Optically active polymers containing side-chain photoreactive benzoin methyl ether moieties

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Optically active copolymers of (−)-menthyl acrylate (MtA) with racemic α-methylolbenzoin methyl ether acrylate (MBA) as well as of (−)-menthyl vinyl ether (MtVE) with racemic α-vinyloxymethylbenzoin methyl ether (MBVE) have been prepared by radical and cationic initiation, respectively. The reactivity of comonomers as well as spectroscopic and fractionation data suggest that acrylic and vinyl ether copolymers show a tendency towards substantial random and block distributions of monomeric units, respectively.

Optical activity at 589 nm of the copolymers seems to exclude any stereoselectivity and stereoelectivity during the copolymerization in both systems. Chiroptical properties indicate that in both series of copolymers an induced optical activity on benzoin-derivative chromophores occurs, which is due to a dissymmetric arrangement of the macromolecules.

Circular dichroism data, connected with the n → π* electronic transition of the keto group, suggest that the observed ellipticity in MBA/MtA copolymers is substantially due to isolated MBA units. In the case of MBVE/MtVE copolymers both isolated and sequential MBVE units give a contribution to the ellipticity, thus suggesting that the induced optical activity is transmitted through short blocks of MBVE units.

INTRODUCTION

A large variety of optically active polymers containing photosensitive or photoreactive groups deriving from naphthalene[1,2], N-vinylcarbazole[3,4], trans-stilbene[5,6], trans-azobenzene[7,8] and benzophenone[9,10] precursors have recently been reported. All the above polymeric products were prepared by copolymerization of achiral unsaturated monomers containing the above-mentioned chromophores with an optically active comonomer. The c.d. spectra of such copolymers display dichroic bands in the same absorption region of the chromophores contained in the achiral monomers, thus clearly showing the occurrence of 'induced optical activity'. The extent of the latter, due to the presence of dissymmetric conformations having a prevailing chirality, was found to be dependent on monomer structure[11] as well as on stereoregularity, composition and sequence distribution of the macromolecules[2,12,13]. By contrast, only a few examples have been reported[14–16] of the copolymerization of an optically active monomer with a racemic comonomer. However, in such cases a heterogeneous stereospecific catalyst and comonomers with peculiar stereochemical requirements were used.

On the other hand, benzoin derivatives, which are known to give rise[17] under u.v. irradiation to free radicals by α-cleavage, are extensively used as polymerization photoinitiators for acrylic coatings[18]. Therefore macromolecular systems containing side-chain benzoin methyl ether moieties are expected to have potential applications both as non-yellowing photoinitiators and for low-odour coatings, due to reduced migration of residual photoreactive groups onto the film surface[19,20].

In this context the synthesis and characterization of optically active copolymers of racemic α-methylolbenzoin methyl ether acrylate (MBA) with (−)-menthyl acrylate (MtA) and of racemic α–vinyloxymethyl benzoin methyl ether (MBVE) with (−)-menthyl vinyl ether (MtVE) (poly(MBA-co-MtA)s and poly(MBVE-co-MtVE)s, respectively) appeared very interesting.

poly(MBA-co-MtA)s

poly(MBVE-co-MtVE)s
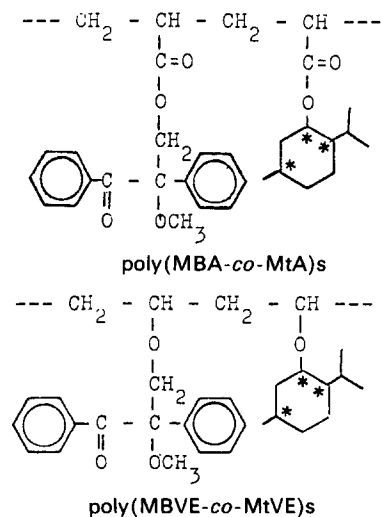
In fact, the investigation of their chiroptical properties could allow one to obtain information on the stereochemical pathway of the copolymerization processes involved, as well as on the secondary structure of the macromolecules[21] and possible cooperative interactions between side-chain benzoin chromophores, which could in principle be responsible for the photoactivation of such polymeric systems.

EXPERIMENTAL

Monomers

(−)-*Menthyl acrylate*. MtA having $[\alpha]_D^{25} = -89$ (neat) was prepared as reported elsewhere[22].

(±)-α-*Methylolbenzoin methyl ether acrylate*. MBA was prepared as previously reported[23].

(−)-*Menthyl vinyl ether*. MtVE having $[\alpha]_D^{25} = -73.5$ (neat) was synthesized by transetherification in the presence of mercuric acetate from (−)-menthol and ethyl vinyl ether[16] and was distilled (b.p. = 112°C/20 mmHg) on Na/K alloy just before use.

(±)-α-*Vinyloxymethylbenzoin methyl ether*. MBVE was obtained in 62% yield by transetherification in the presence of mercuric acetate (3 mmol) from (±)-α-methylolbenzoin methyl ether (39 mmol) and ethyl vinyl ether (720 mmol). After heating at reflux temperature for 4 h, the reaction mixture was treated at room temperature with 1.0 g of solid Na_2CO_3, then washed with aqueous 5% Na_2CO_3 and water in that order. The organic layer, after drying over anhydrous Na_2SO_4, was evaporated at reduced pressure to give crude BMVE as an oily residue still containing the starting alcohol, as checked by t.l.c. analysis. After purification by elution chromatography on neutral silica gel (70–230 mesh), using benzene as eluent, the product was crystallized from ethanol/water (7:3) mixture to give pure BMVE having m.p. = 46°C.

^{1}H n.m.r. (CDCl$_3$): $\delta = 8.2$–8.0 ppm (m, 2H, aromatic protons in *ortho* position to the carbonyl group); 7.7–7.2 ppm (m, 8H, other aromatic protons); 6.7–6.3 ppm (dd, 1H, —CH=); 4.7–3.9 ppm (m, 4H, =CH$_2$ and CH$_2$O—); and 3.4 ppm (s, 3H, O—CH$_3$).

I.r. spectrum (cm^{-1}): 3113–3025, v(C—H) (aromatic rings and vinyl group); 1670, v(C=O); 1614, v(C=C) (vinyl group); 1597, v(C=C) (aromatic rings); 1202, v_{as} (C—O—C) (vinyl ether group); and 1132, v_{as} (C—O—C) (methyl ether).

Low-molecular-weight analogues

(±)-α-*Methylolbenzoin methyl ether acetate*. MBAc was prepared from (±)-α-methylolbenzoin methyl ether as previously reported[23].

(±)-α-*Ethyloxybenzoin methyl ether*. BMEE was synthesized from MBVE by selective hydrogenation of the vinyl group at atmospheric pressure and 25°C in the presence of PtO$_2$ as catalyst. In a round-bottomed two-necked 50 ml flask, connected to a graduated gas burette through a condenser, 4.1 mmol of MBVE dissolved in 15 ml of ethanol and in the presence of a catalytic amount of PtO$_2$ were treated with hydrogen. The reaction was stopped when the absorption of hydrogen was completed (slightly more than the theoretical volume

for the hydrogenation of the vinyl group only). After filtration and removal of the solvent under vacuum, the residual product was crystallized from ethanol/water (7:3) mixture to give in 60% yield pure BMEE having m.p. = 48°C.

^{1}H n.m.r. (CDCl$_3$): $\delta = 8.2$–7.7 ppm (m, 2H, aromatic protons in *ortho* position to the carbonyl group); 7.7–7.2 ppm (m, 8H, other aromatic protons); 4.5–3.8 ppm (dd, 2H, O—CH$_2$); 3.7–3.3 ppm (m, 5H, O—CH$_3$ and O—CH$_2$—CH$_3$); and 1.1 ppm (t, 3H, O—CH$_2$—CH$_3$).

I.r. spectrum (cm^{-1}): 3059–3026, v(C—H) (aromatic rings); 1677, v(C=O); 1597, v(C=C) (aromatic rings); 1130, v_{as} (C—O—C) (methyl ether group); and 1108, v(C—O—C) (ethyl ether group).

Radical initiator

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

Polymerization experiments

Free-radical polymerizations. Free-radical homo- and copolymerizations of MBA and MtA were carried out at 60°C in glass vials using benzene as solvent and AIBN (0.5 wt% with respect to the monomers) as initiator. After introducing the components under nitrogen the vials were degassed several times and sealed under high vacuum. After a certain 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 stored in a refrigerator in the dark.

Cationic polymerizations. Cationic homo- and copolymerizations of MBVE and MtVE were carried out at −78°C using methylene chloride as solvent and a 0.1 M CH$_2$Cl$_2$ solution of BF$_3$·Et$_2$O as initiator, prepared at −78°C just before use. After a suitable time the polymerization was stopped by adding a methanol/concentrated aqueous ammonia (25:1 v/v) mixture. The polymer was completely precipitated by an excess of methanol, redissolved in chloroform and precipitated again by methanol. The polymer after filtration was dried under vacuum at room temperature and stored in a refrigerator in the dark. The polymers obtained by cationic initiation were successively fractionated by solvent extraction at room temperature using n-pentane and chloroform, in that order.

Physicochemical measurements

^{1}H n.m.r. spectra at 60 MHz were carried out in CDCl$_3$ solution on a Varian EM 360L spectrometer, using tetramethylsilane (TMS) as internal standard.

I.r. examinations of the samples were recorded on an *FT*-i.r. Perkin–Elmer 1750 spectrophotometer coupled with a Perkin–Elmer 7700 data station. Cast films on KBr discs or KBr pellets 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 Shodex KF-804 column and a refractive index detector. Monodisperse polystyrene samples were used as standards for calibration.

Optical rotatory measurements were performed at 25°C in CHCl$_3$ solution or on neat samples by using a

Table 1 Preparation[a] and properties of poly(MBA-co-MtA)s

Feed MBA (mol%)	Duration (h)	Conversion[b] (%)	Copolymer characterization		
			MBA units[c] (mol%)	$[\alpha]_D^{25\,d}$	$\bar{M}_n{}^e$
100.0	56	60	100.0	0.0	12 000
75.0	19	69	79.0	−11.0	39 500
50.0	12	67	51.6	−29.8	32 000
37.0	20	65	36.8	−37.6	58 000
25.0	8	51	24.4	−47.0	87 000
13.0	16	36	12.2	−61.6	150 000
0.0	40	68	0.0	−73.9	n.d.

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

Perkin–Elmer 141 spectropolarimeter having a sensitivity of ±0.003°.

Melting point determinations were carried out in glass capillaries using a Büchi 510 apparatus.

U.v. absorption measurements were carried out in chloroform solution on a Jasco Uvidec 510 spectrophotometer by using cell path lengths of 1 cm and 1 mm in the 400–300 and 300–240 nm regions, respectively. Concentrations of about 5×10^{-3} and 8×10^{-4} mol 1^{-1} of benzoin methyl ether chromophore were used, respectively.

C.d. spectra on copolymer samples were performed in chloroform solution on a Jasco J500A dichrograph. Cell path lengths as well as the corresponding solution concentrations and spectral regions were the same as reported for u.v. measurements. The molar differential dichroic absorption coefficient $\Delta\varepsilon$ ($1\,mol^{-1}\,cm^{-1}$) is referred to one benzoin methyl ether-containing monomeric unit and has been calculated as $\Delta\varepsilon = Es/3300cl$, where E is the measured elongation (cm), s is the sensitivity (mdeg cm^{-1}), c is the benzoin methyl ether chromophore concentration (dmol 1^{-1}) and l is the cell path length (cm).

RESULTS AND DISCUSSION

Synthesis and characterization of polymers

Copolymers of (±)-α-methylolbenzoin methyl ether acrylate (MBA) with (−)-menthyl acrylate (MtA) (poly-(MBA-co-MtA)s). Copolymerization experiments, carried out in benzene at 60°C and using AIBN as initiator, are reported in *Table 1*. All runs gave rather high monomer-to-polymer conversion, thus preventing the evaluation of comonomer reactivity ratios.

Copolymer compositions (*Table 1*), estimated by ^{1}H n.m.r. analysis from the signals of aromatic and aliphatic protons, are, within the limits of experimental errors, very close to that of the corresponding comonomer feed, where the conversion is also in the 30–50% range. These results indicate that the reactivity of the two comonomers is very similar, and suggest a substantially random distribution of the monomeric units in the macromolecules.

I.r. spectra (*Figure 1*) of the copolymer samples display the same bands as the corresponding homopolymer mixtures, thus indicating the presence of both monomeric units. In particular, bands at 1735 and 1677 cm^{-1} (C=O stretching of ester and keto aromatic moieties, respectively), at 1597 cm^{-1} (C=C stretching of aromatic rings
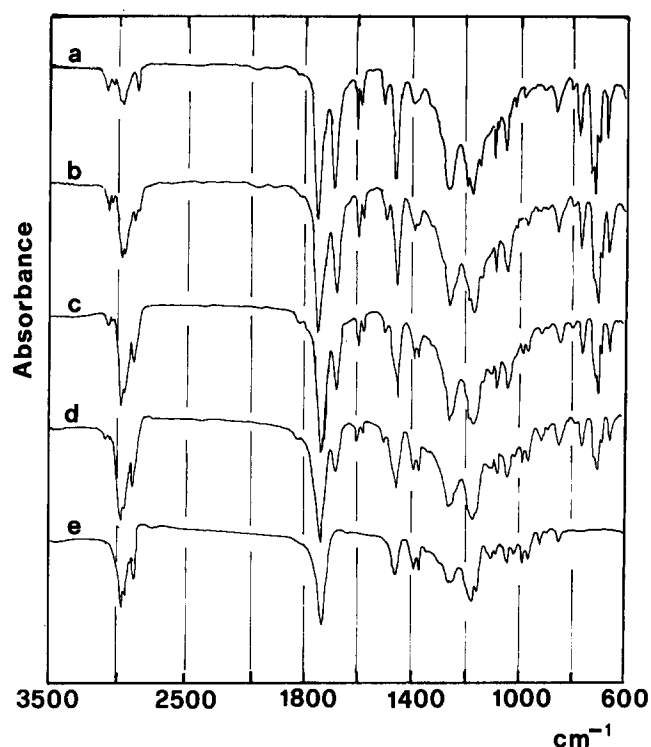
Figure 1 Typical i.r. spectra of the radically prepared copolymers: (a) poly(MBA); (b–d) poly(MBA-co-MtA)s with 79.0, 51.6 and 24.4 mol% MBA units, respectively; (e) poly(MtA)

in MBA units) as well as a doublet at 1388 and 1371 cm^{-1} (C—H bending of *gem*-dimethyl group in MtA units) are observed.

All the copolymer samples display rather high number-average molecular weight ($\bar{M}_n$), which decreases with increasing content of MBA units (*Table 1*), thus suggesting that these latter units favour transfer and/or termination reactions during the polymerization process.

Copolymers of (±)-α-vinyloxymethylbenzoin methyl ether (MBVE) with (−)-menthyl vinyl ether (MtVE) (poly(MBVE-co-MtVE)s). Copolymerization experiments have been carried out in CH$_2$Cl$_2$ solution at −78°C using BF$_3 \cdot$ Et$_2$O as cationic initiator. The data are reported in *Table 2*. All the copolymerization runs display high monomer-to-polymer conversion. The copolymer com-

positions, as checked by ^{1}H n.m.r., show a higher content of MtVE units as compared with the corresponding feed, thus indicating a major reactivity of MtVE with respect to MBVE. This is particularly evident in run 3, where an equimolar mixture of the two comonomers was used and a conversion of only 50% was reached due to short polymerization time (*Table 2*).

I.r. spectra of the crude polymers show the same bands as the corresponding homopolymer mixtures, thus suggesting the presence of both monomeric units (*Figure 2*). In particular the disappearance of the band at 1614 cm^{-1} and the shift of the band of keto-aromatic group from 1670 to 1680 cm^{-1} strongly support that the polymerization of MBVE has involved only the vinyl group and not the ketone moiety. Moreover, the doublet at 1385 and 1371 cm^{-1}, due to the isopropyl group, indicates the contemporary presence of MtVE units.

Fractionation of the copolymerization products by solvent extraction has excluded the presence of homopolymer mixtures, thus confirming the occurrence of copolymeric products. In fact, the copolymerization products are partially soluble in n-pentane and afford A and B fractions containing both MtVE and MBVE units (*Table 3*), whereas poly(MtVE) is soluble in n-pentane at room temperature and poly(MBVE) is completely insoluble in this solvent but soluble in chloroform.

The large difference in composition observed in fractions A and B of poly(MBVE-*co*-MtVE)s, independently of the feed and also for conversions not larger than 50% (run 3, *Tables 2* and *3*), strongly suggests the tendency towards block distribution of both monomeric units in the copolymer macromolecules.

Number-average molecular weights ($\bar{M}_n$) of the copolymer fractions (*Table 3*) are rather high but lower than those observed for the corresponding homopolymers, thus indicating that the presence of both monomers in the feed favours transfer and termination reactions during the polymerization process.

Chiroptical properties

U.v. absorption spectra in chloroform solution of poly(MBA-*co*-MtA)s and poly(MBVE-*co*-MtVE)s show in the 400–240 nm region two distinct bands centred at about 340 and 250 nm (*Figure 3*). The very weak band at lower energy has been definitely associated with the classical n $\rightarrow$ π^* electronic transition of the keto group[24], whereas the strong band at higher energy has been interpreted as related to the lowest energy $\pi \rightarrow \pi^*$ electronic transition of benzene chromophore with an intramolecular charge-transfer (CT) band character[24]. Similar spectral behaviour is observed in poly(MBA), in

Table 2 Homopolymerization and copolymerization of MBVE and MtVE at −78°C in CH$_2$Cl$_2$ solution by using BF$_3$·Et$_2$O as cationic initiator[a]

Run	Feed MBVE (mol%)	Duration (h)	Conversion[b] (%)	Polymer MBVE units[c] (mol%)
1	100.0	1	20	100.0
2	75.0	20	90	65.9
3	50.0	1	50	23.4
4	25.0	20	81	26.7
5	0.0	0.1	88	0.0

[a] Molar ratio monomers/BF$_3$·Et$_2$O = 50
[b] Evaluated as (weight of polymer/weight of starting monomers) × 100
[c] Determined by ^{1}H n.m.r.

Figure 2 Typical i.r. spectra of the cationically prepared copolymers: (a) poly(MBVE); (b–c) poly(MBVE-*co*-MtVE)s with 65.9 and 26.7 mol% MBVE units, respectively; (d) poly(MtVE)

Table 3 Fractionation and properties of homopolymerization and copolymerization products from MBVE and MtVE

|	Pristine polymer MBVE units (mol%)	Polymer fractions[a]							
		A				B			
Run		Amount (%)	MBVE units[b] (mol%)	$[\alpha]_D^{25}$[c]	$\bar{M}_n$[d]	Amount (%)	MBVE units[b] (mol%)	$[\alpha]_D^{25}$[c]	$\bar{M}_n$[d]
1	100.0	0.0	–	–	–	100.0	100.0	0.0	40 500
2	65.9	21.0	15.6	−150.0	20 400	79.0	81.3	−25.3	35 400
3	23.4	83.0	15.3	−169.3	24 200	17.0	n.d.	n.d.	n.d.
4	26.7	69.0	8.0	−180.0	40 900	31.0	71.7	−38.0	28 000
5	0.0	100.0	0.0	−203.4	68 000	0.0	–	–	–

[a] Extracted at room temperature successively with n-pentane (fraction A) and chloroform (fraction B)
[b] Evaluated by ^{1}H n.m.r.
[c] In chloroform solution: $l = 1$ dm
[d] Determined by g.p.c. measurements

poly(MBVE) and in low-molecular-weight analogues BMMAc and BMEE containing a single benzoin methyl ether chromophore per molecule.

CH₃ structures (BMMAc and BMEE)

BMMAc   BMEE
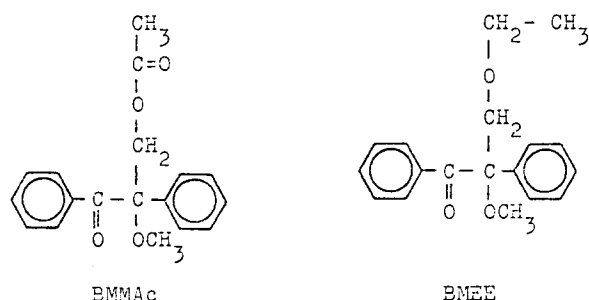
This result can reasonably be considered as an indication that no large electronic interactions occur among
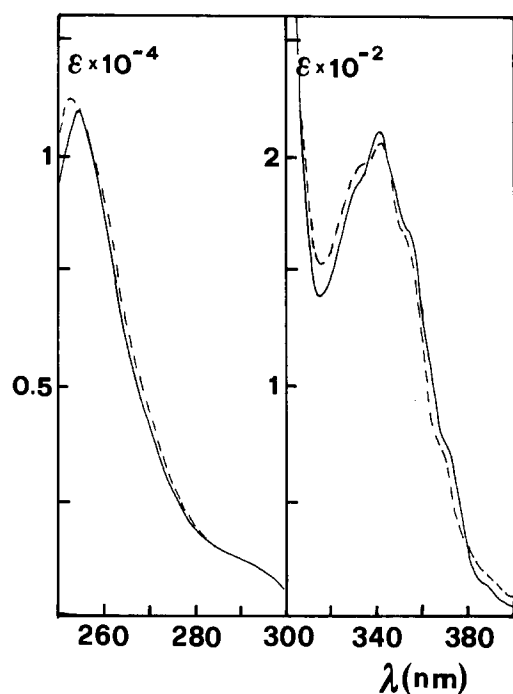
side-chain benzoin-derivative chromophores even if these bands, in particular the one at 340 nm, have a rather low polarizability. However, in poly(MBA-*co*-MtA)s when the content of MBA units decreases from 100 to 12.2 mol% the maximum molar extinction coefficient per MBA unit (ε_{max}) for the $\pi \to \pi^*$ electronic transition increases from 11 000 to 14 000 (*Table 4*). This behaviour has been reported to occur in many polymers containing side-chain aromatic chromophores[4,22] and it was attributed[25,26] to the presence of adjacent interacting aromatic chromophores. On the contrary, in case of poly(MBVE-*co*-MtVE)s no monotonic increase of ε_{max} with decreasing content of MBVE units is observed in the same spectral region.

For a correct interpretation of the chiroptical properties of poly(MBA-*co*-MtA)s and poly(MBVE-*co*-MtVE)s, one must take into account that both copolymers are formed from an optically pure monomer and a racemic comonomer. If a stereoselective[27] process occurs, the optically active monomer copolymerizes with only one single enantiomer of the racemic comonomer, the other enantiomer undergoing homopolymerization. The copolymer thus obtained usually exhibits higher solubility and can be easily separated from the homopolymer by solvent extraction.

In addition, if copolymerization and homopolymerization proceed with different rates, prevailing consumption of one enantiomer of the racemic monomer (stereoelective[27] process) also occurs. Both stereoselectivity and stereoelectivity were found to occur in copolymerization processes involving α-olefins or vinyl ethers, provided that the asymmetric carbon atom in such monomers is in the α or β position with respect to the double bond and heterogeneous isospecific catalysts were used[14-16]. Indeed, homogeneous cationic copolymerization of racemic 1-methylpropyl vinyl ether with optically active 1-phenylethyl vinyl ether by $BF_3 \cdot Et_2O$ at $-78°C$ did not show[16] any stereoselectivity and stereoelectivity, despite the asymmetric carbon atom in the comonomers being in the β position to the double bond. Also the polymerization of racemic 5-methyl-1-heptene, having the asymmetric carbon atom in the γ position to the double bond, by isospecific Ziegler–Natta catalysts proceeds without any appreciable stereoselectivity and stereoelectivity[28,29]. As, in the present paper, both free-radical and cationic copolymerizations

Figure 3 Typical u.v. spectra in the 400–250 nm region of some copolymers in chloroform solution: (——) poly(MBA-*co*-MtA) with 51.6 mol% MBA units; (– – – –) poly(MBVE-*co*-MtVE) with 15.6 mol% MBVE units. (ε is calculated per MBA or MBVE unit)

Table 4 U.v. absorption properties in chloroform solution of poly(MBA-*co*-MtA)s and poly(MBVE-*co*-MtVE)s in the 400–240 nm region

| Sample | Benzoin-derivative units (mol%) | n → π* | | π → π* | |
		λ_{max} (nm)	ε_{max}^a (l mol⁻¹ cm⁻¹)	λ_{max} (nm)	ε_{max}^a (l mol⁻¹ cm⁻¹)
Poly(MBA)	100.0	339	210	253	11 000
	79.0	340	210	254	12 900
	51.6	340	209	254	11 000
Poly(MBA-*co*-MtA)	36.8	339	210	253	12 500
	24.4	340	211	254	13 000
	12.2	340	213	253	14 000
MBAc	–	338	215	253	12 500
Poly(MBVE)	100.0	340	200	251	11 500
	81.3	342	192	252	11 900
	71.7	342	198	252	12 600
Poly(MBVE-*co*-MtVE)	15.6	341	204	252	11 300
	8.0	340	180	252	10 900
MBME	–	339	201	252	11 000

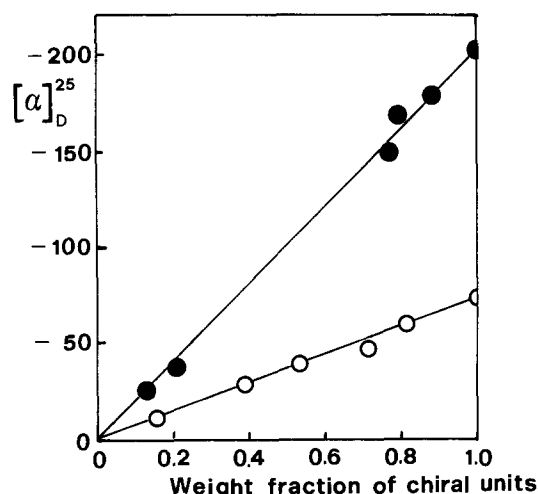^{a} Referred to one benzoin-derivative moiety

Figure 4 Specific rotatory power at the sodium D line vs. composition: (●) poly(MBVE-*co*-MtVE)s; (○) poly(MBA-*co*-MtA)s

Table 5 Differential molar absorption coefficient $\Delta\varepsilon$ in chloroform solution of poly(MBA-*co*-MtA)s and poly(MBVE-*co*-MtVE) in the 400–300 nm spectral region

Sample	Benzoin-derivative units (mol%)	λ_{max} (nm)	$\Delta\varepsilon_{max} \times 10^{2}$ [a]
poly(MBA-*co*-MtA)	79.0	353	−0.5
	51.6	355	−0.9
	24.4	355	−1.9
	12.2	354	−2.2
poly(MBVE-*co*-MtVE)	81.3	340	+0.7
	71.7	342	+2.1
	15.6	343	−8.7
	8.0	342	−8.4

[a] The values are calculated per benzoin-derivative moiety

are carried out by homogeneous initiators and the chiral centres in MBVE and MBA are rather far from the double bond (in γ or δ positions, respectively), both stereoselectivity and stereoelectivity should be negligible, if any.

All the polymeric fractions A and B of poly(MBVE-*co*-MtVE)s display negative optical activity (*Table 3*) and the observed linear dependence of the specific optical rotatory power at the sodium D line as a function of copolymer composition (*Figure 4*) seems to exclude any contribution of MBVE units to the optical activity at 589 nm, thus confirming the above hypothesis. In fact, taking into account the higher reactivity of MtVE with respect to MBVE and the high conversion in the majority of experiments, significant stereoselection and stereoelection should give copolymer fractions A and B containing MBVE units with a relevant enantiomeric excess of opposite chirality, respectively. As a consequence, a large deviation from the above linearity should be observed. Similar results (*Figure 4*) were obtained in the case of poly(MBA-*co*-MtA)s also, thus confirming that in free-radical copolymerization no stereoselectivity and stereoelectivity occur.

However, such a linear dependence does not exclude the possibility that in the above copolymers the repeating units from the optically active monomer can force benzoin co-units deriving from both *R* and *S* enantiomers of the racemic monomer to assume conformations of a prevailing single chirality.

Indeed, circular dichroism (c.d.) spectra show for both copolymeric systems an optically active band in the region of the n → π^* electronic transition of the keto group (*Table 5*). Poly(MBA-*co*-MtA)s display (*Figure 5*) a negative structured c.d. band with relative maxima at 387, 370, 355 and 340 nm, strictly related to u.v. absorption in the same spectral region. The differential molar dichroic absorption per MBA unit ($\Delta\varepsilon$) at 355 nm increases with decreasing content of MBA units in the copolymers, thus suggesting that the main contribution to the 'induced optical activity' comes from MBA units either isolated or flanked by MtA units.

In the 300–240 nm region only the poly(MBA-*co*-MtA) sample containing 12.2 mol% of MBA units shows a positive dichroic band centred at about 290 nm and a more intense negative band with a maximum at 253 nm, in strict correlation with the u.v. absorption spectrum in that region (*Figure 6*). The impossibility of detecting these dichroic bands in the other poly(MBA-*co*-MtA) samples can be attributed to the unfavourable anisotropy ratio $\Delta\varepsilon/\varepsilon$. Indeed, the observation of a change of sign in the c.d. spectra of poly(MBA-*co*-MtA)s in the 325–300 nm region (*Figure 5*) seems to suggest the presence below 300 nm of dichroic bands that are not clearly detectable, due to the high dilution of the copolymer solutions. Also in the case of poly(MBVE-*co*-MtVE)s a structured dichroic band with a maximum at 342 nm is observed in the region connected with the n → π^* electronic transition of the keto group (*Table 5*). However such a band changes sign depending on copolymer composition, being negative
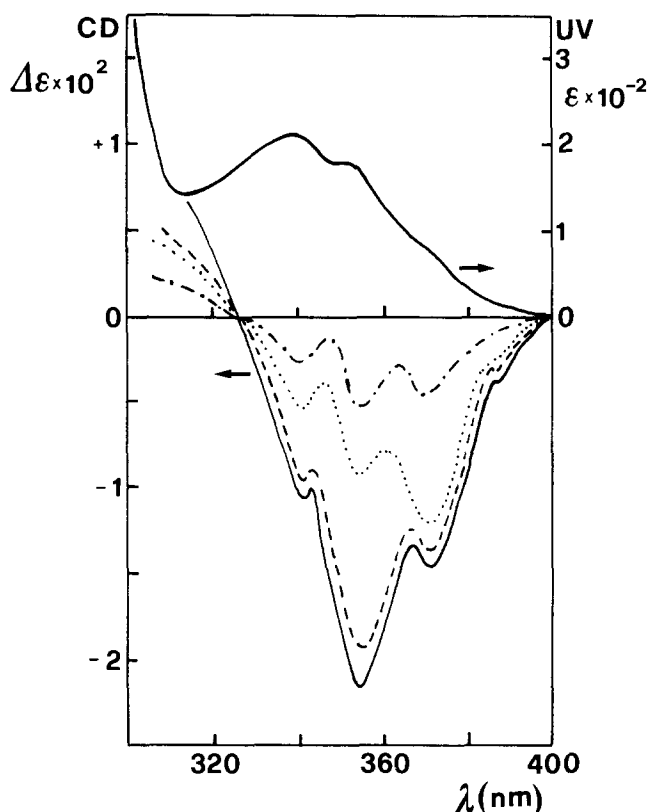

Figure 5 Typical c.d. spectra in the 400–300 nm region and in chloroform solution of poly(MBA-*co*-MtA)s with various amounts of MBA units (mol%): 79.0 (–·–·–), 51.6 (·······), 24.4 (––––) and 12.2 (——). As a general example the u.v. spectrum of poly(MBA-*co*-MtA) with 12.2 mol% MBA units is also reported. ($\Delta\varepsilon$ and ε are calculated per MBA unit)
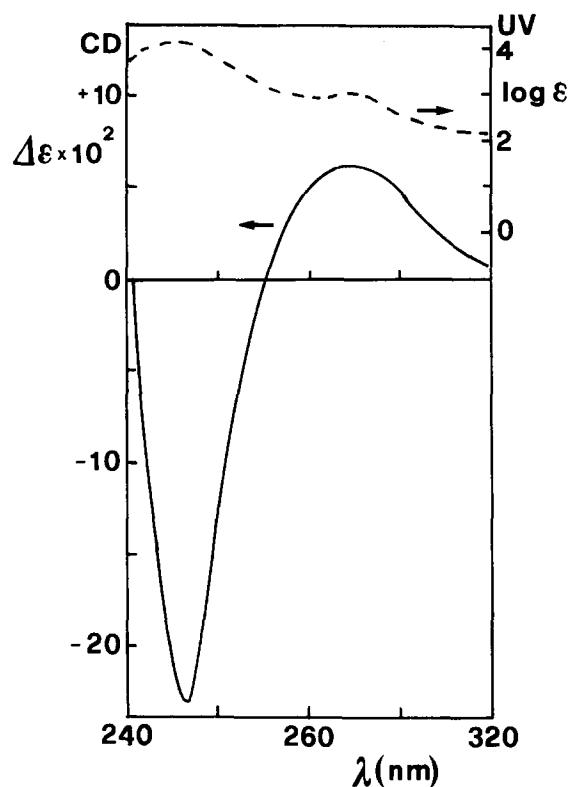
Figure 6 C.d. (——) and u.v. (– – – –) spectra in the 320–240 nm region of poly(MBA-*co*-MtA) with 12.2 mol% MBA units in chloroform solution. (Δε and ε are calculated per MBA unit)

Figure 7 Typical c.d. spectra in the 400–300 nm region and in chloroform solution of poly(MBVE-*co*-MtVE)s with various amounts of MBVE units (mol%): 71.7 (——) and 15.6 (– – – –). As a general example the u.v. spectrum of poly(MBVE-*co*-MtVE) with 71.7 mol% MBVE units is also reported. (Δε and ε are calculated per MBVE unit)

and positive in copolymer samples having low and high content of MBVE units, respectively (*Table 5, Figure 7*). These data clearly indicate that MBVE units, when isolated or in block distribution along the macromolecules, give contributions of opposite sign to c.d. Therefore in poly(MBVE-*co*-MtVE)s the induced chirality is at least partially transmitted along the blocks of MBVE units, due to cooperative effects connected with a higher conformational rigidity of the macromolecules, as compared with poly(MBA-*co*-MtA)s. This picture is also supported by the intensity of ellipticity values of the n → π* electronic transition, which is in general higher in poly(MBVE-*co*-MtVE) than in poly(MBA-*co*-MtA) samples having comparable contents of benzoin-derivative units (*Table 5*).

CONCLUSIONS

On the basis of the results reported, the following concluding remarks can be made.

Free-radical copolymerization of racemic α-methylolbenzoin methyl ether acrylate (MBA) with (−)-menthyl acrylate (MtA) gives rise to substantially random copolymers. By contrast, copolymers of racemic α-vinyloxymethylbenzoin methyl ether (MBVE) with (−)-menthyl vinyl ether (MtVE) having a tendency towards a block distribution of monomeric units are formed by homogeneous cationic initiation.

The linear dependence of optical activity at 589 nm as a function of composition for all the copolymers obtained strongly suggests the lack of stereoselectivity and stereoelectivity during the copolymerization processes. 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
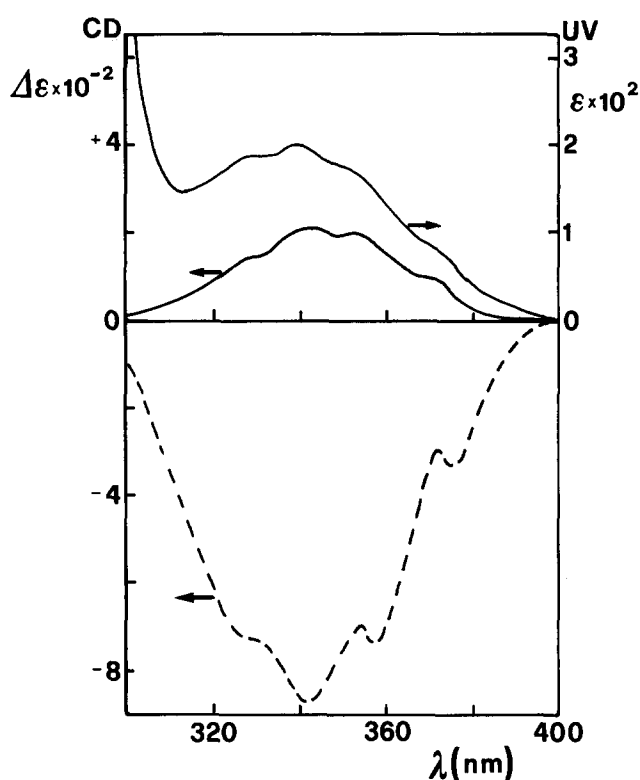
absolute configuration of monomeric units, are chirally perturbed, being inserted in macromolecules that, at least for short sections, assume a dissymmetric conformation of a prevailing chirality. In poly(MBA-*co*-MtA)s mainly isolated MBA units are involved in the induced preferential chirality, whereas in poly(MBVE-*co*-MtVE)s both isolated and sequential MBVE units are chirally perturbed, their contribution to the induced optical activity being of opposite sign. These last results indicate that the dissymmetric perturbation on benzoin chromophores can be transmitted through sequences of MBVE units. This can be attributed to a higher conformational rigidity of the macromolecules, probably due to a closer vicinity of both side-chain benzoin- and menthyl-derivative moieties to the main chain in poly(MBVE-*co*-MtVE)s, as compared with poly(MBA-*co*-MtA)s.

Measurements are in progress to determine the photoinitiating activity in both series of copolymers as compared with the corresponding low-molecular-weight analogues, in order to establish structure–property relationships in terms of distribution and cooperative interactions between benzoin moieties along the macromolecular chain.

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