Optically active polymers bearing side-chain photoreactive moieties: copolymers of racemic 4-acryloyloxy-α-methylbenzoin methyl ether with (−)-menthyl acrylate

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Optically active copolymers of racemic 4-acryloyloxy-α-methylbenzoin methyl ether (AMBE) with (−)-menthyl acrylate (MtA) have been radically prepared. The reactivity of the comonomers suggests that the copolymers display a certain tendency to an alternating distribution of the co-units. Optical activity at 589 nm of the copolymers seems to exclude any stereoselectivity and stereoelectivity during the copolymerization process. Chiroptical properties indicate that an induced optical activity on benzoin methyl ether chromophores occurs. Circular dichroism (c.d.) data, connected with $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions of the benzoin methyl ether moiety, suggest that the observed ellipticity is substantially due to isolated AMBE units. C.d. features indicate that the macromolecules, due to the presence of optically active MtA co-units, assume conformations with a prevailing handedness for sections not sufficiently long to provide cooperative interactions between side-chain benzoin methyl ether chromophores disposed along the backbone with a mutual chiral geometry suitable for exciton couplings.

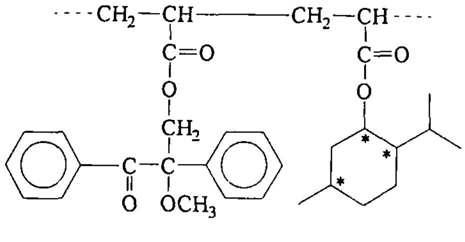
(Keywords: copolymers; optical activity; circular dichroism)

INTRODUCTION

The copolymerization of an optically active monomer with a racemic comonomer may give rise to different polymeric products, depending on the stereochemistry of the reaction. When a stereoselective[1] process occurs, the optically active monomer copolymerizes with only one enantiomer of the racemic comonomer, the other enantiomer undergoing homopolymerization. In this case, the copolymer and the homopolymer display optical activity of opposite sign and can be easily separated by solvent extraction, the former being usually more soluble. Moreover, when copolymerization and homopolymerization of the two individual enantiomers proceed with different rates, a prevailing consumption of one enantiomer of the racemic comonomer also occurs (stereoelective[1] process). Therefore, if the conversion is incomplete, an unreacted optically active monomer, deriving from the starting racemic one, is also recovered.

Copolymerization processes, where both stereoselectivity and stereoelectivity occur, have been reported to involve α-olefins or vinyl ethers, provided that the asymmetric carbon atom in the monomers is in the α or β position to the double bond and heterogeneous stereospecific catalysts are used[2–4]. Accordingly, the homopolymerization of racemic 5-methyl-1-heptene, bearing the asymmetric carbon atom in the γ position to the double bond, by heterogeneous isospecific Ziegler–Natta catalysts, does not exhibit any appreciable stereoselectivity and stereoelectivity[5,6]. Similar results[4] were also obtained in the copolymerization of racemic 1-methylpropyl vinyl ether with optically active 1-phenylethyl vinyl ether by the homogeneous cationic $BF_3.Et_2O$ catalyst at −78°C, although the asymmetric carbon atom in both comonomers was in the β position to the double bond. When the copolymerization process, as in this last case, occurs without any significant stereoselectivity and stereoelectivity, the reaction gives rise to terpolymer macromolecules consisting of repeating units deriving from the optically active monomer and both the enantiomers of the racemic comonomer.

Recently, the above situation was reported to occur in the homogeneous free radical copolymerization of racemic α-methylolbenzoin methyl ether acrylate (MBA) with (−)-menthyl acrylate (MtA) to give poly(MBA-*co*-MtA)s[7].



poly(MBA-*co*-MtA)s

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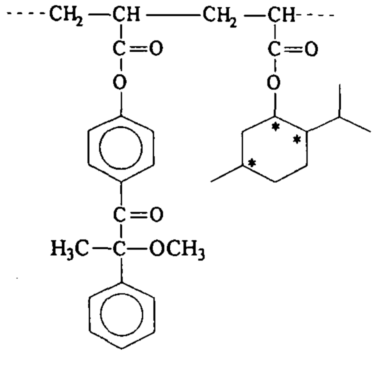
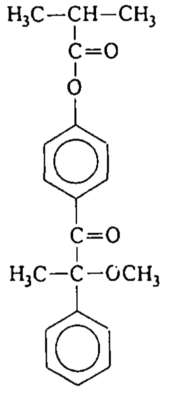
However, circular dichroism (c.d.) spectra of poly(MBA-*co*-MtA)s in the region of the n→π* electronic transition of the ketone group display a negative structured band, thus suggesting that an induced optical activity on the benzoin chromophores occurs. These results have been interpreted as a clear indication that the above moieties, regardless of their (*S*) or (*R*) absolute configuration, are inserted in macromolecules which assume a dissymmetric conformation of a prevailing chirality, at least for short sections, owing to the presence of the optically active MtA co-units. Moreover, the lack of an exciton splitting in the above copolymers seems to suggest that no significant cooperative interaction between side-chain benzoin methyl ether chromophores occurs. Accordingly, poly(MBA-*co*-MtA)s[8] are active as photoinitiators in the u.v. curing of acrylic coatings independently of the content of MBA co-units, thus indicating that side-chain benzoin methyl ether moieties behave, under irradiation, as isolated free radical generating species with an α-cleavage mechanism of the same type[9] as for low molecular weight analogues.

In this context, the synthesis and characterization of optically active copolymers of racemic 4-acryloyloxy-α-methylbenzoin methyl ether (AMBE) with MtA [poly(AMBE-*co*-MtA)s] appeared very interesting. In fact, in poly(AMBE-*co*-MtA)s, in contrast to poly(MBA-*co*-MtA)s, the benzoin methyl ether moieties are directly attached to the backbone through the *para* position of the benzoyl group, thus providing in principle a higher conformational rigidity of the macromolecules. Therefore the investigation of their chiroptical properties could allow one to obtain information on the potential presence in the macromolecules of a conformational homogeneity with a prevailing chirality, and hence on possible cooperative interactions involving side-chain benzoin methyl ether moieties which may affect the photochemical and photophysical behaviour of the above polymeric systems as u.v. curing agents.

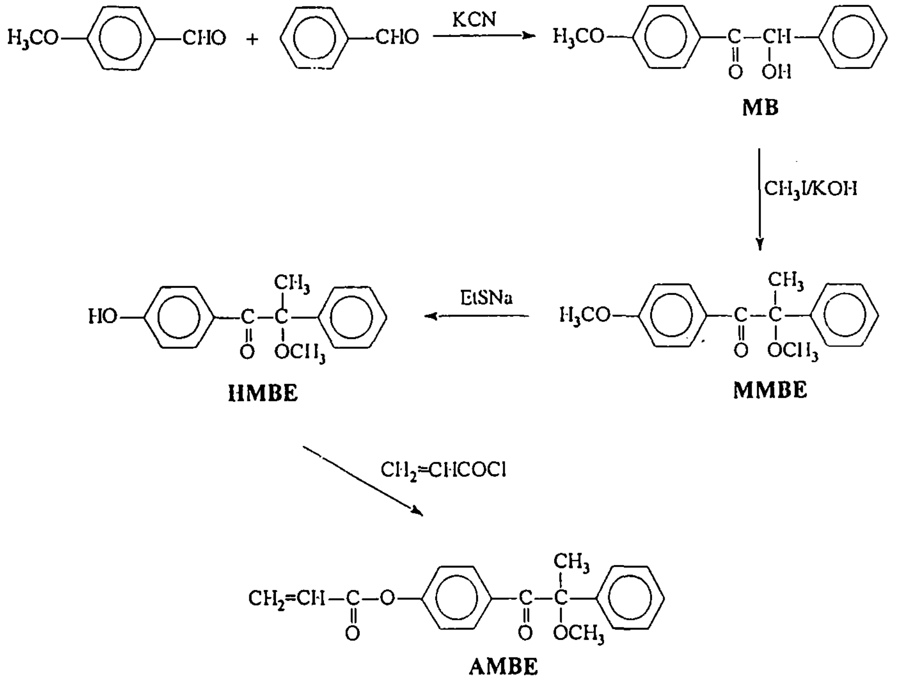


poly(AMBE-*co*-MtA)s

The synthesis of AMBE has been realized according to *Scheme 1*. In addition, racemic 4-(2-methylpropionyloxy)-α-methylbenzoin methyl ether (PMBE) has also been synthesized as a low molecular weight model compound.



PMBE



Scheme 1

EXPERIMENTAL

Monomers

(−)-Menthyl acrylate. MtA, having $[\alpha]_D = -88.3$ (neat, at 25°C), was synthesized as previously reported[10]. It was distilled under vacuum just before use.

^{1}H n.m.r. ($CDCl_3$): $\delta = 6.4$ and 5.8 ppm (2dd, 2H, $CH_2{=}$); 6.1 ppm (dd 1H, $CH{=}$); 4.7 ppm (m, 1H, CH–O); 2.1–0.7 ppm (m, 18 H, residual protons of the menthyl moiety).

I.r. spectrum (liquid film, cm^{-1}): 2956, 2930 and 2871 ν(C–H) (aliphatic); 1723, ν(C=O) (ester group); 1634 and 1619, ν(C=C) (vinyl group); 1388 and 1371, δ(C–H) (geminal methyls of isopropyl group); 1200, ν_{as}(C–O) (ester group); 985 and 905, δ(C–H) (vinyl group).

(±)-4-Acryloyloxy-α-methylbenzoin methyl ether. AMBE was prepared as follows: pure (±)-4-methoxybenzoin (MB) was obtained in 43% yield (after recrystallization from ethanol) by condensation of 4-methoxybenzaldehyde with benzaldehyde in the presence of potassium cyanide as previously described[11].

^{1}H n.m.r. ($CDCl_3$): $\delta = 8$–7.9 ppm (m, 2H, aromatic protons in *ortho* position to the carbonyl group); 7.4–7.2 ppm (m, 5H, aromatic protons of the phenyl ring adjacent to the carbinol carbon atom); 6.9–6.8 ppm (m, 2H, aromatic protons in *ortho* position to the methoxy group); 5.9 ppm (d, 1H, CH); 4.7 ppm (d, 1H, OH); and 3.8 ppm (s, 3H, OCH_3).

MB (0.08 mol) and CH_3I (0.34 mol) were added to a suspension of powdered KOH (0.68 mol) in anhydrous dimethylsulfoxide (340 ml), according to a mild procedure for alkylation of phenols and alcohols[12]. The reaction mixture became deeply blue-coloured, the colour progressively fading and disappearing after half an hour at room temperature when the alkylation was complete, as tested by thin layer chromatography using chloroform as eluent. The reaction mixture was poured into 1.5 l of water and extracted with CH_2Cl_2. After drying with anhydrous Na_2SO_4 and removing the solvent under vacuum, (±)-4-methoxy-α-methylbenzoin methyl ether (MMBE) was obtained in 93% yield as an oily product.

^{1}H n.m.r. ($CDCl_3$): $\delta = 8.0$–7.9 ppm (m, 2H, aromatic protons in *ortho* position to the carbonyl group); 7.5–7.2 ppm (m, 5H, aromatic protons of the phenyl ring in the substituted benzyl group); 6.8–6.7 ppm (m, 2H, aromatic protons in *ortho* position to the methoxy group); 3.8 ppm (s, 3H, CH_3O–Ph); 3.3 ppm (s, 3H, C–OCH_3); 1.7 ppm (s, 3H, CH_3).

MMBE (0.06 mol) was reacted, under nitrogen, with EtSNa (0.21 mol) in 600 ml of anhydrous dimethylformamide at the refluxing temperature for 3 h, according to a procedure adopted for the demethylation of aryl methyl ethers[13]. After cooling at room temperature, 400 ml of HCl 2 M were added and the reaction mixture was extracted with diethyl ether.

The ethereal layer was treated several times with aq. NaOH, then the combined aqueous layers were acidified with aq. HCl and finally extracted with diethyl ether. After drying with Na_2SO_4, the solvent was removed under vacuum and the residue purified by elution chromatography on silica gel, using a $CHCl_3/CH_3OH$ (9/1, v/v) mixture as eluent. After removing the solvent under vacuum, pure (±)-4-hydroxy-α-methylbenzoin methyl ether (HMBE) was obtained (84% yield) as an oily product.

^{1}H n.m.r. ($CDCl_3$): $\delta = 8$–7.9 ppm (m, 2H, aromatic protons in *ortho* position to the carbonyl group); 7.5–7.2 ppm (m, 5H, aromatic protons of the phenyl ring in the substituted benzyl group); 6.7–6.6 ppm (m, 2H, aromatic protons in *ortho* position to the hydroxy group); 6.0 ppm (s, 1H, OH); 3.3 ppm (s, 3H, OCH_3); 1.7 ppm (s, 3H, CH_3).

Acryloyl chloride (0.11 mol) dissolved in 40 ml of anhydrous tetrahydrofuran (THF) was dropped at 0°C under nitrogen into 0.04 mol of HMBE mixed with 0.05 mol of triethyl amine dissolved in 160 ml of anhydrous THF. The reaction mixture was allowed to remain at room temperature for 2 h and then filtered. The solution was evaporated to dryness and the residue was crystallized from ethanol to give pure AMBE with 54% yield (total yield with respect to MB 18%).

^{1}H n.m.r. ($CDCl_3$): $\delta = 8.1$–8.0 ppm (m, 2H, aromatic protons in *ortho* position to the ketone group); 7.5–7.2 ppm (m, 5H, aromatic protons of the phenyl ring in the substituted benzyl group); 7.1–7.0 ppm (m, 2H, aromatic protons in *ortho* position to the ester group); 6.6–6.0 ppm (2dd, 2H, $CH_2{=}$); 6.3 ppm (dd, 1H, $CH{=}$); 3.3 ppm (s, 3H, OCH_3); and 1.7 ppm (s, 3H, CH_3).

I.r. spectrum (cm^{-1}): 3084–3010, ν(C–H) (aromatic rings and vinyl group); 2934–2834, ν(C–H) (aliphatic); 1730, ν(C=O) (ester group); 1683, ν(C=O) (ketone group); 1625, ν(C=C) (vinyl group); 1598 ν(C=C) (aromatic rings); 1412, $\delta(CH_2{=})$ (scissoring, vinyl group); 996 and 912, $\delta(CH_2{=})$ (out of plane bendings, vinyl group); 856, δ(C–H) (1,4-disubstituted phenyl ring); 768 and 703, δ(C–H) (monosubstituted phenyl ring).

Model compound

(±)-4-(2-Methylpropionyloxy)-α-methylbenzoin methyl ether. PMBE was prepared from HMBE and 2-methylpropionyl chloride with the same procedure as reported for AMBE. The crude product was crystallized from ethanol to give pure PMBE in 43% yield.

^{1}H n.m.r. ($CDCl_3$): $\delta = 8.1$–8.0 ppm (m, 2H, aromatic protons in *ortho* position to the ketone group); 7.5–7.2 ppm (m, 5H, aromatic protons of the phenyl ring in the substituted benzyl group); 7.0–6.9 ppm (m, 2H, aromatic protons in *ortho* position to the ester group); 3.3 ppm (s, 3H, OCH_3); 2.75 ppm [hept, 1H, $CH(CH_3)_2$]; 1.7 ppm (s, 3H, α-CH_3); 1.25 ppm [d, 6H, $CH(CH_3)_2$].

I.r. spectrum (cm^{-1}): 3067–3010, ν(C–H) (aromatic rings); 2978–2836, ν(C–H) (aliphatic); 1756, ν(C=O) (ester group); 1683, ν(C=O) (ketone group); 1597, ν(C=C) (aromatic rings); 1387 and 1370, δ(C–H) (geminal methyls of isopropyl group); 842, δ(C–H) (1,4-disubstituted phenyl ring); 767 and 699, δ(C–H) (monosubstituted phenyl ring).

Radical initiator

2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol just before use.

Polymerization experiments

Free radical homo- and copolymerizations of AMBE and MtA were carried out at 60°C in dark adapted glass vials using benzene as solvent and AIBN (0.5 wt% with respect to the monomers) as initiator. Monomer or comonomer concentration was about 10 wt%. After

Table 1 Preparation and properties of poly(AMBE-*co*-MtA)s and corresponding homopolymers[a]

Feed AMBE (mol%)	Duration (h)	Conversion[b] (%)	Copolymer characterization: AMBE co-units[c] (mol%)	$[\alpha]_D$[d]	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]
0.0	137	68	0.0	−73.9	n.d.	n.d.
10.0	22	22	15.0	−63.9	46800	1.6
17.0	18	46	22.0	−55.4	55100	2.6
39.0	28	59	43.0	−39.3	43100	2.2
59.0	88	26	58.0	−24.6	59700	1.9
80.0	92	76	79.0	−16.7	33400	1.8
100.0	91	40	100.0	0.0	21900	1.8

[a] In benzene solution at 60°C, using AIBN as free radical initiator; monomers concentration 10 wt%
[b] Evaluated as (weight of polymer/weight of monomers) × 100
[c] Determined by ^{1}H n.m.r. analysis
[d] In chloroform solution at 25°C, l = 1 dm
[e] Determined by g.p.c. measurements

introducing the components under nitrogen, the vials were submitted to several freeze–thaw cycles and sealed under high vacuum. After a proper period of time the reaction mixture was poured into a large excess of methanol. The coagulated polymer was filtered, redissolved in chloroform and then reprecipitated with methanol. The polymer was isolated by filtration, dried under vacuum and finally stored in a refrigerator in the dark.

Physicochemical measurements

^{1}H n.m.r. spectra were performed at 200 MHz in $CDCl_3$ solution on a Varian Gemini 200 spectrometer, using tetramethylsilane (TMS) as internal standard.

I.r. examinations were recorded on a *FT*i.r. Perkin–Elmer 1750 spectrophotometer equipped with a Perkin–Elmer 7700 data station. Cast films on KBr discs or KBr pellets of the samples were used.

Average molecular weights of the polymers were evaluated by g.p.c. measurements in $CHCl_3$ solution using an h.p.l.c. Waters Millipore 590 chromatograph equipped with a TSK gel G4000HXL column, a Waters model U6K injector and a Perkin–Elmer LC95 u.v. detector. Monodisperse polystyrene samples were used for the calibration curve. Optical rotatory measurements were performed at 25°C in $CHCl_3$ solution or on neat samples by using a Jasco DIP-360 polarimeter.

U.v. absorption measurements were carried out in $CHCl_3$ solution on a Kontron Instruments model UVICON 860 spectrophotometer by using cell path lengths of 1 and 0.1 cm in the 400–300 and 300–240 nm regions, respectively. Concentrations of about 5×10^{-3} and 8×10^{-4} mol l^{-1} of benzoin methyl ether chromophore were used, respectively.

C.d. spectra on copolymer samples were carried out in $CHCl_3$ solution on a Jasco J500A dichrograph. Cell path lengths as well as the corresponding solution concentrations and spectral regions were the same as for u.v. measurements. The molar differential dichroic absorption coefficient $\Delta\varepsilon$ (l mol^{-1} cm^{-1}) was calculated by the following equation: $\Delta\varepsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ (degree cm^2 dmol^{-1}) refers to one benzoin methyl ether chromophore.

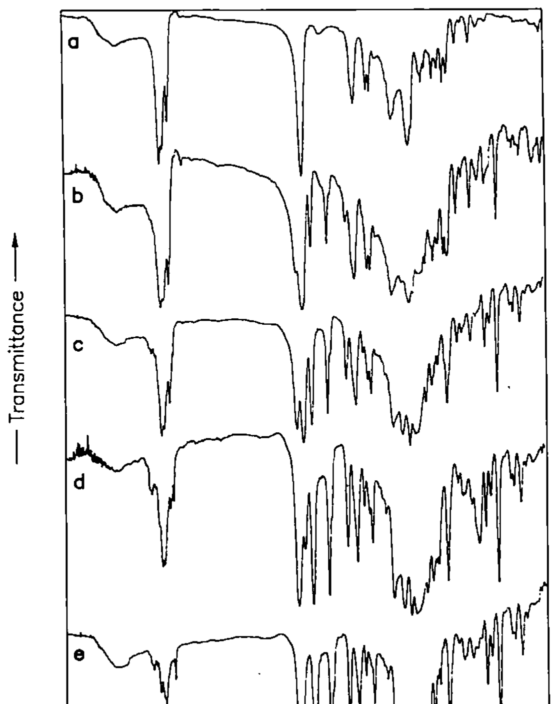


Figure 1 I.r. spectra in the 4000–400 cm^{-1} region: (a) poly(MtA); (b)–(d) poly(AMBE-*co*-MtA)s with 15.0, 43.0 and 79.0 mol% of AMBE co-units, respectively; (e) poly(AMBE)

RESULTS AND DISCUSSION

Synthesis and characterization of the polymers

Poly(AMBE-*co*-MtA)s were prepared by free radical initiation starting from different relative amounts of the comonomers in the feed. Relevant properties of the copolymers are reported in *Table 1*.

I.r. spectra (*Figure 1*) of the copolymer samples display the same bands as the corresponding homopolymer mixtures. Moreover, the higher solubility of the former with respect to the latter systems suggests the presence of both monomeric units in the same macromolecule. In particular, bands at 1760 and 1684 cm^{-1} (C=O stretching of ester and ketone moieties, respectively, in AMBE co-units), at 1732 cm^{-1} (C=O stretching of ester group in MtA co-units), at 1599 cm^{-1} (C=C stretching of aromatic rings in AMBE co-units), as well as at 1388 and 1371 cm^{-1} (C–H bending of *gem*-dimethyl group in MtA co-units) are observed, their relative intensity changing on composition. In addition, the shift towards higher frequencies of the bands of the carbonyl of the aromatic and aliphatic ester groups (about 30 and 10 cm^{-1}, respectively) in the polymeric products with respect to the corresponding monomers, as well as the disappearance of the bands at 1634 and 1625 cm^{-1}, related to the acrylic groups of AMBE and MtA comonomers, confirms that the free radical polymerization occurred involving the double bond of the acrylic functions. Accordingly, in the ^{1}H n.m.r. spectra of poly(AMBE-*co*-MtA)s, no signals related to the protons of the vinyl group of the corresponding comonomers are observed in the 7.0–6.0 ppm region.

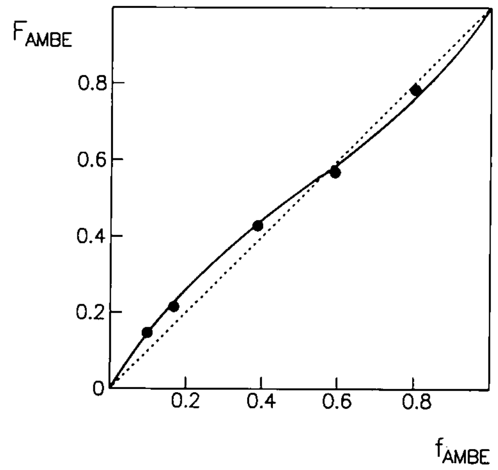


Figure 2 Copolymerization diagram for the (±)-4-acryloyloxy-α-methylbenzoin methyl ether (AMBE)/(−)-menthyl acrylate (MtA); f_{AMBE} and F_{AMBE} are the AMBE molar fractions in the feed and in the copolymerization product, respectively

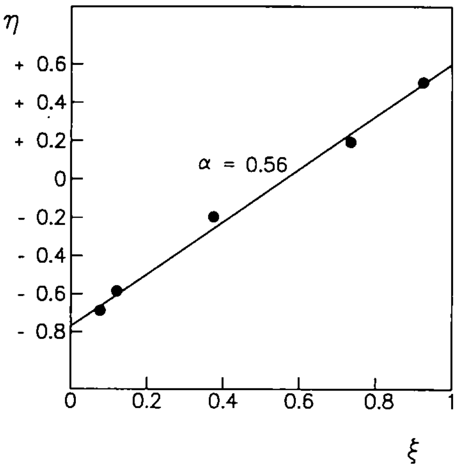


Figure 3 Kelen–Tüdos plot for the system (±)-4-acryloyloxy-α-methylbenzoin methyl ether (AMBE)/(−)-menthyl acrylate (MtA): $\eta = (r_{AMBE} + r_{MtA}/\alpha)\xi - r_{MtA}/\alpha$

Copolymer composition was determined by ^{1}H n.m.r. analysis based on the integrated areas of the signals of aromatic and aliphatic protons.

In all the copolymerization runs the monomer to polymer conversion was usually in the range 20-80% (*Table 1*), thus preventing a precise determination of the reactivity ratios. However, an approximate evaluation of the above parameters was performed by using the modified Kelen–Tüdos method[14,15] which considers for calculation the average monomer feed between the beginning and the end of the copolymerization process for each experiment.

The copolymerization diagram (*Figure 2*) clearly indicates the presence of a well defined azeotropic point, thus strongly suggesting that the reactivity ratios of the comonomers are both lower than unity[16]. Indeed, the calculated values (*Figure 3*) are found to be: $r_{AMBE} = 0.60$ and $r_{MtA} = 0.43$. These findings, therefore, indicate a certain tendency to an alternating distribution of the two co-units along the polymer chain.

All the copolymer samples display a rather high number-average molecular weight ($\bar{M}_n$), which, although without a regular trend, decreases on increasing the content of AMBE co-units (*Table 1*). This is particularly evident in poly(AMBE) and in the copolymer containing about 80 mol% of AMBE co-units. These findings seem to suggest that, on increasing the amount of AMBE in the feed to at least over 60 mol%, AMBE favours transfer and/or termination reactions during the free radical polymerization process. However, it cannot be excluded that this behaviour may be, at least partially, ascribed to the presence of a gel effect.

Chiroptical properties

U.v. absorption spectra in chloroform solution of poly(AMBE) and poly(AMBE-*co*-MtA)s show two distinct bands in the 400–240 nm region, centred at about 340 and 255 nm (*Figure 4*). The structured weak band at lower energy, with shoulders at about 370, 350, 325 and 315 nm, has been associated with the n→π* electronic transition of the ketone moiety[17]. The strong band at higher energy, centred near 255 nm and having a shoulder at about 270 nm, has been assigned to the lowest energy π→π* electronic transition of the benzene chromophore with an intramolecular charge-transfer band character[17]. Analogous results were obtained for poly(MBA-*co*-MtA)s[7]. The low molecular weight analogue PMBE, containing a single benzoin methyl ether moiety per molecule, displays a similar absorption spectrum (*Figure 4*).

In addition, when the content of AMBE units decreases from 100 to 15 mol%, the maximum molar extinction coefficient (ε_{max}) for the π→π* electronic transition changes from 12 500 to 15 500 without any monotonic trend (*Table 2*). These findings can reasonably be considered as an indication that no large electronic interactions occur between side-chain benzoin methyl ether chromophores along the backbone[18,19]. However, a slight progressive bathochromic effect is observed for the same band on decreasing the content of AMBE co-units (*Table 2*).

All the copolymer samples display a negative optical activity at the sodium D line, the specific rotatory power

Table 2 U.v. absorption properties in chloroform solution of poly(AMBE-*co*-MtA)s, poly(AMBE) and PMBE in the 400–240 nm region

Sample	AMBE co-units (mol%)	n→π* λ_{max} (nm)	n→π* $\varepsilon_{max}{}^{a}$ ($l\,mol^{-1}\,cm^{-1}$)	π→π* λ_{max} (nm)	π→π* $\varepsilon_{max}{}^{a}$ ($l\,mol^{-1}\,cm^{-1}$)
Poly(AMBE)	100.0	341	219	253	12 500
Poly(AMBE-*co*-MtA)	79.0	340	219	254	14 100
	58.0	340	218	255	15 500
	43.0	340	215	255	14 400
	22.0	338	223	256	13 400
	15.0	338	209	257	12 700
PMBE	–	339	232	257	13 700

[a] Referred to one benzoin methyl ether moiety

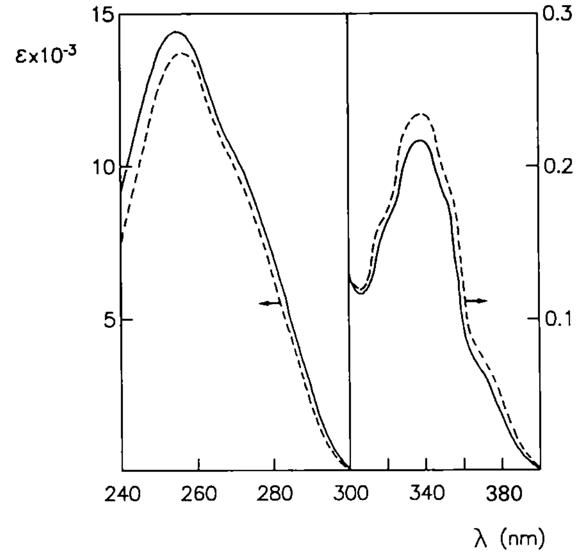


Figure 4 U.v. spectra in the 400–240 nm region and in chloroform solution: (———) poly(AMBE-*co*-MtA) with 43.0 mol% of AMBE co-units; (-----) the model compound PMBE

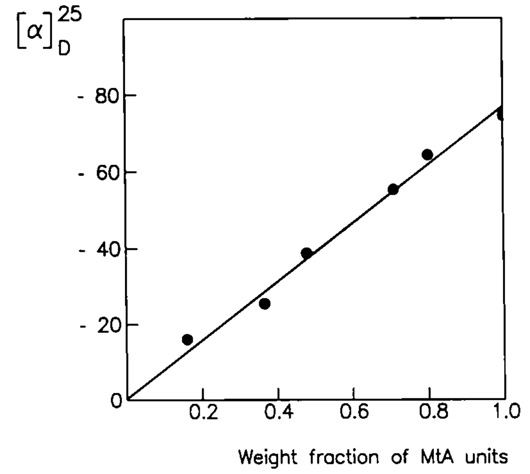


Figure 5 Specific rotatory power in chloroform solution at the sodium D line and 25°C for poly(AMBE-*co*-MtA)s vs. composition

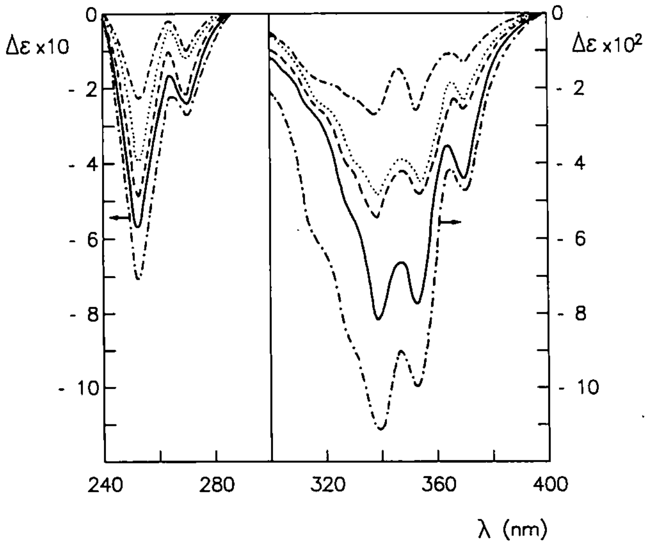


Figure 6 C.d. spectra in the 400–240 nm region and in chloroform solution of poly(AMBE-*co*-MtA)s with various amounts of AMBE co-units (mol%): 79.0 (—·—·—), 58.0 (·····), 43.0 (-----), 22.0 (———), and 15.0 (-·-·-)

depending linearly on composition (*Figure 5*). This result is in accordance with those previously obtained for free radically prepared copolymers of MtA with several vinyl aromatic monomers such as styrene[20], 1-vinylnaphthalene[21] and 4-vinylpyridine[22] as well as with different acrylates, namely 4-hydroxybenzophenone acrylate[23], *trans*-4-hydroxystilbene acrylate[24], 4-acryloxyazobenzene[25] and α-methylolbenzoin methyl ether acrylate (MBA)[7].

The linear trend of $[\alpha]_D$ *versus* the content of MtA units, independently from the extent of copolymerization conversions, indicates that no significant stereoelectivity and stereoselectivity occur during the process and that AMBE co-units do not give any contribution to the optical activity at 589 nm. However, this does not exclude the occurrence of an asymmetric perturbation on the benzoin methyl ether moiety in poly(AMBE-*co*-MtA)s, due to the presence of the chiral MtA co-units, as well established in the case of the above-mentioned different copolymers.

Indeed, poly(AMBE-*co*-MtA)s show in the 400–300 nm region, connected with the n→π* electronic transition of the benzoin methyl ether chromophore, a negative structured dichroic band with relative maxima and shoulders strictly related to u.v. absorption in the same spectral region (*Figure 6*). The differential dichroic absorption coefficient per AMBE co-unit (Δε) at about 340 nm increases in absolute value with decreasing the

Table 3 Circular dichroism between 400 and 240 nm of side-chain benzoin methyl ether chromophores in poly(AMBE-*co*-MtA)s[a]

Sample AMBE co-units (mol%)	C.d. maxima					
	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$			
	λ	$\Delta\varepsilon \times 10^2$	λ	$\Delta\varepsilon \times 10^2$	λ	$\Delta\varepsilon \times 10^2$
79.0	339	−2.7	270	−9.5	253	−22.9
58.0	340	−4.8	270	−12.0	254	−38.6
43.0	339	−5.4	270	−21.9	255	−49.1
22.0	338	−8.2	270	−23.9	255	−57.0
15.0	338	−11.2	269	−26.5	255	−70.7

[a] In chloroform solution; λ expressed in nm; $\Delta\varepsilon$ expressed in $l\,mol^{-1}\,cm^{-1}$ and referred to one AMBE repeating unit

content of AMBE units in the copolymers (*Table 3*), thus suggesting that the main contribution to the induced optical activity comes from AMBE co-units either isolated or flanked by optically active MtA co-units. The c.d. spectra of poly(AMBE-*co*-MtA)s in the above region, as compared with those of poly(MBA-*co*-MtA)s[7] having similar content of benzoin methyl ether units, clearly show $\Delta\varepsilon$ values larger than almost one order of magnitude, in accordance with a higher conformational rigidity of the macromolecules in solution. This is confirmed also by the presence of two intense negative dichroic bands, centred at about 270 and 255 nm, in the spectral region connected with the $\pi \rightarrow \pi^*$ electronic transition of the benzoin methyl ether chromophore, in close relation to the corresponding absorption spectra (*Figures 4* and *6*). $\Delta\varepsilon$ values for the above bands also increase in absolute value with decreasing the content of AMBE co-units in the copolymers (*Table 3*). These bands were not observed in poly(MBA-*co*-MtA)s for compositions in the 80-25 mol% range of benzoin methyl ether containing units and were detectable only in the copolymer sample having the lowest content of MBA co-units (12.2 mol%)[7].

All these results strongly support the existence of higher conformational homogeneity in poly(AMBE-*co*-MtA)s as compared with poly(MBA-*co*-MtA)s. However, the lack of any exciton splitting of the dichroic bands in both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ spectral regions seems to exclude the possibility that long sections of macromolecules assume a dissymmetric conformation with a prevailing screw sense. Therefore it may be concluded that in the macromolecules of poly(AMBE-*co*-MtA)s the optically active MtA co-units are able to force AMBE co-units, independently of their (*R*) or (*S*) absolute configuration, to assume conformations with a prevailing chirality for sections longer than in poly(MBA-*co*-MtA)s, but not enough to give cooperative dipole–dipole interactions along the backbone between side-chain benzoin methyl ether chromophores with a mutual chiral geometry suitable for exciton couplings.

CONCLUSIONS

Free radical copolymerization of racemic 4-acryloyloxy-α-methylbenzoin methyl ether (AMBE) with (−)-menthyl acrylate (MtA) affords copolymeric products having a certain tendency to an alternating distribution of both co-units along the polymer chain.

The linear dependence of the specific optical rotatory power at the sodium D line in poly(AMBE-*co*-MtA)s as a function of the composition, independently of the extent of conversion in the individual copolymerization experiments, strongly suggests the lack of stereoselectivity and stereoelectivity during the copolymerization process. However, the induced optical activity on benzoin methyl ether chromophores, as checked by c.d. measurements, clearly shows that the above moieties, regardless of the (*S*) or (*R*) absolute configuration of the monomeric units, are chirally perturbed, being inserted in macromolecules having a dissymmetric conformation with a predominant handedness.

The higher ellipticity in both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ dichroic bands for poly(AMBE-*co*-MtA)s, as compared with poly(MBA-*co*-MtA)s, indicates a higher conformational rigidity of the macromolecules in solution for the former system. However, the lack of exciton couplets in the above dichroic bands seems to suggest that the macromolecules assume conformations with a prevailing screw sense for sections insufficiently long to provide cooperative dipole–dipole interactions between side-chain benzoin methyl ether chromophores disposed along the backbone in a mutual chiral geometry.

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