

# Optically active polymers containing side-chain benzophenone chromophores

Carlo Carlini and Francesco Gurzoni

Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica Industriale, University of Pisa, Via Risorgimento 35, 56100 Pisa, Italy

(Received 24 February 1982)

Optically active copolymers of (-)-menthyl acrylate (MtA) with 4-hydroxybenzophenone acrylate (ABP) have been prepared by radical initiation. Reactivity ratios, mean sequence lengths and the statistical distribution of the sequence lengths of both co-units have been evaluated. Chiroptical properties of the copolymers indicate that a chiral perturbation of side-chain benzophenone chromophores occurs, due to the dissymmetric arrangement of the macromolecules. C.d. data in the spectral region connected with the  $n \rightarrow \pi^*$  electronic transition of benzophenone chromophore, combined with statistical distribution of sequence lengths of monomeric units in the macromolecules suggest that the observed ellipticity is essentially due to the isolated ABP units, inserted in blocks of chiral MtA units.

**Keywords** Optically active copolymers; menthyl acrylate; 4-hydroxybenzophenone acrylate; 4-hydroxybenzophenone-2-methylpropanoate; circular dichroism; sequence length; induced optical activity

## INTRODUCTION

Optically active polymers containing photosensitive side-chain chromophoric groups deriving from 1-vinylnaphthalene<sup>1,2</sup>, 6-vinylchrysene<sup>3</sup>, *N*-vinylcarbazole<sup>4,5</sup>, 4- or 3-(9-carbazolylmethyl)styrene<sup>6</sup> and *trans*-4-hydroxystilbene acrylate<sup>7</sup> have recently been described.

All these polymers have been prepared by copolymerization of the above-mentioned achiral monomers with an optically active comonomer. The copolymer macromolecules show dichroic bands in the u.v. absorption region of the chromophore present in the achiral comonomer, the 'induced optical activity' depending on the monomer structure<sup>8</sup>, as well as on stereoregularity, composition and sequence distribution of the macromolecules<sup>2,9,10</sup>.

Benzophenone derivatives are well known photoinitiators of radical polymerization<sup>11</sup>, the efficiency of the photoinitiated polymerization of acrylic derivatives having been shown<sup>12</sup> to be higher with polymeric systems than with low molecular weight analogues.

In this context it was of interest to prepare optically active copolymers of (-)-menthyl acrylate (MtA) with 4-hydroxybenzophenone acrylate (ABP), poly(MtA-co-ABP)s,

where chiroptical properties could allow one to obtain information about the secondary structure of the macromolecules<sup>13</sup> and about the cooperative interactions between side-chain benzophenone chromophores, which could in principle be responsible for the enhanced efficiency of poly(4-hydroxybenzophenone acrylate) (poly(ABP)) as a photoinitiator compared with 4-hydroxybenzophenone-2-methylpropanoate (IBP)<sup>12</sup>.

## EXPERIMENTAL

### Monomers

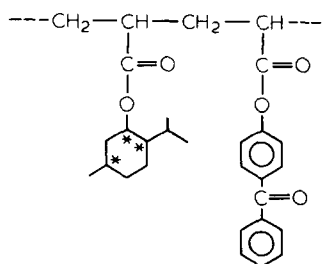
(-)-Menthyl acrylate (MtA) having  $[\alpha]_D^{25} = -89$  (neat) was prepared and purified as reported elsewhere<sup>14</sup>.

4-Hydroxybenzophenone acrylate (ABP) was prepared as follows. 23 g (0.25 mol) of acryloyl chloride (Fluka) were added dropwise with stirring to a mixture of 30 g (0.15 mol) of 4-hydroxybenzophenone (Fluka) and 29 g (0.29 mol) of triethylamine in 250 ml of anhydrous diethyl ether solution. The addition rate was adapted to maintain a gentle reflux of the solvent. The reaction mixture after cooling was hydrolysed with dilute aqueous HCl. The organic layer was washed with 5% aqueous NaOH solution and water in that order. After drying over anhydrous  $\text{Na}_2\text{SO}_4$ , the solvent was removed under vacuum to give 30 g of a red crude solid (79% yield). This product was solubilized in boiling ethanol and the resulting solution, treated with activated charcoal, was filtered while still maintaining it warm. After two crystallizations from ethanol at 0°C, 23 g (0.091 mol) of white crystals of ABP were obtained (m.p. = 50°–51°C).

<sup>1</sup>H n.m.r. ( $\text{CCl}_4$ ):  $\delta = 8\text{--}7$  ppm (m; aromatic protons) and 6.8–5.8 ppm (m; vinyl protons). Intensity ratio 9:3.

### Low molecular weight model

4-Hydroxybenzophenone-2-methylpropanoate (IBP)



poly(MtA-co-ABP)s

Table 1 Preparation<sup>a</sup> and properties of poly(MtA-co-ABP)s

Feed ABP (mol %)	Conversion <sup>b</sup> (%)	Copolymer characterization			
		ABP units <sup>c</sup> (mol %)	$[\alpha]_D^{25d}$	$\bar{l}_{MtA}^e$	$\bar{l}_{ABP}^e$
100.0	43.5	100.0	0.0	—	—
89.8	10.5	92.5	-5.4	1.08	12.62
75.5	7.3	80.0	-12.8	1.22	5.07
50.6	5.5	57.6	-27.8	1.66	2.35
25.1	3.2	32.5	-51.9	3.03	1.44
10.1	16.8	13.9	-64.6	7.05	1.15
0.0	91.4	0.0	-77.2	—	—

<sup>a</sup> In benzene at 60°C using AIBN as radical initiator; duration 1.5–2.5 h

<sup>b</sup> Calculated as (weight of polymer/weight of starting comonomers) × 100

<sup>c</sup> Determined by <sup>1</sup>H n.m.r. analysis

<sup>d</sup> In chloroform solution; *l* = 1 dm

$$^e \bar{l}_{MtA} = \frac{[MtA]}{[ABP]} \times r_{MtA} + 1$$

$$\bar{l}_{ABP} = \frac{[ABP]}{[MtA]} \times r_{ABP} + 1$$

where [MtA] and [ABP] are molar concentrations of MtA and ABP in the feed, respectively

has been obtained in a 67% yield as a white crystalline compound (m.p. = 68°–69°C) starting from 4-hydroxybenzophenone and 2-methylpropionyl chloride following the same procedure described for ABP.

<sup>1</sup>H n.m.r. (CCl<sub>4</sub>): δ = 8–7 ppm (m; aromatic protons), 3.0–2.4 ppm (m; CH) and 1.3 ppm (d; CH<sub>3</sub>). Intensity ratio 9:1:6.

#### Radical initiator

2,2'-Azobisobutyronitrile (AIBN) was recrystallized from ethanol just before use.

#### Polymerization experiments

Free radical copolymerizations were performed in benzene solution and the monomers, the solvent and AIBN were added under nitrogen in a glass vial which was then sealed under vacuum. After maintaining the reaction mixture at 60°C for a suitable period, the polymerization was stopped by pouring the contents of the vial into a large excess of methanol. The coagulated polymer was purified by dissolving in chloroform and reprecipitation from methanol several times. Finally the polymeric product was filtered and dried under vacuum at room temperature. All the polymeric samples were stored in a refrigerator and handled as far as possible in the dark.

#### Physicochemical measurements

<sup>1</sup>H n.m.r. spectra at 60 MHz were carried out in CDCl<sub>3</sub> solution on a Varian T-60 spectrometer, using TMS as internal standard.

I.r. examinations of polymer samples were recorded on a Perkin-Elmer model 180 spectrophotometer using thin films on KBr discs, prepared from polymer solutions in CHCl<sub>3</sub> or CCl<sub>4</sub> by evaporating the solvent.

The optical densities of the bands at 1500 and 1370 cm<sup>-1</sup>, for determining the copolymer composition by i.r. measurements, have been evaluated by drawing a baseline between 1530 and 1350 cm<sup>-1</sup>.

U.v. spectra of polymers and IBP were performed in

CHCl<sub>3</sub> solution on a Varian DMS80 spectrophotometer in the range 400–240 nm using a cell path length of 1 cm. In the spectral regions 400–300 nm and 300–240 nm, sample concentrations of about 5 × 10<sup>-3</sup> and 5 × 10<sup>-5</sup> mol l<sup>-1</sup> of benzophenone chromophore were used, respectively.

C.d. spectra on copolymer samples in CHCl<sub>3</sub> solution were carried out on a Jobin-Yvon Mark III dichrograph in the range 400–240 nm. Cell path lengths of 0.1 and 0.01 dm were used for 400–300 nm and 300–240 nm spectral regions, respectively. Concentrations of 5 × 10<sup>-3</sup> and 5 × 10<sup>-4</sup> mol l<sup>-1</sup> of ABP units were used in the two regions, respectively. Differential molar dichroic absorption coefficients (Δε) are referred to one ABP monomeric unit and expressed in l mol<sup>-1</sup> cm<sup>-1</sup>.

Optical rotatory measurements of polymers in CHCl<sub>3</sub> solution were performed at 25°C on a Perkin-Elmer model 141 spectropolarimeter having a sensitivity of ±0.003°.

Melting point determinations were carried out on a hot-plate Köfler microscope with a 3°C min<sup>-1</sup> heating rate.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The copolymerization experiments were carried out in benzene at 60°C using AIBN as radical initiator. All the runs were stopped at low conversion (<20%) in order to obtain polymeric materials having as far as possible homogeneous composition (Table 1). This was estimated by <sup>1</sup>H n.m.r. from the signals of the aromatic and aliphatic protons. I.r. spectra (Figure 1) of the copolymers display the same bands as the corresponding homopolymer mixtures. The ratio between the optical densities of i.r. bands at 1500 and 1370 cm<sup>-1</sup> (arising from the stretching vibrations of carbon-carbon bonds in the aromatic rings of ABP units and from symmetrical bending vibration of methyls in the isopropyl group of MtA units, respectively) as a function of composition gives a monotonic curve (Figure 2) which can be used to evaluate copolymer composition directly from i.r. measurements.

All the copolymer samples exhibit a content of ABP units higher than that of the corresponding initial comonomer mixtures (Figure 3 and Table 1). Accordingly the reactivity ratios, calculated by least-squares evaluation of the Kelen-Tüdös parameters<sup>15</sup> (Figure 4) are  $r_{ABP} = 1.32$  and  $r_{MtA} = 0.68$ . The above values indicate that the ABP radical slightly favours its own monomer rather than MtA, the opposite occurring for the MtA radical. However, as the value of the product of reactivity ratios is very close to 1 ( $r_{ABP}r_{MtA} = 0.9$ ), the co-units are inserted into the copolymers in a substantially random manner<sup>16</sup>.

The mean sequence lengths of both co-units ( $\bar{l}_{ABP}$  and  $\bar{l}_{MtA}$ ) were evaluated according to Mayo and Walling<sup>17</sup> (Table 1). The molar fractions (%) of ABP and MtA units ( $X_{ABP(n)}$  and  $X_{MtA(n)}$ ) inserted in sequence lengths of *n* units deriving from ABP and MtA, respectively, were also calculated<sup>18</sup> (Table 2).

In the region between 400 and 240 nm the u.v. spectrum of the low molecular weight model compound IBP in chloroform solution exhibits two absorption bands centred at 336 and 258 nm related to the  $n \rightarrow \pi^*$  ( $\epsilon = 208$ )

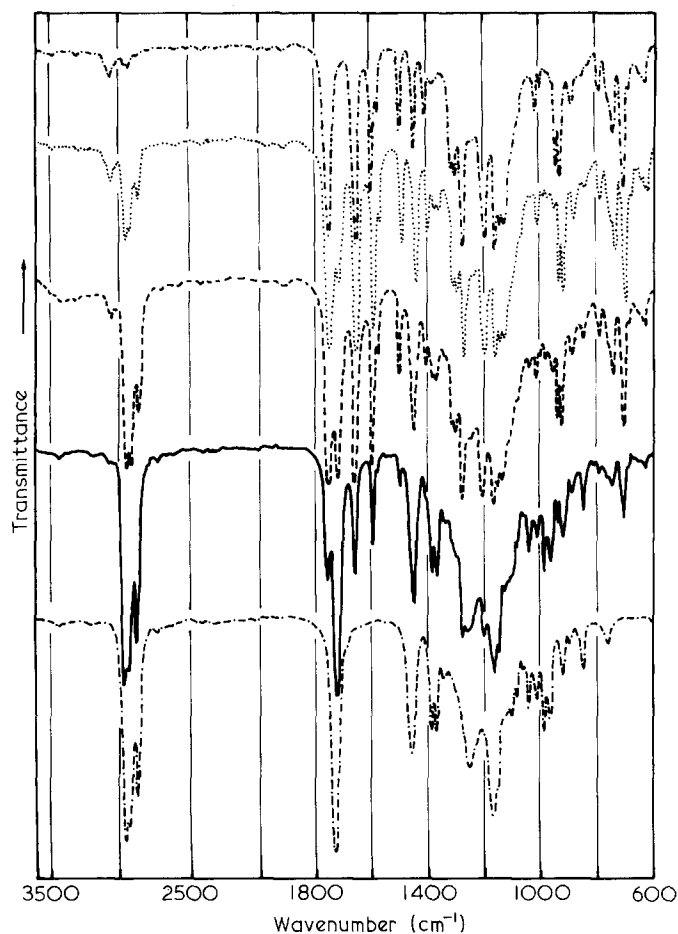


Figure 1 Typical i.r. spectra of the radically prepared copolymers: —, poly(ABP); ·····, poly(MtA-co-ABP) with 80.0 mol% ABP units; - - - - , poly(MtA-co-ABP) with 57.6 mol% ABP units; ———, poly(MtA-co-ABP) with 13.9 mol% ABP units; - - - - , poly(MtA)

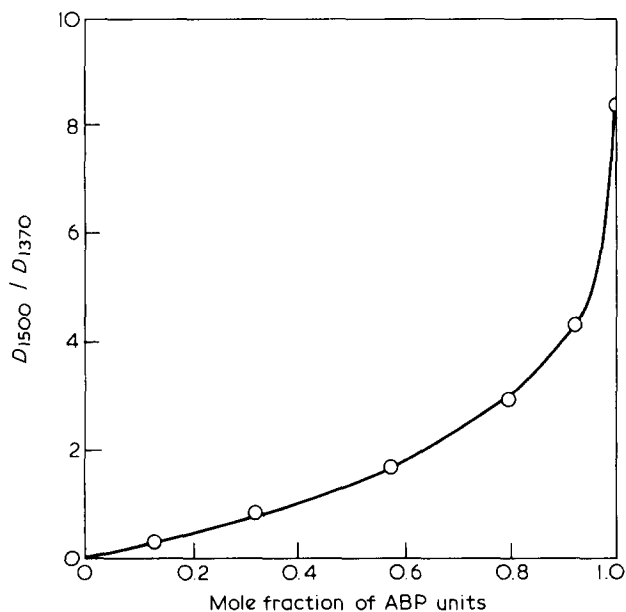


Figure 2 Ratio between i.r. optical densities at 1500 and 1370 cm<sup>-1</sup> ( $D_{1500}/D_{1370}$ ) vs. copolymer composition

and to a  $\pi \rightarrow \pi^*$  ( $\epsilon = 20\,400$ ) electronic transitions of benzophenone<sup>19</sup>, respectively (Figure 5 and Table 3). In the case of poly(4-hydroxybenzophenone acrylate) (poly(ABP)), the former band shows a maximum at 337 nm with  $\epsilon = 168$ , whereas the second one is centred at

256.5 nm with  $\epsilon = 17\,400$  per ABP unit (Figure 5 and Table 3). The molar extinction coefficient of poly(MtA-co-ABP)s for the band connected with the  $n \rightarrow \pi^*$  electronic transition changes between 178 and 276, depending on the content of ABP units, but without any regular trend. At the same time a shift of the absorption maximum to lower wavelength with increasing molar extinction coefficient is observed (Figure 5 and Table 3).

Even if u.v. measurements were performed on freshly prepared polymer solutions and the polymeric products handled as far as possible in the dark, this behaviour could

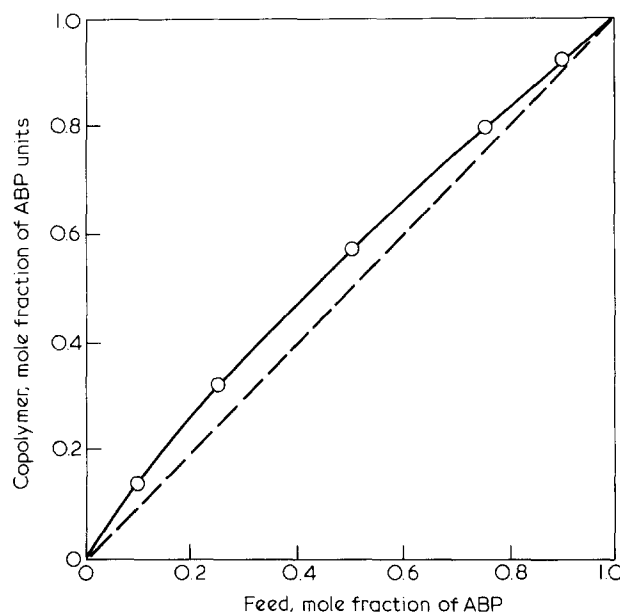


Figure 3 Copolymerization diagram for (-)-menthyl acrylate(MtA)/4-hydroxybenzophenone acrylate (ABP) system

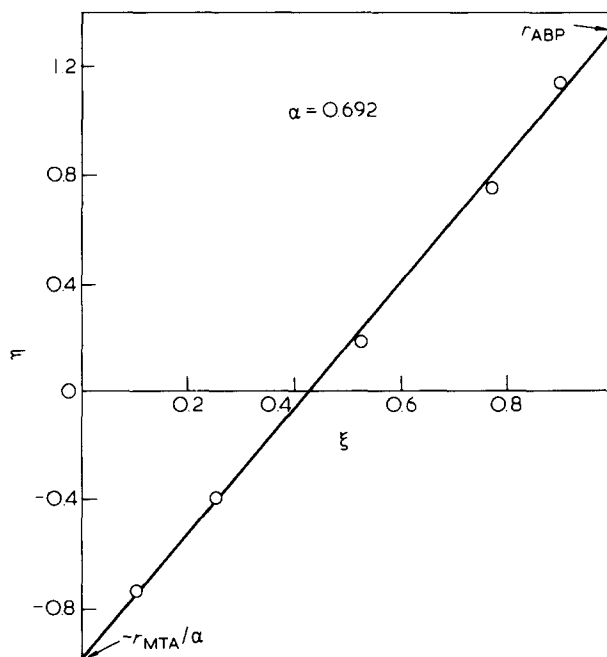


Figure 4 Kelen-Tüdös plot of the (-)-menthyl acrylate(MtA)/4-hydroxybenzophenone acrylate (ABP) system:

$$\eta = \left( r_{ABP} + \frac{r_{MtA}}{\alpha} \right) \xi - \frac{r_{MtA}}{\alpha}$$

be explained on the basis of the high photoreactivity of side-chain benzophenone chromophores<sup>11</sup>. Accordingly in the 400–300 nm region u.v. spectra, performed on the same sample, show a progressive increase of the molar extinction coefficient on ageing the solution and the absorption maximum at the same time shifts towards higher energy becoming progressively a shoulder of the much more intense band connected with the  $\pi \rightarrow \pi^*$

electronic transition (Figure 6). This last band shows a monotonic decrease of the molar extinction coefficient of the maximum from 20 400 to 17 600 with increasing content of ABP units (Table 3). A slight bathochromic effect is also observed with decreasing content of ABP units (Table 3). This shift could be at least partially

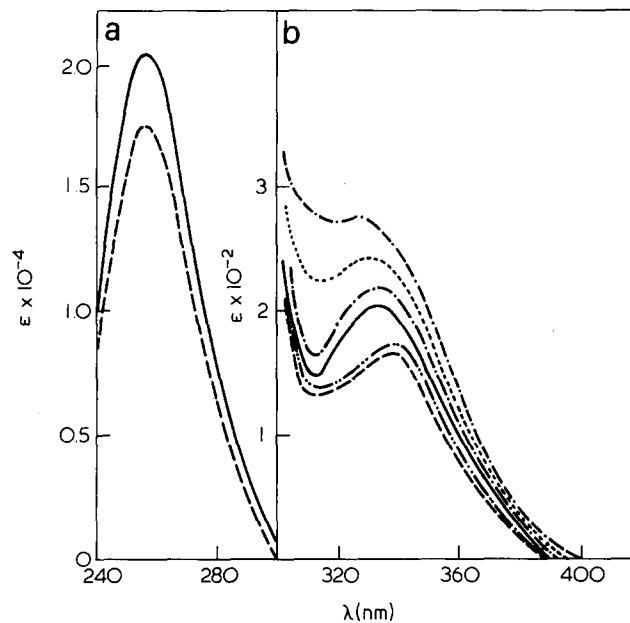


Figure 5 Typical u.v. spectra in chloroform solution of low and high molecular weight benzophenone derivatives. (a) 300–240 nm spectral region: —, 4-hydroxybenzophenone-2-methylpropanoate (IBP); ---, poly(ABP). (b) 400–300 nm spectral region: ---, poly(ABP); - · - · - ·, poly(MtA-co-ABP) with 92.5 mol% ABP units; —, IBP; · · · · ·, poly(MtA-co-ABP) with 57.6 mol% ABP units; - · - · - ·, poly(MtA-co-ABP) with 32.5 mol% ABP units; - · - · - ·, poly(MtA-co-ABP) with 13.9 mol% ABP units

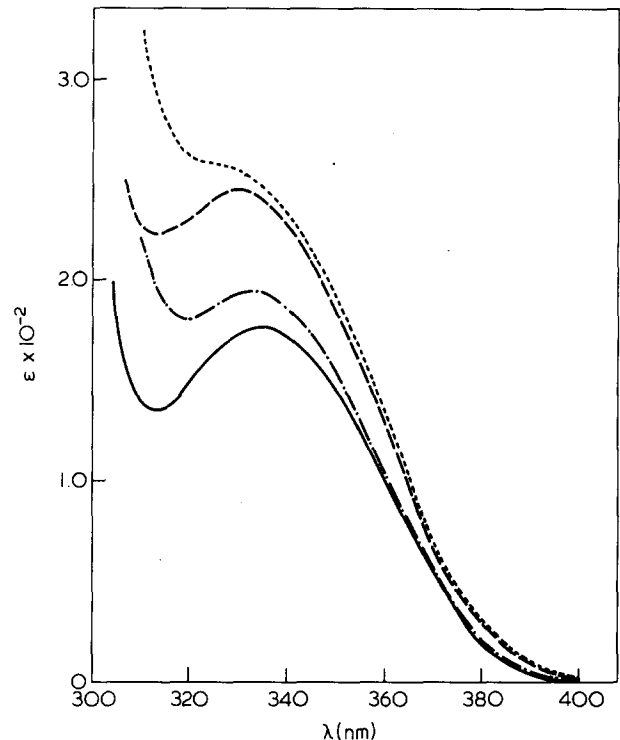


Figure 6 U.v. spectra in the 400–300 nm region of some copolymers in freshly prepared and aged chloroform solutions. Poly(MtA-co-ABP) with 57.6 mol% ABP units: freshly prepared (---) and 1 week aged (· · · · ·) solutions, respectively. Poly(MtA-co-ABP) with 80.0 mol% ABP units: freshly prepared (—) and 1 week aged (- · - · - ·) solutions, respectively

Table 2 Molar fraction (%) of ABP and MtA units in sequence lengths  $n$  ( $X_{ABP}(n)$  and  $X_{MtA}(n)$ )<sup>a</sup> for poly(MtA-co-ABP)s

Poly(MtA-co-ABP) ABP units (mol %)	$X_{ABP}(n)$						$X_{MtA}(n)$					
	$n = 1$	2	3	4	5	>5	$n = 1$	2	3	4	5	>5
92.5	0.6	1.1	1.6	2.0	2.2	92.5	86.2	12.3	1.3	0.1	0.01	0.09
80.0	3.9	6.2	7.5	8.0	8.1	66.3	67.1	24.2	6.6	1.6	0.3	0.2
57.6	18.0	20.8	17.9	13.7	9.8	19.8	36.1	28.8	17.2	9.2	4.6	4.1
32.5	48.0	29.5	13.5	5.5	2.1	1.4	10.9	14.6	14.7	13.1	11.0	35.7
13.9	75.8	19.6	3.8	0.6	0.1	0.1	2.0	3.5	4.4	5.1	5.4	79.6

<sup>a</sup> Evaluated according ref. 18

Table 3 U.v. absorption spectra in chloroform solution in the range 400–240 nm of low and high molecular weight benzophenone derivatives

Sample	ABP units (mol %)	$\lambda_1$ (nm)	$\epsilon_1$ (mol l <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_2$ (nm)	$\epsilon_2$ (mol l <sup>-1</sup> cm <sup>-1</sup> )
IBP	—	336	208	258	20 400
	13.9	335	220	258	20 400
	32.5	325	276	257.5	19 700
Poly(MtA-co-ABP)	57.6	330	246	257	19 000
	80.0	332	223	256.5	17 700
	92.5	337	178	256.5	17 600
Poly(ABP)	100.0	337	168	256.5	17 400

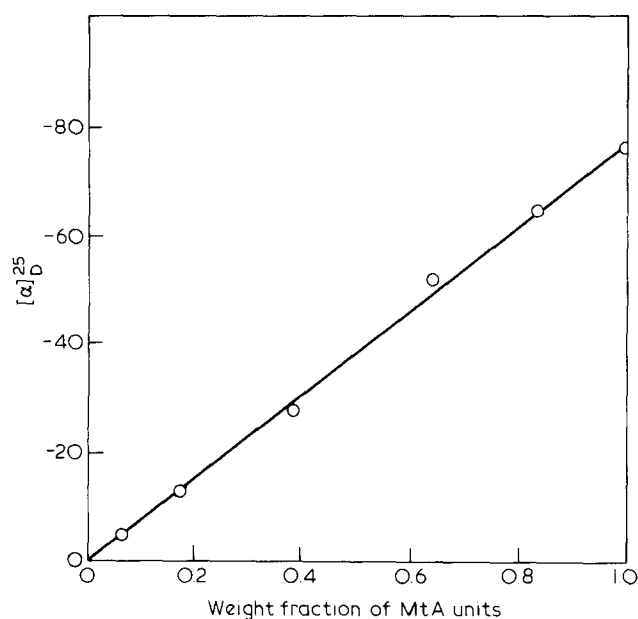


Figure 7 Specific rotatory power at sodium D line of poly(MtA-co-ABP)s vs. composition

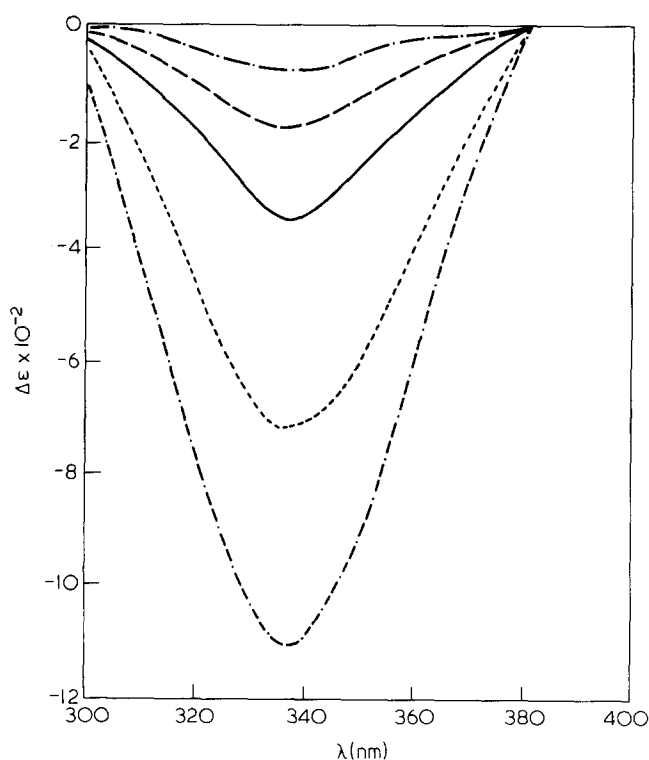


Figure 8 C.d. spectra in the 400–300 nm region of poly(MtA-co-ABP)s in chloroform solution: — — — —, 13.9 mol% ABP units; ······, 32.5 mol% ABP units; ————, 57.6 mol% ABP units; - · - · - ·, 80.0 mol% ABP units; - · - · - ·, 92.5 mol% ABP units

responsible for the particular behaviour of the  $n \rightarrow \pi^*$  electronic transition band. The observed hypochromism and bathochromic shift have already been reported for optically active copolymers of MtA with different vinyl aromatic comonomers such as styrene and *N*-vinylcarbazole<sup>5,14</sup> and have been attributed to electronic interactions between neighbouring chromophores<sup>20,21</sup>.

#### Chiroptical properties

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

depending linearly on composition (Figure 7), as in the case of radically prepared copolymers of MtA with styrene<sup>14</sup>, 1-vinylnaphthalene<sup>2</sup> and *trans*-4-hydroxystilbene acrylate<sup>7</sup>. However the investigation of c.d. spectra in chloroform solution shows a dichroic band of negative sign centred at 338 nm (Figure 8), corresponding to the u.v. absorption band related to the  $n \rightarrow \pi^*$  electronic transition of benzophenone chromophore. The molar differential dichroic absorption per ABP unit of the band increases in absolute value with decreasing content of ABP units, whereas no shift of the dichroic maximum is observed with varying copolymer composition.  $\Delta\epsilon_{338}$  of the copolymer samples increases regularly with increasing mean sequence length of the chiral co-units, ( $\bar{l}_{MtA}$ ) (Figure 9). The remarkable difference between the value of  $\Delta\epsilon_{338}$  of poly(MtA-co-ABP)s containing 13.9 and 32.5 mol% of ABP units, where  $\bar{l}_{ABP}$  is 1.15 and 1.44 respectively, seems to suggest that the induced optical activity is highest for isolated ABP units and that the dissymmetry effect is practically not transmitted through even short sequences of ABP units (substantially sequences of two ABP units). Accordingly  $\Delta\epsilon_{338}$  of the copolymers depends linearly on the molar fraction (%) of isolated ABP units ( $X_{ABP(1)}$ ), even if it is not exactly zero for  $X_{ABP(1)}=0$  (Figure 10 and Table 2). In

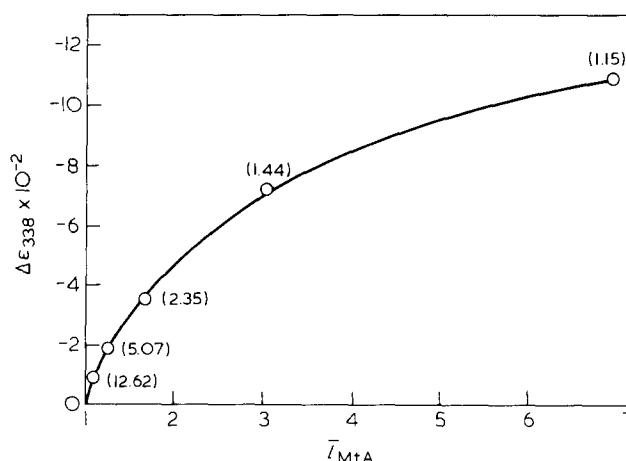


Figure 9 Differential molar dichroic absorption coefficient at 338 nm ( $\Delta\epsilon_{338}$ ) of poly(MtA-co-ABP)s in chloroform solution vs. mean sequence length of MtA units ( $\bar{l}_{MtA}$ ); mean sequence lengths of ABP units are reported in parentheses

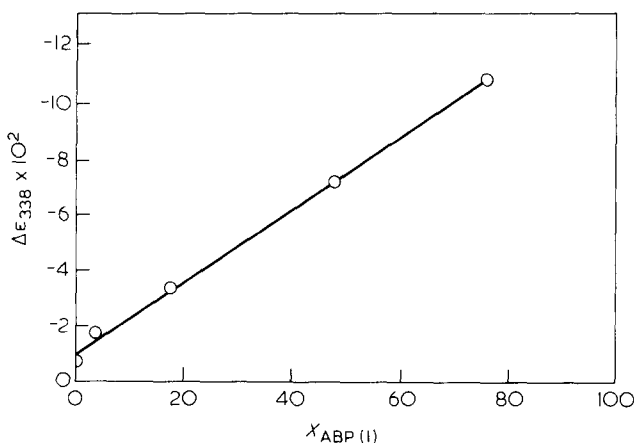


Figure 10 Differential molar dichroic absorption coefficient at 338 nm ( $\Delta\epsilon_{338}$ ) of poly(MtA-co-ABP)s in chloroform solution vs. molar fraction (%) of ABP units in sequence length of 1 ( $X_{ABP(1)}$ )

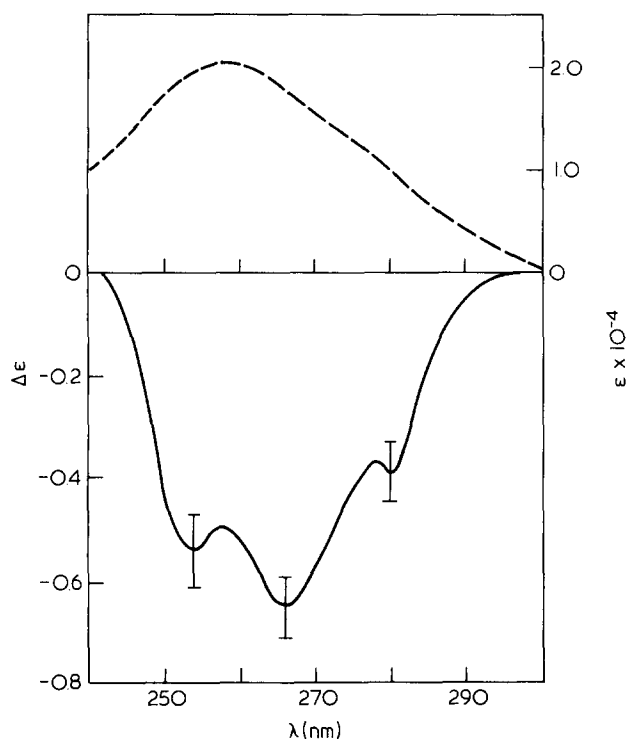


Figure 11 U.v. (---) and c.d. (—) spectra in the 300–240 nm region of poly(MtA-co-ABP) with 13.9 mol% ABP units in chloroform solution

contrast, in the analogous copolymers of MtA with 4-vinylpyridine (4VP)<sup>22</sup> the induced chirality is substantially the same for the isolated 4VP units as well as for sequences of two units from this non-chiral monomer. Such a difference can be attributed to the larger conformational mobility of benzophenone chromophores related to the rotational freedom of the ester group which links them to the main chain.

C.d. investigation of poly(MtA-co-ABP)s in chloroform solution in the 300–240 nm spectral region is rather difficult due to the unfavourable dissymmetry factor  $\Delta\epsilon/\epsilon$ . However, in the copolymers containing 32.5 mol% or less of ABP units, a structured dichroic band with negative sign and relative maxima at about 280, 266 and 254 nm is observed corresponding to the  $\pi \rightarrow \pi^*$  electronic transition of benzophenone chromophore (Figure 11). In the copolymers containing more than 32.5 mol% of ABP units, a negative dichroic band is also detectable, but no quantitative evaluation of ellipticity is possible due to the large noise/elongation ratio. However, the above results confirm that an induced prevailing chirality occurs in side-chain benzophenone chromophores due to the dissymmetric structure of the copolymer macromolecules.

## CONCLUSIONS

On the basis of the reported results the following concluding remarks can be drawn:

(i) The radically initiated copolymerization of 4-hydroxybenzophenone acrylate (ABP) with (–)menthyl acrylate (MtA) gives rise to the formation of substantially random copolymers where the side-chain benzophenone chromophores are chirally perturbed.

(ii) C.d. measurements combined with statistical distribution of co-unit sequences in the copolymers suggest that the induced preferential chirality ('induced optical activity') involves mainly the isolated ABP units. These results indicate that the dissymmetric perturbation of side-chain benzophenone chromophores cannot be transmitted along sequences of two or more ABP units, probably because of the rather high conformational mobility of the macromolecules. These data therefore seem to exclude the existence of even short sequences of ABP units disposed in an ordered conformation giving rise to c.d. bands by dipole–dipole electrostatic interactions between chromophoric side chains of different units<sup>8</sup>.

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