

Methacrylic polymers bearing side-chain permanent dipole azobenzene chromophores spaced from the main chain by chiral moieties, 3^a Synthesis and chiroptical properties of the homopolymer of (*R*)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine and of copolymers with the enantiomeric monomer (*S*)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine

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Abstract: The optically active photochromic homopolymer deriving from radical polymerization of the monomer (R)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)-pyrrolidine, containing a chiral group of one prevailing configuration interposed between the methacrylic moiety and the photochromic azoaromatic chromophore, has been synthesized and characterized. Copolymers with the enantiomeric monomer (S)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine have also been prepared in order to evaluate the effect on the overall optical activity of side chain chiral groups of opposite configuration in various ratios. The spectroscopic and chiroptical properties in solution of the polymeric derivatives have been assessed.

Introduction

It is well known that polymeric materials containing photochromic moieties are of remarkable potential interest for several technological applications, such as devices for the optical storage of information, waveguides, optical switches, chemical photo-receptors and in general as materials exhibiting photoresponsive properties when irradiated with light of suitable frequency and intensity [1-3]. In particular, when the photochromic moiety is the *trans*-azoaromatic group bearing strong electron donor and electron acceptor substituents conjugated through the aromatic rings, a rapid *trans-cis* isomerization at the azo double bond takes place upon irradiation, which is followed by thermal reverse reaction to the more stable *trans* form, so as to produce repeated *trans-cis-trans* isomerization cycles of the conjugated system, with concomitant conformational rearrangements of the material. If the irradiation of thin films of

^a Part 1: cf. ref. [10]

the material is performed with linearly polarized (LP) laser light, a net excess of dipoles perpendicularly oriented with respect to the direction of the electric field of the light is produced, as a consequence of the inability of these last species to absorb the irradiating light and undergo the *trans-cis-trans* isomerization cycle. This order can be successively erased by using circularly polarised (CP) pump radiation. Such a behaviour, which allows to obtain a reversible photoinduced orientation of the dipoles in the polymeric material, can be therefore exploited to produce the photomodulation of NLO properties [4], of birefringence [5] or of the linear or circular dichroic properties of the material [6-8].

The presence of chiral groups of one prevailing configuration, interposed in the side chain between the polymer backbone and the *trans*-azoaromatic chromophore, provides the macromolecules with the further possibility to assume a conformational dissymmetry of one prevailing screw sense which can be revealed by the presence in the circular dichroism (CD) spectra of dichroic bands related to the electronic transitions of the chromophore. If electrostatic interactions are present between the *trans*-azoaromatic chromophores disposed according to a chiral geometry, it is also possible to observe in the CD spectra exciton splittings of the dichroic bands to an extent connected to the amount of the interactions present and hence to the overall amount of chiral conformations assumed by the macromolecules [9,10].



Fig. 1. Chemical structure of the polymers investigated

In this context, we have recently observed [11] that it is possible to photomodulate also the chiroptical properties of thin films of the above chiral photochromic polymers by irradiation with CP light of one single R or L rotation sense. In particular, when the methacrylic homopolymer poly[(*S*)-**MAP-N**], obtained by radical polymerization of (*S*)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine [(*S*)-**MAP-N**] (Fig. 1, x = 0), is irradiated with LP light followed by CP-L light, a reversible net inversion of the sign of the related CD bands is produced, the original shape being restored by pumping with R-polarised CP radiation. This behaviour has been tentatively attributed to the ability of the CP-L light to invert the prevailing helicity of the macromolecules originated by the presence of chiral centres of absolute configuration S in the side chain. To confirm this hypothesis it was necessary to check whether the homopolymer poly[(R)-**MAP-N**], having side-chain chiral moieties of opposite absolute configuration with respect to poly[(S)-**MAP-N**] and hence with an opposite helicity sense, would exhibit the same behaviour as that observed with its enantiomer poly[(S)-**MAP-N**] when submitted to pumping with CP light irradiation.

With this aim we report in the present paper the characterization of the homopolymer derived from the monomer (R)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)-pyrrolidine [(R)-**MAP-N**] as well as of copolymers with the enantiomeric monomer (S)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine [(S)-**MAP-N**] so as to obtain the corresponding polymeric derivatives with different amounts of side-chain chiral moieties of opposite configuration, useful to assess the effect on the chiroptical properties of the reduction of the enantiomeric excess of either of the optically active co-monomers (Fig. 1).

All polymeric products have been characterized by ¹H and ¹³C NMR, FT-IR, UV-Vis spectroscopy and thermal analysis. The chiroptical properties have been investigated by CD spectroscopy.

Experimental part

Chemicals

Methacryloyl chloride (Aldrich) was distilled (b.p. 95°C) under dry nitrogen in the presence of traces of 2,6-di-*tert*-butyl-*p*-cresol as polymerization inhibitor before use.

Methylene dichloride, tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) were purified and dried according to reported procedures [12] and stored over molecular sieves (4 Å) under nitrogen.

Triethylamine (Aldrich) was refluxed over dry CaCl₂ for 8 h, and then distilled (b.p. 89°C).

2,2'-Azobisisobutyronitrile (AIBN) (Aldrich) was crystallized from abs. ethanol before use. All other reagents and solvents (Aldrich) were used as received.

Synthesis of monomer

(*R*)-3-Methacryloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine [(R)-**MAP-N**] was prepared according to the procedure previously reported for (*S*)-**MAP-N** [13], starting from (*R*)-(+)-malic acid instead of (*S*)-(-)-malic acid, with an overall yield of 24.2%. m.p. 163 - 165°C.

¹H NMR: 8.35 (dd, 2H, arom. 3'-H), 7.95 (m, 4H, arom. *metha* to amino group and 2'-H), 6.65 (dd, 2H, arom. *ortho* to amino group), 6.15 and 5.60 (2d, 2H, CH₂=), 5.55 (m, 1H, 3-CH), 3.85 - 3.50 (m, 4H, 2- and 5-CH₂), 2.35 (m, 2H, 4-CH₂), 1.95 (s, 3H, CH₃) ppm.

FT-IR: 3107 (v_{CH} , arom.), 2954, 2857 (v_{CH} , aliph.), 1717 (v_{CO} , ester), 1635 ($v_{C=C}$, methacrylic), 1605 and 1507 ($v_{C=C}$, arom), 850 and 819 (δ_{CH} 1,4-disubst. arom. ring) cm⁻¹.

Polymers

Homo- and copolymerization reactions were carried out in glass vials using AIBN (2 wt.-% with respect to the monomers) as thermal initiator and dry THF as solvent (1 g of monomer in 15 ml of THF). 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, and allowed to polymerize at 60°C for 72 h. The polymerization was stopped by pouring the reaction mixture into a large excess of methanol and collected by filtration. The solid polymeric product was repeatedly redissolved in DMF, precipitated again with methanol and submitted to a further purification from monomeric and oligomeric impurities by Soxhlet continuous extraction with methanol. The material was finally dried at 60°C for 4 days under high vacuum to constant weight. All products were structurally characterized by FT-IR, ¹H and ¹³C NMR and size exclusion chromatography. Glass transition temperature (T_g) and thermal stability were also determined.

Physico-chemical measurements

NMR spectra of monomers and low molecular weight intermediates were recorded with a Varian Gemini 300 spectrometer at room temperature in 5 - 10% CDCl₃ solutions. Polymeric derivatives were measured at 80°C in *p*-nitrobenzene- d_5 solutions in order to achieve a better signal resolution. Tetramethylsilane (TMS) was used as internal reference. ¹H NMR spectra were performed at 300 MHz, using the following experimental conditions: 24 000 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, using the following experimental conditions: 24 000 data points, 20 kHz spectral width, 0.6 s acquisition time, 64 000 transients.

Number-average molecular weights of the polymers (M_n) and polydispersity (M_w/M_n) were determined by size exclusion chromatography (SEC) in DMA solution eluted with THF using a HPLC Lab Flow 2000 apparatus, equipped with a Rheodyne 7725i injector, a Phenomenex Phenogel 5 μ MXL column and a UV-Vis detector Linear Instruments model UVIS-200, working at 254 nm. Calibration curves were obtained from several monodisperse polystyrene standards.

FT-IR spectra were recorded with 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.

UV-Vis absorption spectra of the samples were recorded at 25°C in DMA solutions with a Perkin-Elmer Lambda 19 spectrophotometer in the 250 - 650 nm spectral region with cell path lengths of 0.1 cm. Azobenzene chromophore concentrations of about $5 \cdot 10^{-4}$ mol·L⁻¹ were used.

Optical activity experiments were accomplished at 25° C in CHCl₃, ethanol, or methanol solutions with a Jasco DIP-360 digital polarimeter, equipped with a Toshiba sodium bulb, using a cell path length of 1 dm. Specific rotation values at the sodium D line are expressed in deg·dm⁻¹·g⁻¹·dL.

CD spectra of the samples were recorded at 25°C with a Jasco 810 A dichrograph, using the same spectral regions, cell path lengths and concentrations as for UV measurements. $\Delta\epsilon$ values, expressed in L·mol⁻¹·cm⁻¹, were calculated via the following equation: $\Delta\epsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in deg·cm²·dmol⁻¹ refers to one azobenzene chromophore.

The glass transition temperatures of polymers (T_g) were determined by differential scanning calorimetry (DSC) with a TA Instruments DSC 2920 Modulated apparatus adopting a temperature program consisting of three heating and two cooling ramps starting from room temperature (heating/cooling rate 10°C/min under nitrogen atmosphere). The initial thermal decomposition temperature (T_d) was determined on polymer samples with a Perkin-Elmer TGA-7 thermogravimetric analyser by heating the samples in air at a rate of 20°C/min.

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

Results and discussion

The radical homo- and copolymerization reaction of (*R*)-**MAP-N** with (*S*)-**MAP-N** afforded in all cases polymeric products with comparable yields, molar masses and polydispersities (Tab. 1). Both FT-IR and ¹H NMR spectra confirmed the occurrence of polymerization. In particular, the signals related to the methacrylic double bond were absent in the spectra of the products, a new band at 1729 cm⁻¹ (methacrylic ester C=O stretching) with a shift to higher frequency of about 12 cm⁻¹ with respect to the monomeric precursor appeared in the IR spectrum, and an upfield shift from 1.95 to 1.2 - 0.6 ppm of the methacrylic methyl resonance was displayed in the ¹H NMR spectrum. As expected, no difference between homo- and copolymers was noticed in the spectra. The narrow value of polydispersity displayed by all samples can be attributed to the exhaustive purification method adopted for the polymeric derivatives.

Feed in mol-%		Yield ^{a)} $M_n^{b)}$		$M_{\rm w}/M_{\rm n}$	$T_{d}^{c)}$	T_{g}^{d}
(<i>R</i>)- MAP-N	(S)- MAP-N	AP-N in % in g/mol			in °C	in °C
100	0	75	22 900	1.3	283	206
75	25	78	21 000	1.3	281	189
50	50	74	19400	1.2	285	194
25	75	68	20 600	1.3	286	197

Tab. 1. Characterization of polymeric derivatives

^{a)} Calculated as (g polymer/g monomers)·100. ^{b)} Determined with SEC. ^{c)} Initial decomposition temperature determined via TGA. ^{d)} Glass transition temperature determined with DSC.

In order to verify if the presence of the chiral centre in the monomer molecule could affect to some extent the stereoregularity of the main chain, an assessment of the microtacticity of the polymers was performed on the basis of the ¹³C NMR integrated resonances of the methacrylic methyl group, located at 20.2 and 18.4 ppm, respectively, for the *mr* (heterotactic) and *rr* (syndiotactic) triads present in the main chain [14]. It is thus possible to calculate the probability of presence of *meso* and *racemo* dyads (P_m and P_r , respectively) in the backbone, as well as the amounts of *mm*, *mr* (*rm*) and *rr* triads. As reported in Tab. 2, it appears that all polymeric derivatives display a substantially heterotactic microstructure, with a predominance of syndiotactic triads, around 55%, in agreement with previous results obtained with poly-(methyl methacrylate) macromonomers [15] and closely related to the data of

poly[(*S*)-**MAP-N**] [13] and analogous photochromic polymethacrylates with various electron acceptor substituents in the 4' position of the azoaromatic chromophore [16]. It is also confirmed that the addition of monomer to the growing chain is not affected by the structure of the last repeating unit, but follows a Bernoullian statistics, as indicated by the close similarity of $P_{m/r}$ with $P_{m/m}$ (the probability for a *m* dyad to follow a *r* or a *m* dyad) and of $P_{r/m}$ with $P_{r/r}$ (the probability for a *r* dyad to follow a *m* or a *r* dyad). It can therefore be concluded that a very low or negligible contribution to the overall optical activity of the macromolecules is made by the stereogenic centres located in the methacrylic backbone.

Differently from the well known case of polyisocyanates, where the presence of few chiral units in the side chain induces a remarkable optical activity to the whole macro-molecule (the so-called 'sergeant and soldier' effect) [17] attributable to the orienting ability of chiral units towards achiral adjacent groups, in these polymers the presence of chiral groups of one single configuration in each repeating unit should prevent the occurrence of a similar effect.

Polymer	P _m	P _r	mm	<i>mr</i> (<i>rm</i>) in %	rr	P _{m/r}	P _{r/m}	P _{m/m}	P _{r/r}
poly[(<i>R</i>)- MAP-N]	0.26	0.74	7	38	55	0.26	0.73	0.26	0.74
copol 75/25 ^{a)}	0.26	0.74	7	38	55	0.26	0.73	0.26	0.74
copol 50/50 ^{b)}	0.27	0.73	7	40	53	0.27	0.74	0.26	0.73
copol 25/75 ^{c)}	0.26	0.74	7	38	55	0.26	0.73	0.27	0.74

Tab. 2. Microtacticity of polymers investigated, as determined by ¹³C NMR

^{a)} Poly[(*R*)-**MAP-N**-*co*-(*S*)-**MAP-N**]75/25. ^{b)} Poly[(*R*)-**MAP-N**-*co*-(*S*)-**MAP-N**]50/50. ^{c)} Poly[(*R*)-**MAP-N**-*co*-(*S*)-**MAP-N**] 25/75.

TGA data of the homopolymer of (R)-**MAP-N** and of its derivatives with various contents of (S)-**MAP-N** (Tab. 1) indicate that all materials show very high decomposition temperatures, close to 300°C, regardless of the composition. This behaviour suggests that remarkable dipolar interactions originated by the strongly conjugated side-chain donor-acceptor azoaromatic moieties are present in the solid state.

Only thermal transitions of the second order, ranging around $190 - 200^{\circ}$ C, attributed to glass transitions, are observed in the DSC thermograms of the polymers investigated (Tab. 1). No endothermic peaks related to melting transitions are present, in agreement with the substantially amorphous state of the macromolecules in the solid state. The T_g value of poly[(R)-**MAP-N**] is very close to that previously found (208°C) for the enantiomeric poly[(S)-**MAP-N**] [13], whereas slightly lower values are observed for polymers obtained from different mixtures of enantiomeric monomers, probably as a consequence of a lower conformational homogeneity, suggesting the presence in the same macromolecule of side chain moieties of opposite configuration. In any case, all values appear particularly high, and confirm the very stiff character of these compounds, attributable to the presence both of the conformationally rigid pyrrolidine ring interposed between the backbone and the azoaromatic group, and of extended dipolar interactions between the azoaromatic chromophores in the solid state.

The UV-Vis spectra in DMA solution (Tab. 3) of poly[(R)-MAP-N] and of the copolymers, guite similar to each other, exhibit two absorption bands in the spectral region 250 - 650 nm. The former one, more intense, is located at 470 - 480 nm and is attributed to electronic transitions such as $n-\pi^*$, $\pi-\pi^*$ and internal charge transfer of the azoaromatic chromophore. The latter, around 290 nm, is attributed to the π - π^* electronic transition of the aromatic ring [18]. It appears from the data that a gradual change of the prevailing chirality in the macromolecules does not appreciably affect the spectroscopic behaviour, however slightly higher values of the extinction coefficient related to the first absorption band can be noticed for the copolymers in comparison with the homopolymers. If one takes into account the ε_{max} value (Tab. 3) of the low molecular weight structural model (S)-3-pivaloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine [(S)-PAP-N] [13], it appears that when dipolar interactions between chromophores vicinally located in the side chain of a macromolecular solute are absent, a remarkable increase of ε_{max} does occur [19-21]. Thus, it could be inferred that the slight increase of ε_{max} could be due to a reduction of these interactions, more likely if chiral groups of opposite configuration are contemporarily present in the side chains, as observed in similar chiral copolymers [22].

Sample	<u>1st abso</u>	orption band	2 nd absorption band		
	λ _{max} in nm	ε _{max} ·10 ⁻³ in L·mol ⁻¹ ·cm ⁻¹	λ _{max} in nm	ε _{max} ·10 ⁻³ in L·mol ⁻¹ ·cm ⁻¹	
poly[(<i>R</i>)- MAP-N] ^{a)}	479	28.4	287	11.0	
poly[(<i>R</i>)- MAP-N - <i>co</i> -(<i>S</i>)- MAP-N] 75/25	477	29.8	288	11.4	
poly[(<i>R</i>)- MAP-N - <i>co</i> -(<i>S</i>)- MAP-N] 50/50	475	28.9	287	11.2	
poly[(<i>R</i>)- MAP-N - <i>co</i> -(<i>S</i>)- MAP-N] 25/75	478	28.4	288	10.9	
(S)- PAP-N ^{a)}	491	33.8	289	11.0	
a) rof [12]					

Tab.	3.	UV-Vis	spectra in	DMA	solution	of pol	ymers and	model ((S)	-PAP-N	٧
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^{a)} ref. [13]

The chiroptical properties of poly[(R)-MAP-N] and of the copolymers have been investigated in DMA solution by CD in the spectral region 250 - 650 nm in order to understand the effect on the conformational homogeneity of the macromolecules induced by the introduction of progressively increasing amounts of the enantiomeric co-monomer (S)-MAP-N. As expected, the CD spectrum of poly[(R)-MAP-N] (Tab. 4 and Fig. 2) is the mirror image of the previously [13] measured spectrum of poly[(S)-**MAP-N**], with two strong dichroic bands of opposite sign located in the spectral region related to the first UV-Vis band, and a crossover point at 479 nm, corresponding to the UV-Vis maximum wavelength. The negative Cotton effect shown by poly[(R)-MAP-N] can be ascribed to the presence of dipole-dipole interactions between the azoaromatic chromophores disposed according to a prevailing screw sense [9,23] and is in fact absent in the structural model (S)-PAP-N, which displays only two single bands of low intensity in correspondence to the UV-Vis maxima. It is therefore confirmed that the homopolymers assume in solution, for chain sections, enantiomeric conformations of one prevailing screw sense characterized by a much higher optical activity than that one displayed by the related monomeric species, as depicted in Fig. 3, where the actual helix sense of poly[(R)-MAP-N] and poly[(S)-MAP-N] is undetermined.



Fig. 2. CD spectra in DMA solution of poly[(S)-MAP-N] (a), poly[(R)-MAP-N-co-(S)-MAP-N] 25/75 (b), poly[(R)-MAP-N-co-(S)-MAP-N] (c), poly[(R)-MAP-N] (d) and (S)-PAP-N (----)

The CD spectra of the polymers deriving from the 75/25 and 25/75 feeds are qualitatively identical to those of the homopolymers, but reduced in intensity, due to the lower relative content of repeating units of one prevailing configuration, no dichroic signal being of course displayed by the product deriving from the racemic monomer mixture 50/50.

It appears however that the optically active derivatives still exhibit exciton splitting originated by the dipole-dipole interactions of chirally arranged side chain chromophores. If one takes into consideration the 50% enantiomeric excess present in the 75/25 or 25/75 compositions, a corresponding lowering of the intensity of the dichroic bands would be expected, in the case of a mixture of enantiomeric homopolymers in the same ratios. Actually, the observed intensity decrease is higher than 50%, on the average about 58%, and can be interpreted as due to a reduction of the average length of chain sections of one chiral sense originated by the introduction of repeating units of opposite configuration, in agreement with the mainly conformational character of the optical activity displayed by these macromolecules.

Sample		1 st ab	2 nd absorption band				
	λ_1	$\Delta \epsilon_1$	$\lambda_0^{\ b)}$	λ_2	$\Delta\epsilon_2$	λ_3	$\Delta \epsilon_3$
poly[(<i>R</i>)- MAP-N]	522	-8.63	471	431	+6.36	279	+1.21
copol 75/25 ^{c)}	519	-3.40	465	429	+2.66	281	+0.45
copol 50/50 ^{d)}	-	-	-	-	-	-	-
copol 25/75 ^{e)}	516	+3.93	465	428	-2.43	290	+0.27
poly[(<i>S</i>)- MAP-N] ^{f)}	515	+8.49	469	428	-6.04	285	-0.37
(S)- PAP-N ^{f)}	495	-0.67	-	-	-	284	+0.28

Tab. 4. CD spectra in DMA solution of polymers and model (S)-PAP-N^{a)}

^{a)} Wavelength λ and $\Delta \varepsilon$ values of dichroic maxima are expressed in nm and L·mol⁻¹·cm⁻¹, respectively. $\Delta \varepsilon$ values are calculated for one repeating unit of chromophore. ^{b)} Wavelength in nm of the crossover of dichroic bands. ^{c)} Poly[(*R*)-**MAP-N**-*co*-(*S*)-**MAP-N**] 75/25. ^{d)} Poly[(*R*)-**MAP-N**-*co*-(*S*)-**MAP-N**] 50/50; ^{e)} poly[(*R*)-**MAP-N**-*co*-(*S*)-**MAP-N**] 25/75. ^{f)} ref. [13]



Fig. 3. Idealised conformation of enantiomeric poly[(*R*)-**MAP-N**] and poly[(*S*)-**MAP-N**]

Studies concerning the photochromic behaviour of these macromolecular systems in the solid state are currently in progress. In particular, the possibility of photomodulation of the chiroptical properties of thin films of material, both optically active and racemic, by using one-handed CP light of suitable wavelength will be investigated. These experiments should also enable one to univocally assign by direct CD measurements the screw sense of macromolecular chains of one prevailing helix conformation.

Conclusions

The homopolymer of (R)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine, obtained by radical polymerization, displays the same spectroscopic properties as the

enantiomeric homopolymer derived from (S)-3-methacryloyloxy-1-(4'-nitro-4-azobenzene)pyrrolidine, previously investigated, and a thermal stability suitable for technological applications, due to their particularly elevated T_d and T_q values. The CD spectra confirm that the chiroptical properties of these macromolecules are related to the configuration of the side chain optically active moiety, which determines the screw sense assumed by chain sections of the methacrylic main chain. The derivatives obtained by copolymerization of the enantiomeric monomers exhibit CD spectra qualitatively similar to the homopolymers, but with intensities reduced to a larger extent than expected, which indicates that the optical activity of these systems is not linearly related to the content of optically active co-units, as would be the case for enantiomeric homopolymers mixtures, but rather to the average length of the chain sections with one prevailing helical conformation, in accordance with the conformational origin of chirality in these systems. A significant amount of chain sections of one predominant handedness, sufficient to provide the strong dichroic effects observed, would be therefore maintained in the copolymers. On the other hand, the possibility of stereoselective (stereospecific) polymerization of both enantiomeric monomers to give the S- and the R-homopolymer would be rather surprising, given the radical mechanism of this polymerization.

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