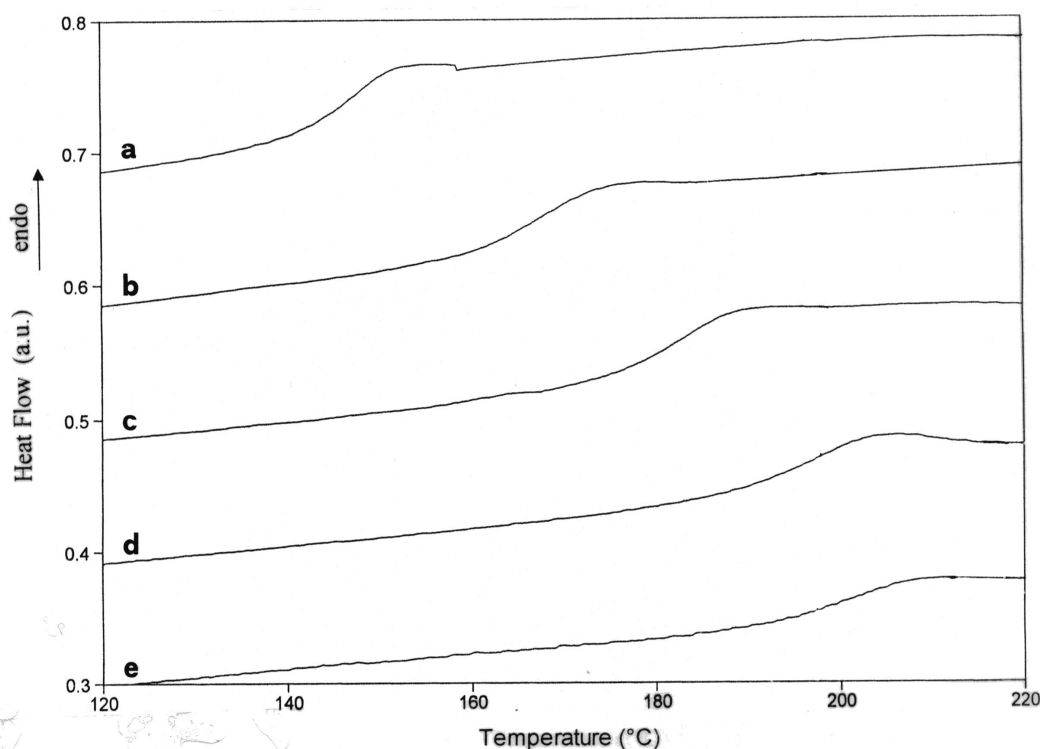


Fig. 3. DSC thermograms of poly[(**S**)-**MAP-S**-co-**MMA**]s at 12 mol-% (a); 26 mol-% (b); 46 mol-% (c); 67 mol-% (d) content of (**S**)-**MAP-S** co-units and of poly[(**S**)-**MAP-S**] (e)

All polymeric compounds exhibited two absorption bands in the UV-Vis spectra in *N,N*-dimethylacetamide (DMA) solution (Tab. 2), the first one, more intense and significant, located at 480-500 nm, related to the $n-\pi^*$, $\pi-\pi^*$ and internal charge

transfer electronic transitions of the conjugated azoaromatic chromophore, the second one, located around 320 nm, related to the $\pi\text{-}\pi^*$ electronic transition of the aromatic ring [16]. In contrast to what observed [11] when comparing the absorption spectrum of poly[(S)-**MAP-S**] with the spectrum of the corresponding low molecular weight model compound (S)-**PAP-S** (Tab. 2), the first absorption band of poly[(S)-**MAP-S-co-MMA**] copolymers did not display particularly evident hypochromic effects with respect to (S)-**PAP-S**, their spectroscopic features appearing more similar to those exhibited by the low molecular weight model compound rather than to those of the homopolymer.

The presence of hypochromic effects in polymeric derivatives bearing side chain aromatic chromophores is attributed to the presence of electrostatic dipolar interactions between neighbouring aromatic chromophores [17-19], while the occurrence of hypsochromism is related to the anti-parallel [20] or parallel (H-aggregates) [21,22] intramolecular stacking of adjacent dipolar chromophores. Thus it appears that separating from each other the azoaromatic chromophores by insertion of non-chromophoric **MMA** co-units in the macromolecular chain – although it lowers the possibility of intramolecular interactions, giving rise to a behaviour more similar to that of the model, where the lack of structural restraints originates a random distribution in dilute solution of the chromophores – yet does not completely cancel the existence of an appreciable extent of such interactions, even at the lowest chromophore composition, as shown by the λ_{max} values of the first absorption band.

Tab. 2. UV-Vis spectra in DMA solution of polymers and model (S)-**PAP-S** ^{a)}

Sample	1 st absorption band		2 nd absorption band	
	λ_{max} in nm	$\epsilon_{\text{max}} \cdot 10^3$ in L·mol ⁻¹ ·cm ⁻¹	λ_{max} in nm	$\epsilon_{\text{max}} \cdot 10^3$ in L·mol ⁻¹ ·cm ⁻¹
poly[(S)- MAP-S] ^{a)}	486	32.3	318	12.3
copol 75/25 ^{b)}	493	36.8	320	12.9
copol 50/50 ^{c)}	484	34.2	319	11.3
copol 25/75 ^{d)}	498	37.7	320	13.1
copol 10/90 ^{e)}	496	35.6	318	11.9
(S)- PAP-S ^{a)}	500	36.6	323	12.6

^{a)} Ref. [11]. ^{b)} Poly[(S)-**MAP-S-co-MMA**] at 67 mol-% content of (S)-**MAP-S** co-units. ^{c)} Poly[(S)-**MAP-S-co-MMA**] at 46 mol-% content of (S)-**MAP-S** co-units. ^{d)} Poly[(S)-**MAP-S-co-MMA**] at 26 mol-% content of (S)-**MAP-S** co-units. ^{e)} Poly[(S)-**MAP-S-co-MMA**] at 12 mol-% content of (S)-**MAP-S** co-units.

The circular dichroism (CD) spectra in DMA solution of polymeric derivatives (Fig. 4) exhibit two intense bands of opposite sign, particularly in the spectral region related to the first absorption band, with a crossover point roughly corresponding to the UV-Vis maximum absorption, indicative of the existence of exciton splitting originated by dipole-dipole cooperative interactions between the side-chain chromophores disposed according to a chiral arrangement with one prevailing handedness [23].

The intensities of dichroic absorptions decrease upon decreasing the content of azoaromatic co-units (Tab. 3), thus confirming that the presence of achiral **MMA** co-units progressively reduces the extent of the interactions between dipoles ordered according to a chiral arrangement. It can be noted that the exciton splitting is well visible at a content of azoaromatic chromophore as low as 26 mol-%, and that the copolymer of the lowest composition still shows a couplet of very low intensity, with a behaviour similar to the model, that exhibits in dilute solution a completely disordered distribution of chromophores with consequent absence of any couplet (Tab. 3).

The high optical activity displayed by polymeric derivatives can be ascribed to the presence of conformational dissymmetry induced in the main chain by the side chain (S)-3-hydroxypyrrolidine moiety, which is characterized by a sufficiently rigid structure to force the macromolecules to assume a chiral arrangement, at least for chain sections. Indeed, the dichroic bands decrease in intensity upon increasing the content of the achiral, weakly hindering **MMA** co-units to a larger extent than that one calculated on the basis of composition, thus suggesting the prevailing conformational nature of the dissymmetry of the macromolecules.

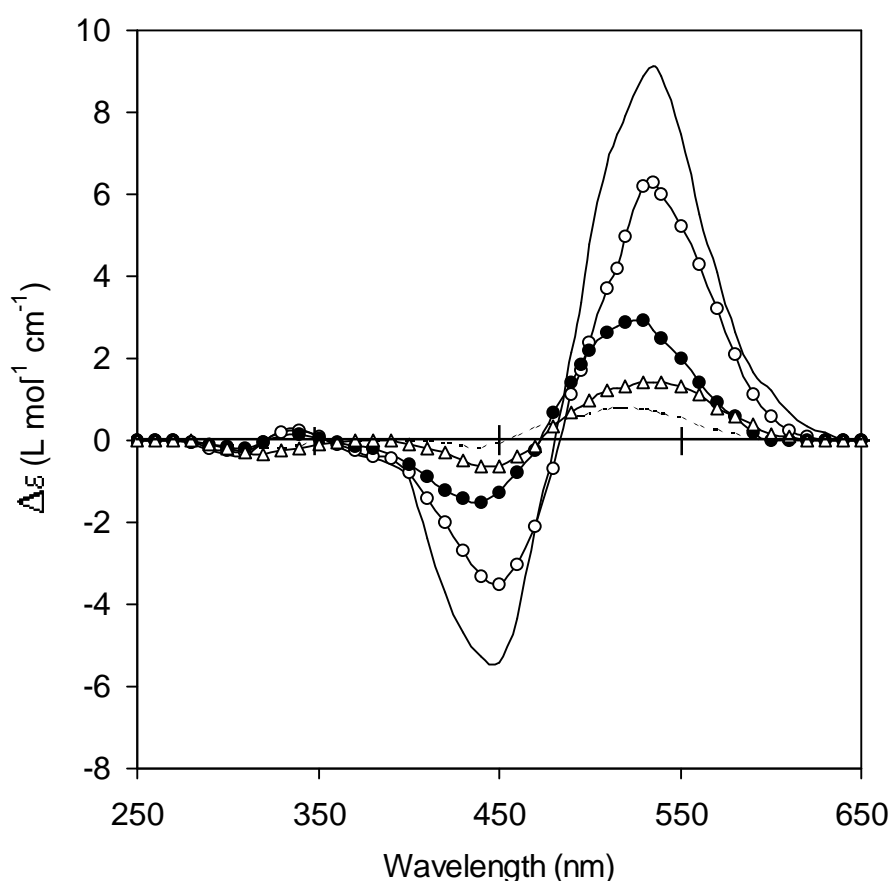


Fig. 4. CD spectra in DMA of poly[(S)-**MAP-S-co-MMA**]s at 12 mol-% (---); 26 mol-% (-Δ-); 46 mol-% (-●-); 67 mol-% (-o-) content of (S)-**MAP-S** co-units and of poly[(S)-**MAP-S**] (—)

Tab. 3. CD spectra in DMA solution of polymers and model (S)-PAP-S^{a)}

Sample	1 st absorption band				2 nd absorption band			
	λ_1	$\Delta\epsilon_1$	λ_2	$\Delta\epsilon_2$	λ_3	$\Delta\epsilon_3$	λ_4	$\Delta\epsilon_4$
poly[(S)-MAP-S] ^{b)}	537	+9.06	446	-5.28	337	+0.33	307	-0.40
copol 75/25 ^{c)}	535	+6.31	448	-3.53	340	+0.31	310	-0.42
copol 50/50 ^{d)}	524	+2.94	442	-1.42	342	+0.14	314	-0.21
copol 25/75 ^{e)}	531	+1.42	446	-0.65	325	-0.29	-	-
copol 10/90 ^{f)}	510	+0.85	430	-0.15	318	-0.18	-	-
(S)-PAP-S ^{b)}	502	+0.60	-	-	325	-0.30	-	-

^{a)} Wavelength λ and $\Delta\epsilon$ values of dichroic maxima are expressed in nm and $L \cdot mol^{-1} \cdot cm^{-1}$, respectively; $\Delta\epsilon$ values are calculated for one repeating unit of chromophore. ^{b)} Ref. [11] ^{c)} Poly[(S)-MAP-S-co-MMA] at 67 mol-% content of (S)-MAP-S co-units. ^{d)} Poly[(S)-MAP-S-co-MMA] at 46 mol-% content of (S)-MAP-S co-units. ^{e)} Poly[(S)-MAP-S-co-MMA] at 26 mol-% content of (S)-MAP-S co-units. ^{f)} Poly[(S)-MAP-S-co-MMA] at 12 mol-% content of (S)-MAP-S co-units.

In principle, the relevant optical activity of polymeric derivatives could also be due to a prevailing configuration of the stereogenic centers located in the main chain, giving rise to stereoregular sections of the backbone. To this regard, however, the microtacticity of poly[(S)-MAP-S-co-MMA] copolymers, as evaluated by integration of the ¹³C NMR signals related to the methacrylic methyl groups at ca. 20 and 18 - 19 ppm, belonging to *meso-racemo* (*mr*) and *racemo-racemo* (*rr*) triads [24], respectively, indicates (Tab. 4) a content of syndiotactic (*rr*) triads in the range 52 - 54%, which suggests a substantially stereoirregular configuration of the stereogenic centers, in agreement with literature reports concerning the radical polymerization of MMA [25]. It also appears from Tab. 4 that the radical copolymerization of monomer (S)-MAP-S with MMA obeys a Bernoullian statistics, as indicated by the close similarity of $P_{r/m}$ to $P_{r/r}$ and of $P_{m/r}$ to $P_{m/m}$.

 Tab. 4. Microtacticity of copolymers as determined by ¹³C NMR^{a)}

Sample	P_m	P_r	<i>mm</i> (%)	<i>mr</i> (<i>rm</i>) (%)	<i>rr</i> (%)	$P_{m/r}$	$P_{r/m}$	$P_{m/m}$	$P_{r/r}$
copol 75/25 ^{b)}	0.27	0.73	7	40	53	0.27	0.73	0.26	0.73
copol 50/50 ^{c)}	0.27	0.73	7	39	54	0.27	0.73	0.26	0.73
copol 25/75 ^{d)}	0.28	0.72	8	40	52	0.28	0.73	0.25	0.72
copol 10/90 ^{e)}	0.27	0.73	7	40	53	0.27	0.73	0.26	0.74

^{a)} P_m and P_r represent the probability of *meso* and *racemo* dyads formation, respectively; *mm*, *mr*(*rm*) and *rr* are the % amount of triads found in the polymers; $P_{m/r}$, $P_{r/m}$, $P_{m/m}$ and $P_{r/r}$ are the calculated probabilities that a given dyad follows a dyad having the same or the opposite relative configuration. ^{b)} Poly[(S)-MAP-S-co-MMA] at 67 mol-% of (S)-MAP-S co-units. ^{c)} Poly[(S)-MAP-S-co-MMA] at 46 mol-% of (S)-MAP-S co-units. ^{d)} Poly[(S)-MAP-S-co-MMA] at 26 mol-% of (S)-MAP-S co-units. ^{e)} Poly[(S)-MAP-S-co-MMA] at 12 mol-% of (S)-MAP-S co-units.

It can be therefore stated that the optical activity of copolymeric derivatives is essentially of conformational origin, rather than related to the presence of a predominant configuration of the asymmetric centers in the main chain, in line with previous results obtained with analogous methacrylic homopolymers bearing in the side-chain strongly conjugated azoaromatic chromophores [11]. However, different from the well known polyisocyanates, where the introduction of even small amounts of chiral units in the side chain induces a remarkable optical activity of the copolymers with the chiral units forcing the achiral ones to adopt a helical conformation of the same sense as that one of the chiral moieties (the so called sergeant and soldier copolymers) [26], in our copolymers the chiral units appear substantially unable to maintain the conformational dissymmetry of the homopolymers, when achiral co-units of MMA are present along the main chain. This behaviour is therefore attributable to the lower stiffness of polymethacrylates with respect to polyisocyanates.

Considering the mean sequence lengths of the chiral co-units, $\bar{l}_{(S)\text{-MAP-S}}$, calculated according to Mayo and Walling [27] and the molar fractions, $X_{(S)\text{-MAP-S}(n)}$, of sequences of length n [28] (Tab. 5), it appears that even few adjacent chiral units or a low fraction of sequences of sufficiently high length are able to produce a remarkable conformational dissymmetry in the macromolecules. In fact, the copolymer poly[(S)-MAP-S-co-MMA] at 12 mol-% content of (S)-MAP-S shows an optical activity appreciably larger than the model compound (S)-PAP-S, although it is constituted by 90.7% of isolated units ($X_{(S)\text{-MAP-S}(1)}$) and only 0.1% of sequences with length 4 ($X_{(S)\text{-MAP-S}(4)}$). In this context, it will be of interest to investigate in more detail the chiro-optical properties of oligomeric models possessing a known amount of adjacent azoaromatic repeating units.

Tab. 5. Mean sequence lengths, \bar{l} , and mole fractions, $X_{(n)}$ (in %), of (S)-MAP-S and MMA co-units having sequence lengths of n units in poly[(S)-MAP-S-co-MMA]s

Sample	$\bar{l}_{(S)\text{-MAP-S}}$	\bar{l}_{MMA}	$X_{(S)\text{-MAP-S}(n)}$					$X_{\text{MMA}(n)}$				
			$n=1$	2	3	4	>4	$n=1$	2	3	4	>4
copol 75/25 ^{a)}	2.92	1.19	11.7	15.4	15.2	13.3	44.4	70.8	22.4	5.3	1.2	0.3
copol 50/50 ^{b)}	1.53	1.64	40.8	29.5	15.9	7.7	6.1	37.2	29.0	17.0	8.8	8.0
copol 25/75 ^{c)}	1.16	3.24	74.4	20.6	4.3	0.8	0.1	9.5	13.1	13.6	12.6	51.2
copol 10/90 ^{d)}	1.04	8.24	90.7	8.6	0.6	0.1	0.0	1.5	2.6	3.4	4.0	88.5

^{a)} Poly[(S)-MAP-S-co-MMA] at 67 mol-% content of (S)-MAP-S co-units. ^{b)} Poly[(S)-MAP-S-co-MMA] at 46 mol-% of (S)-MAP-S. ^{c)} Poly[(S)-MAP-S-co-MMA] at 26 mol-% of (S)-MAP-S. ^{d)} Poly[(S)-MAP-S-co-MMA] at 12 mol-% of (S)-MAP-S.

Experimental part

Materials

Monomer (S)-3-methacryloyloxy-1-[4'-(β-cyano-β-(methylsulfonyl)vinyl)-4-azobenzene]pyrrolidine [(S)-MAP-S] was synthesized as previously reported [10]. Methyl methacrylate (MMA) (Merck) was purified by distillation under reduced pressure (b.p. 46° C at 100 mmHg) in the presence of traces of 2,6-di-*tert*-butyl-*p*-cresol as polymerization inhibitor before use. *N,N*-Dimethylformamide (DMF) and

N,N-dimethylacetamide (DMA) were purified and dried according to reported procedures [29] and stored over molecular sieves (4 Å) under nitrogen. 2,2'-Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use.

Copolymerizations

All copolymerization reactions were carried out in glass vials in dry DMF (25 ml/g of monomers) in the presence of AIBN (2 wt.-% with respect to monomers) as thermal initiator. Feeds of molar composition as reported in Tab. 1 were prepared and introduced into the vial under nitrogen atmosphere, submitted to several freeze-thaw cycles in order to eliminate any trace of dissolved oxygen, and heated at 60°C for 72 h. The crude product was precipitated from solution by pouring the reaction mixture into a large excess of methanol (100 ml) and collected by filtration. The solid material was then repeatedly dissolved in DMF and reprecipitated in methanol. The last traces of unreacted monomer were eliminated from the product by Soxhlet extraction with methanol. The purified products were finally thoroughly dried to constant weight under vacuum at 80°C for 4 days. Relevant data for the synthesized products are reported in Tab. 1. All products were characterized by FT-IR, ¹H and ¹³C NMR. As an example, spectroscopic data for poly[(*S*)-**MAP-S**-co-**MMA**] at 46 mol-% content of (*S*)-**MAP-S** co-units are here reported:

¹H NMR (in nitrobenzene-*d*₅ at 80°C, ppm): 8.25 (s, 1H, vinyl CH), 8.05 (m, 2H, arom. *ortho* to vinyl group), 7.85-7.60 (m, 4H, arom. 3-H and 2'-H), 6.70 (m, 2H, arom. *ortho* to amino group), 5.70-5.45 (m, 1H, pyrrolidine 3-CH), 3.90-3.50 (m, 7H, OCH₃ and pyrrolidine 2- and 5-CH₂), 3.40 (s, 3H, SO₂CH₃), 2.60-1.10 (m, 12H, pyrrolidine 4-CH₂ and backbone CH₃ and CH₂).

¹³C NMR (in nitrobenzene-*d*₅ at 80° C, ppm): 178.8-176.8 (CO), 157.1 (arom. C-CH=), 152.4 (CH=), 151.4, 148.8, 145.1 (arom. C-N=N-C and C-NCH₂), 132.7 (arom. 3'-C), 131.2 (C(CN)(SO₂CH₃)), 126.7, 123.5 (arom. 2'-C and 3-C), 114.2 (CN), 112.6 (arom. 2-C), 75.4 (CH-O), 55.4 (main chain CH₂-C), 53.4 (CH-CH₂-N), 52.0 (CH₃O), 46.6 (CH₂-CH₂-N), 46.2 (main chain CH₂-C), 42.4 (SO₂CH₃), 31.4 (CH-CH₂-CH₂), 20.1 and 18.5 (main chain CH₃).

FT-IR (cm⁻¹): 3085 (ν_{CH}, arom.), 2925, 2861 (ν_{CH}, aliph.), 2212 (ν_{CN}), 1728 (ν_{C=O}, ester), 1602 and 1515 (ν_{C=C}, arom.), 1131 (ν_{C-O}), 842 (δ_{CH}, 1,4-disubst. arom. ring), 821 (δ_{CH}, 1,4-disubst. arom. ring).

Physicochemical measurements

NMR spectra of polymeric derivatives were recorded on 5 - 10% nitrobenzene-*d*₅ solutions at 80° C, using a Varian NMR Gemini 300 spectrometer. Tetramethylsilane (TMS) was used as internal reference. ¹H NMR spectra were measured at 300 MHz by using the following experimental conditions: 24000 data points, 4.5 kHz spectral width, 2.6 s acquisition time, 16 transients. ¹³C NMR spectra were recorded at 75.5 MHz, under full proton decoupling, by using the following experimental conditions: 24000 data points, 20 kHz spectral width, 0.6 s acquisition time, 64000 transients.

FT-IR spectra were carried out on a Perkin Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station, on samples prepared as KBr pellets.

UV-Vis absorption spectra were recorded at 25°C in the 650 - 250 nm spectral region with a Perkin Elmer Lambda 19 spectrophotometer on DMA solutions by using cell

path lengths of 0.1 cm. For all samples concentrations in azobenzene chromophore of about $8 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ were used.

CD spectra were recorded at 25°C on a Jasco 500 A dichrograph, using the same cell pathlength and solution concentrations as for UV measurements. $\Delta\epsilon$ values, expressed in $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, were calculated by the following equation: $\Delta\epsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in $\text{deg} \cdot \text{cm}^2 \cdot \text{dmol}^{-1}$ refers to one azobenzene chromophore.

Number average molecular weight of polymers, \bar{M}_n , and polydispersity, \bar{M}_w / \bar{M}_n , were determined in THF solution by size exclusion chromatography (SEC) using a HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725i, a Phenomenex Phenogel 5 micron MXL column and a UV-Vis detector Linear Instruments model UVIS-200, working at 254 nm. Calibration curves were obtained by using several monodisperse polystyrene standards.

The glass transition temperatures of polymers (T_g) were measured by differential scanning calorimetry (DSC) on a TA Instruments DSC 2920 Modulated apparatus adopting a temperature program consisting of two heating and one cooling ramps starting from room temperature (heating/cooling rate $10^\circ \text{C}/\text{min}$ under nitrogen atmosphere). Each sample was heated up to only 250°C in order to avoid thermal decomposition. The initial thermal decomposition temperature (T_d) was determined on the polymer samples with a Perkin-Elmer TGA-7 thermogravimetric analyzer by heating the samples in air at a rate of $20^\circ \text{C}/\text{min}$.

Conclusions

The radical copolymerization of the optically active monomer (S)-**MAP-S** with achiral methyl methacrylate produces copolymers possessing lower optical activity, per repeating unit of azoaromatic chromophore, with respect to the homopolymer of (S)-**MAP-S**, as a consequence of the conformational origin of the dissymmetry of the macromolecules. However the derivatives with contents of chiral co-units as low as 26 mol-% still display relevant dichroic effects originated by dipolar interactions between the azoaromatic chromophores disposed according to a helical conformational arrangement. This behaviour can be attributed to the combined effects of the strongly dipolar conjugated donor-acceptor azoaromatic system with the conformational stiffness of the pyrrolidine ring, favouring the adoption of chiral conformations of chain sections of the macromolecules with a prevailing handedness. The presence of strong polar interactions between chromophores in the solid state also produces relevant thermal properties with high values of T_g which can be of interest for technological applications of these copolymers.

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