Optically active polymers containing side-chain *trans*-stilbene chromophores

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(*Received* 10 *September* 1981)

Optically active copolymers of (−)menthyl acrylate (MtA) with *trans*-4-hydroxystilbene acrylate (SA), with a wide composition range, have been prepared using AIBN as the radical initiator. Reactivity ratio values of the comonomers, evaluated by the Kelen–Tüdös method, have allowed us to show that SA exhibits a higher reactivity compared with MtA. Mean sequence lengths of both co-units and their distribution in the macromolecules have been evaluated by statistical calculations. Chiroptical properties of side-chain stilbene chromophores have been investigated by circular dichroism measurements and related to the composition and distribution of monomeric units.

Keywords Optically active copolymers; (-)menthyl acrylate; *trans*-4-hydroxystilbene acrylate; *trans*-4-hydroxystilbene 2-methylpropanoate; circular dichroism; conformational properties

INTRODUCTION

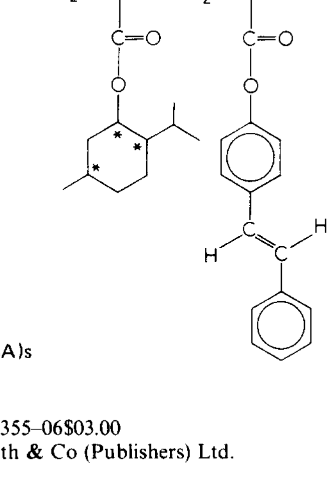
The physical and chemical behaviour of photochromic probes in macromolecular systems have been reported as being related to the free volume and microviscosity of the polymer matrix both in solution and in bulk[1].

In this context the photochemical and thermal *trans* → *cis* isomerization of side-chain double bonds has been largely investigated and the isomerization rate has been shown to depend on the structure and the physical state of the macromolecular system[2-5].

Moreover, in the case of polypeptides containing side chain azobenzene moieties, the *trans* → *cis* photoisomerization can induce conformational transitions as confirmed by circular dichroism (c.d.) measurements[6,7].

However in copolymers of optically active monomers with different vinyl aromatic comonomers, the electronic transitions of the aromatic chromophores can become optically active, the chirality and the magnitude of the induced dissymmetry being dependent on the primary and secondary structure of the macromolecules[8-15].

The same is expected, in principle, for copolymers of (−)menthyl acrylate (MtA) with *trans*-4-hydroxystilbene acrylate (SA) [poly(MtA-*co*-SA)s].



poly(MtA–*co*–SA)s

In this connection the introduction of photochromic groups into optically active synthetic macromolecular chains could be a very sensitive tool in the investigation of the secondary structure in polymer solutions and in the obtaining of information about the use of polymeric systems in energy photo-conversion.

Here synthesis by radical initiation, the structural characterization and chiroptical properties of poly(MtA-*co*-SA)s are reported, and investigation of their fluorescence and photochemical behaviour will be the subject of a future paper.

EXPERIMENTAL

Monomers

(−)*Menthyl acrylate* (*MtA*). MtA having $[\alpha]_D^{25} = -89.0$ (neat) was prepared and purified as previously reported[9].

trans-*4-Hydroxystilbene acrylate* (*SA*). SA was synthesized by reacting commercial (Fluka) *trans*-4-hydroxystilbene (HS) with acryloyl chloride in the presence of triethylamine as follows: to a mixture of 20.0 g (101.9 mmoles) HS, 150 ml anhydrous diethylether and 21.7 g (215.0 mmoles) Et_3N, 13.8 g (153.0 mmoles) of acryloyl chloride were added dropwise with stirring at room temperature. After 4 h stirring the reaction mixture was extracted with chloroform and the extracts, washed with dilute HCl, $NaHCO_3$ aqueous solution and water in that order, were dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was eluted with chloroform over silica gel (70–230 mesh) and then recrystallized from n-hexane to give 18.2 g (71.4% yield) pure SA as white lamellae having m.pt. = 123°–124°C. *Figure 1A* shows the i.r. spectrum of SA in a pressed mixture with KBr. ^1H n.m.r. ($CDCl_3$): $\delta = 7.7$–7.0 (*m*, stilbene protons, 11H) and 6.8–5.8 ppm (*m*, acrylic protons, 3H).

trans-4-Hydroxystilbene 2-methylpropanoate (*SP*).

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SP was synthesized from HS and 2-methylpropanoyl chloride in the presence of triethylamine by the same procedure as reported for the preparation of SA. After purification by elution over silica gel and subsequent recrystallization from n-hexane, pure SP was obtained in 75.0% yield as white crystals having m.pt. 134°–136°C. *Figure 1B* shows the i.r. spectrum of SP in a pressed mixture with KBr. ^{1}H n.m.r. ($CDCl_3$): $\delta = 7.7$–7.0 (*m*, stilbene protons, 11H); 2.8 (*m*, $C\underline{H}(CH_3)_2$, 1H) and 1.3 ppm (*d*, $CH(C\underline{H}_3)_2$, 6H).

2,2′-Azobisisobutyronitrile (*AIBN*). The commercial product from 'Fluka' was recrystallized from ethanol.

Polymerization experiments

Free radical copolymerization experiments were performed in benzene at 60°C in vials sealed under high vacuum, using AIBN as initiator. After a suitable period of time the polymerization was interrupted by pouring the reaction mixture into a large excess of methanol. The coagulated polymer was purified by repeated precipitation in methanol. Finally the polymeric product was filtered and dried under vacuum at room temperature.

Physicochemical measurements

60 MHz ^{1}H n.m.r. spectra were recorded in $CDCl_3$ solution with a Varian T-60 spectrometer using TMS as the internal standard.

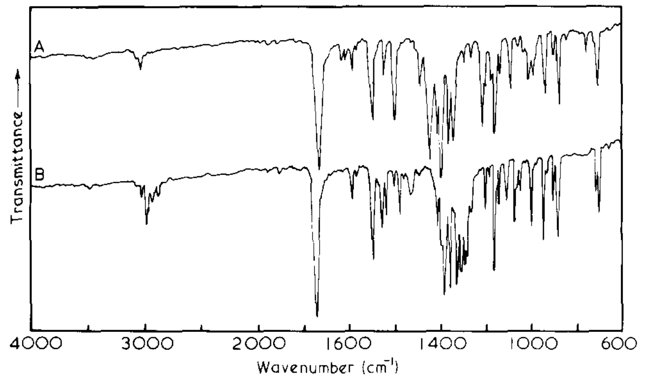

Figure 1 I.r. spectra of: (A) *trans*-4-hydroxystilbene acrylate (SA); (B) *trans*-4-hydroxystilbene-2-methylpropanoate (SP)

I.r. examinations of low and high molecular weight samples were carried out on a Perkin-Elmer 283 B spectrophotometer on a pressed mixture with KBr or on cast film respectively.

U.v. spectra were performed in $CHCl_3$ solution on a Cary 14 spectrophotometer in the range 400–240 nm.

C.d. spectra in the range 400–240 nm were performed in $CHCl_3$ solution with a Jobin-Yvon Dichrograph III.

Optical rotatory measurements were performed on polymer solution in $CHCl_3$ at 25°C with a Perkin-Elmer 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^{-1} heating rate.

Average molecular weights of polymer samples were determined by g.p.c. measurements on a Perkin-Elmer Model 2/2 HPLC, equipped with two Shodex columns A 802/S and A 803/S connected in series, and with a variable wavelength Perkin-Elmer LC75 u.v. detector. Polystyrene standards were used for calibration.

RESULTS AND DISCUSSION

Synthesis and characterization

The radically initiated copolymerization experiments were carried out in benzene at 60°C using AIBN as initiator. Some copolymerization runs were performed at high conversion to have at our disposal large amounts of copolymer samples. An analogous set of low conversion (<12%) runs were carried out in order to determine the reactivity ratios of the comonomers involved and to obtain copolymers having substantially homogeneous composition and distribution of monomeric units. Whenever possible spectroscopic investigation was performed on these latter samples. Copolymerization data and some properties of poly(MtA-*co*-SA)s are reported in *Table 1*. The copolymer composition was estimated on the basis of ^{1}H n.m.r. analysis by comparing the area of the signals due to the protons of stilbene moieties with that relevant to the saturated aliphatic protons.

I.r. spectra of poly(MtA-*co*-SA)s show the same bands as the corresponding homopolymer mixtures, indicating that both co-units are present in the macromolecules. Some typical i.r. spectra are reported in *Figure 2*.

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

Feed (mole fraction of SA in %)	Duration (h)	Conversion[b] (%)	Copolymer[c] (mole fraction of units from SA in %)	$[\alpha]_D^{25}$[d]	$\bar{M}_w$[e]	$\bar{M}_w/\bar{M}_n$
100.0	29.0	26.6	100.0	0.0	65000	2.8
75.0	4.0	4.3	87.0	−9.9	31000	1.7
50.0	2.5	2.5	68.6	−25.1	39000	1.9
50.0	20.0	47.4	62.3	−29.3	84000	2.2
25.0	4.0	12.2	38.9	−45.8	55000	1.7
25.0	20.0	51.7	26.4	−55.3	79000	2.3
15.0	5.0	1.0	25.0	−55.4	71000	1.8
15.0	7.0	31.8	21.8	−63.0	84000	1.9
7.5	5.0	6.5	12.6	−69.0	96000	1.6
0.0	24.0	91.4	0.0	−77.2	n.d.	–

[a] In benzene (30 ml) at 60°C using AIBN (1% w/w) as initiator; starting comonomer mixture: 3 g

[b] Calculated as (weight of polymer/total weight of starting comonomers) x 100

[c] Evaluated by ^{1}H n.m.r. analysis

[d] In chloroform solution at 25°C, $l = 1$ dm

[e] Determined by g.p.c. measurements

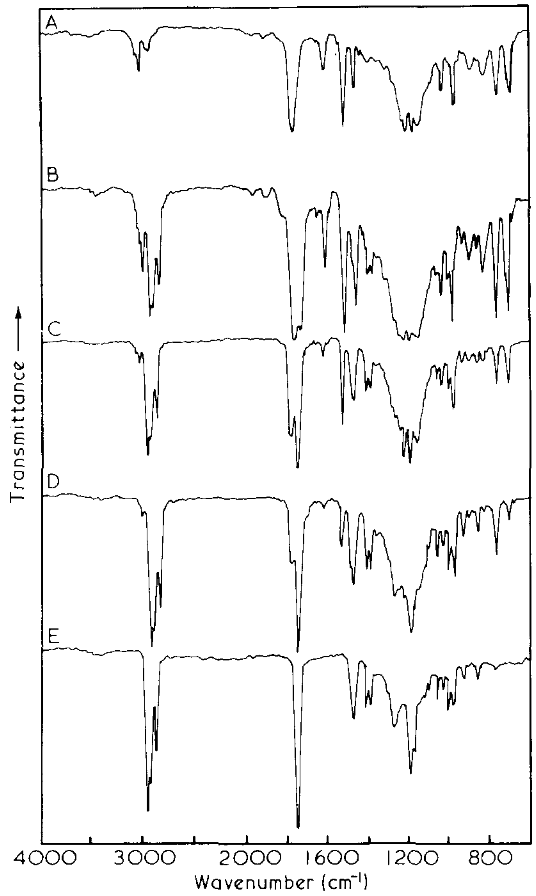

Figure 2 I.r. spectra of: (A) poly(SA); (B), (C), (D) poly(MtA-*co*-SA)s containing 68.6, 38.9 and 12.6 mol% of units from SA, respectively; (E) poly(MtA)

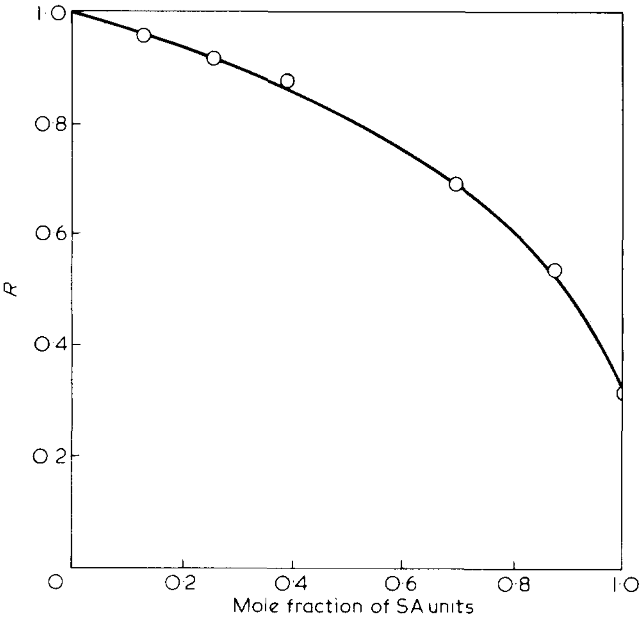

Figure 3 Plot of the ratio of i.r. absorbances at 2950 and 3020 cm^{-1}: $R = [D_{2950}/(D_{2950} + D_{3020})]$ of poly(MtA-*co*-SA)s *versus* composition

The optical densities of i.r. bands at 2950 and 3020 cm^{-1}, due to the stretching vibrations of aliphatic and aromatic C–H bonds, respectively, allow us to evaluate the ratio $R=[D_{2950}/(D_{2950}+D_{3020})]$. A plot of R *versus* composition of poly(MtA-*co*-SA)s (*Figure 3*) gives a smooth monotonic curve which can be used to evaluate copolymer composition directly from i.r. measurements.

The copolymerization diagram (*Figure 4*) shows that all the copolymer samples have a higher content of units from SA than the corresponding comonomer mixtures, according to a larger reactivity of SA with respect to MtA.

The reactivity ratios were calculated by the least-squares evaluation of the Kelen–Tüdös parameters[16] (*Figure 5*). The values obtained ($r_{SA}=2.38$ and $r_{MtA}=0.59$) indicate that the SA radical greatly favours its own monomer rather than MtA, the opposite occurring for the MtA radical. The product of the reactivity ratios is moderately larger than unity ($r_{SA} \cdot r_{MtA}=1.4$).

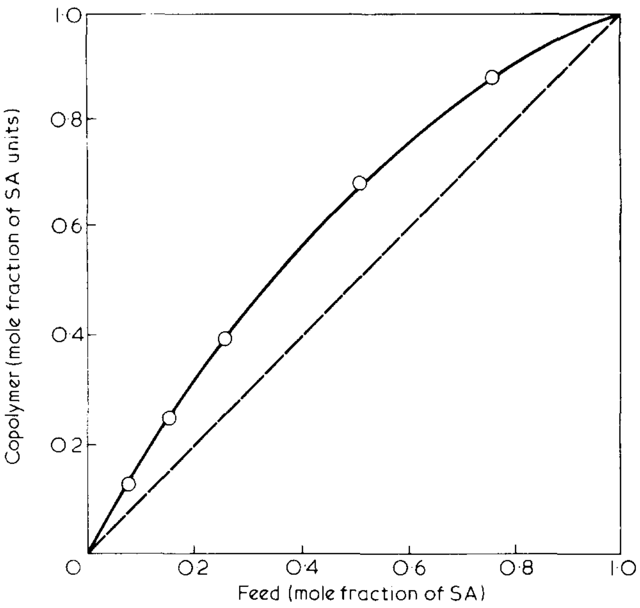

Figure 4 Copolymerization diagram of the system (–)menthyl acrylate (MtA)/*trans*-4-hydroxystilbene acrylate(SA)

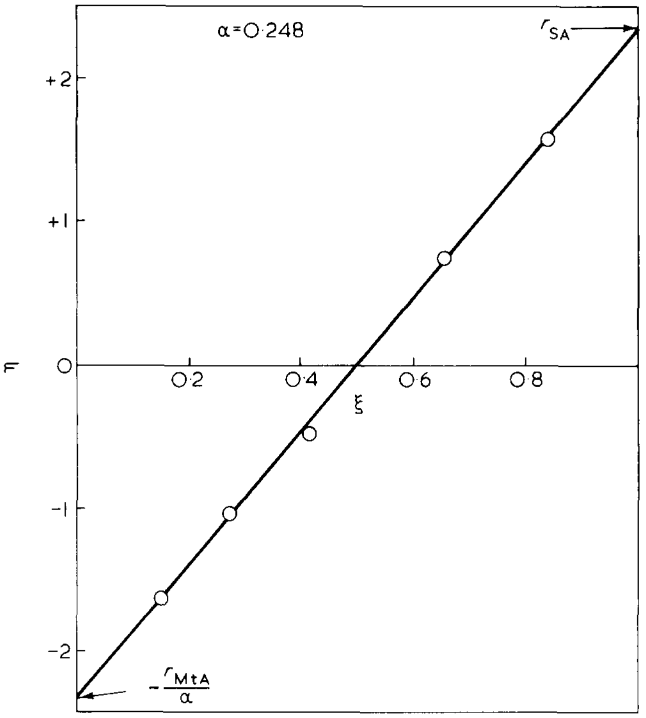

Figure 5 Kelen–Tüdös plot of the system (–)menthyl acrylate(MtA)/*trans*-4-hydroxystilbene acrylate(SA): $\eta = (r_{SA} + r_{MtA}/\alpha)\xi - r_{MtA}/\alpha$

Table 2 Mean sequence lengths[a] ($\bar{l}_{SA}$ and $\bar{l}_{MtA}$) and molar fractions (%)[a] [$X_{SA(n)}$ and $X_{MtA(n)}$] of units from SA and MtA in sequence lengths of n units, for poly(MtA-*co*-SA)s

Mole fraction of units from SA (%)	$\bar{l}_{SA}$	$\bar{l}_{MtA}$	$X_{SA(n)}$ $n=1$	2	3	4	5	>5	$X_{MtA(n)}$ $n=1$	2	3	4	5	>5
87.0	8.1	1.2	1.5	2.6	3.5	4.1	4.5	83.8	70.0	22.8	5.6	1.2	0.3	0.1
68.6	3.4	1.6	8.7	12.3	13.0	12.2	10.7	43.1	39.8	29.4	16.3	8.0	3.7	2.8
38.9	1.8	2.7	30.6	27.3	18.3	10.9	6.1	6.8	13.5	17.1	16.2	13.7	10.8	28.7
25.0	1.4	4.3	49.8	29.3	12.9	5.1	1.9	1.0	5.3	8.2	9.4	9.7	9.3	58.1
12.6	1.2	8.2	70.4	22.7	5.5	1.2	0.2	0.0	1.5	2.6	3.4	3.9	4.4	84.2

[a] Calculated according to ref. 18

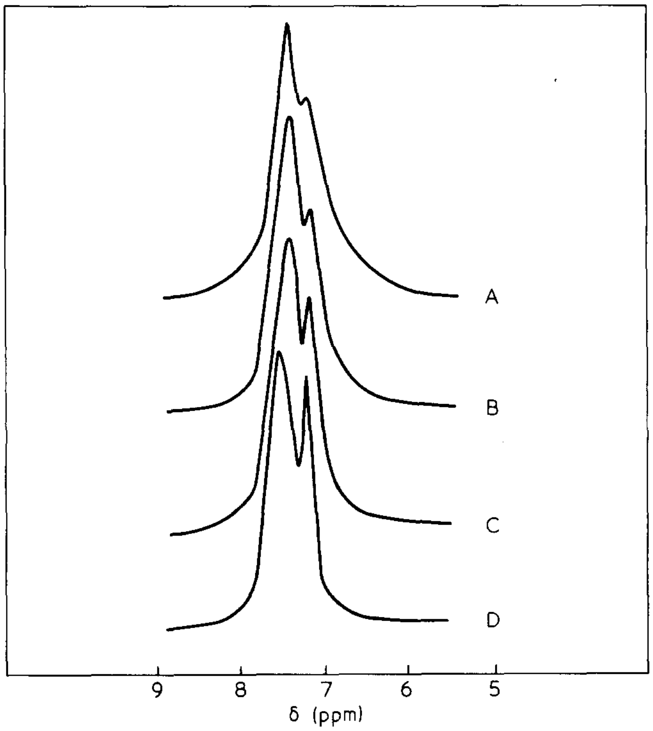

Figure 6 ^{1}H n.m.r. signals of stilbene moieties for: (A) poly(SA); (B), (C), (D) poly(MtA-*co*-SA)s containing 68.6, 38.9 and 12.6 mol% of units from SA, respectively

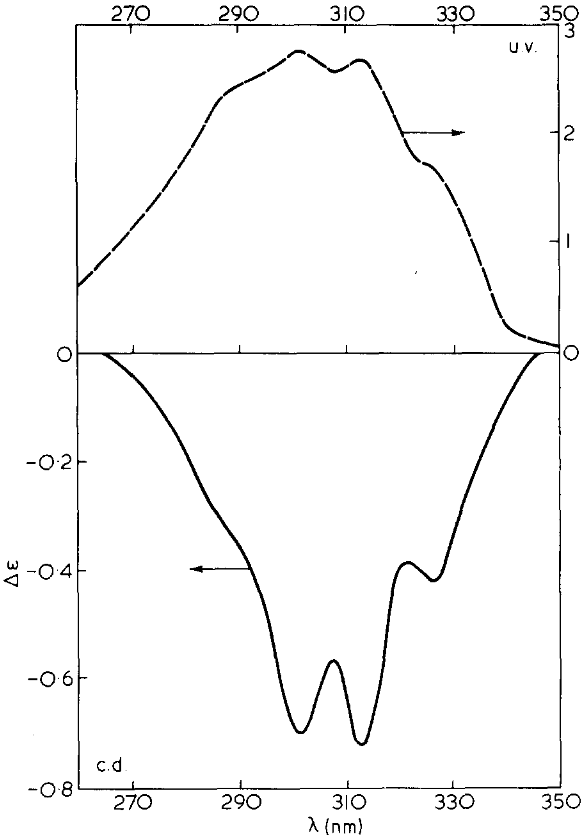

Figure 7 U.v. (– – – –) and c.d. (———) absorption spectra of poly(MtA-*co*-SA) containing 12.6 mol% of units from SA

The average sequence length of both co-units ($\bar{l}_{SA}$ and $\bar{l}_{MtA}$), evaluated according to Mayo and Walling[17] are reported in *Table 2*.

Molar fractions (%) of SA and MtA units ($X_{SA_{(n)}}$ and $X_{MtA_{(n)}}$) inserted in sequences of n units deriving from SA and MtA respectively were also evaluated[18]. These data give a better insight into the distribution of the two monomeric units in the copolymer macromolecules. Selected values of $X_{SA_{(n)}}$ and $X_{MtA_{(n)}}$ varying n in the range 1–5 are reported in *Table 2*.

^{1}H n.m.r. spectra in the region of stilbyl protons show two overlapping signals at 7.5 and 7.2 ppm which are not substantially affected by the composition of the copolymer sample, contrary to what was observed in several copolymers containing side-chain aromatic chromophores[9,19]. However a more detailed analysis of the spectra indicates that a line broadening occurs with increasing SA content (*Figure 6*). Such broadening can be related to the interactions between stilbene chromophores in sequences of SA units, the mean length of which increases with increasing SA content (*Table 2*).

In the region between 350 and 250 nm, the u.v. spectra of poly(MtA-*co*-SA)s in chloroform solution exhibit a structured absorption band having a maximum at about 300 nm (*Figure 7*) corresponding to the $\pi \rightarrow \pi^*$ ($^1B \leftarrow {}^1A$) electronic transition of the stilbene chromophore[20], analogous to that observed for the low molecular weight structural model *trans*-4-hydroxystilbene-2-methylpropanoate (SP). Decreasing the content of SA units from 100 to 12.6%, the molar extinction coefficient at 300 nm (ε_{max}) increases from 17800 to 28500 l mol^{-1} cm^{-1} (*Figure 8*), this last value being very close to that observed for SP ($\varepsilon_{max} = 28700$). An analogous behaviour has been reported to occur in polymers containing side-chain aromatic chromophores[9,13] and has been attributed to the occurrence of chromophore–chromophore interactions[21,22] which lower the molar extinction coefficient of SA units in sequences with respect to isolated units.

Chiroptical properties

All the copolymer samples exhibit a negative optical rotation at sodium D line as observed for poly(MtA). A plot of specific optical rotation at 589 nm *versus* content of MtA units (*Figure 9*) shows a linear trend, thus excluding any contribution of stilbene moieties to the optical rotatory power at 589 nm. An analogous behaviour was observed in several optically active copolymers containing aromatic side chains[9,10,15].

As in previous cases this finding does not exclude an asymmetric perturbation of stilbene moieties; indeed c.d. spectra show in all samples the presence of a negative structured dichroic band with relative maxima at 327, 313 and 301 nm, in close agreement with u.v. absorption spectra (*Figure 7*). C.d. data relevant to poly(MtA-*co*-SA)s obtained at low conversion and having content of units from SA between 12.6 and 87.0 mol % are reported in *Table 3*. The molar dichroic absorption coefficients referred to one stilbene group ($\Delta\varepsilon$) are of the same order of magnitude as those reported for other copolymers of MtA with several comonomers containing different aromatic side-chain chromophores[9,10,12,15].

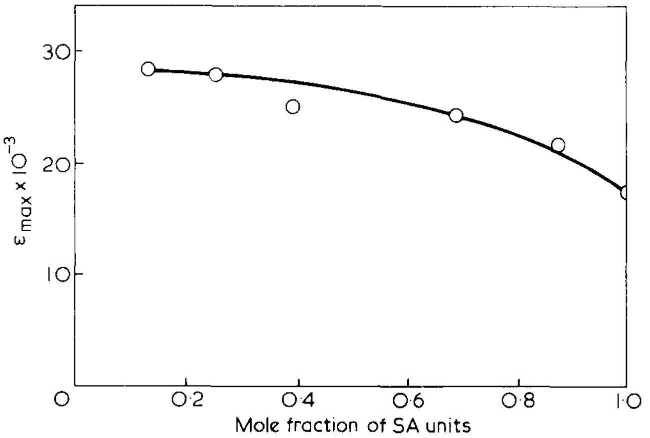

Figure 8 Molar extinction coefficient at 300 nm (ε_{max}) of poly(MtA-*co*-SA)s *versus* composition

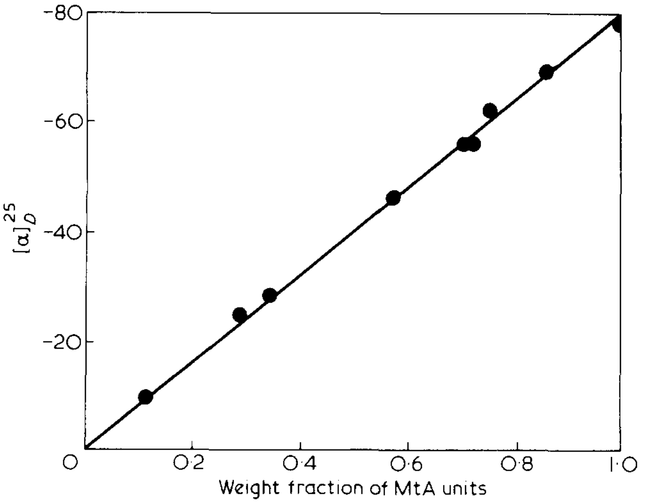

Figure 9 Specific optical rotation at sodium D-line of poly(MtA-*co*-SA)s *versus* composition

Within the limit of experimental error, the observed $\Delta\varepsilon_{max}$ at 301 nm decreases with decreasing content of chiral co-units, indicating that the highest asymmetric perturbation is attained when substantially isolated SA units are flanked by relatively long blocks of MtA co-units. However the still rather high value of $\Delta\varepsilon_{max}$ for the copolymer containing a very large amount of SA units in long sequences [$X_{SA_{(n>5)}} = 88.3\%$ (*Table 2*)] seems to suggest that the induced dissymmetry can be also partially transmitted to chromophores not adjacent to chiral co-units. This effect can be favoured by the local conformational regidity, as evidenced by ^{1}H n.m.r. spectra, even if a contribution to c.d. may also arise from dipole–dipole coupling between adjacent aromatic chromophores disposed in a mutual chiral arrangement[8].

CONCLUSIONS

The results obtained indicate that the radically initiated copolymerization of (−)menthyl acrylate (MtA) with *trans*-4-hydroxystilbene acrylate (SA) gives rise to the formation of copolymers with chirally perturbed side-chain stilbene chromophores.

Reactivity ratio values show that substantially random copolymers are obtained, even if SA has some tendency to a block distribution.

C.d. measurements suggest that isolated SA units inserted between blocks of chiral co-units exhibit the highest induced dissymmetry. However the asymmetric perturbation on side-chain stilbene moieties can also be transmitted to chromophores not adjacent to chiral co-units, probably due to a local conformational rigidity of the macromolecules in solution. However a contribution to the asymmetric induction by dipole–dipole interactions of stilbene chromophores cannot be excluded.

ACKNOWLEDGEMENT

The authors wish to express their grateful appreciation to Dr C. Bertucci for his valuable experimental support on the c.d. measurements.

Table 3 Circular dichroism between 350 and 250 nm of side-chain *trans*-stilbene chromophores in poly(MtA-*co*-SA)s[a]

Mole fraction of units from SA (%)	λ_{max} (nm)	$\Delta\varepsilon^b$	λ_{max} (nm)	$\Delta\varepsilon^b$	λ_{max} (nm)	$\Delta\varepsilon^b$
12.6	327	−0.40	313	−0.70	301	−0.70
25.0	327	−0.35	313	−0.65	301	−0.60
38.9	327	−0.30	313	−0.60	301	−0.55
68.6	327	−0.20	313	−0.35	301	−0.30
87.0	327	−0.10	313	−0.30	301	−0.25

[a] Copolymers obtained from low conversion experiments

[b] Expressed in $l\ mol^{-1}\ cm^{-1}$ and referred to one SA monomeric unit

REFERENCES

1 Williams, J. L. R. and Daly, R. C. *Progr. Polym. Sci.* 1977, **5**, 61

2 Eisenbach, C. D. *Makromol Chem.* 1978, **179**, 2439

3 Eisenbach, C. D. *Makromol. Chem.* 1979, **180**, 565

4 Mikes, F., Strop, P. and Kàlal, J. *Makromol. Chem.* 1974, **175**, 2375

5 Bednàr, B., Kàlal, J., Mikes, F. and Strop, P. *Proc. IUPAC Symposium on Macromolecules*, Dublin, 1977, vol. 2, p. 515

6 Ueno, A., Takahashi, K., Anzai, J. and Osa, T. *Makromol. Chem. Rapid. Comm.* 1981, **182**, 693

7 Pieroni, O., Houben, J. L., Fissi, A., Costantino, P. and Ciardelli, F. *Preprints IUPAC Symposium on Macromolecules*, Florence, 1980, vol. 2, p. 515

8 Ciardelli, F., Chiellini, E., Carlini, C., Pieroni, O., Salvadori, P. and Menicagli, R. *J. Polym. Sci., Polym. Symp.* 1978, **62**, 143

9 Majumdar, R. N. and Carlini, C. *Makromol. Chem.* 1980, **181**, 201

10 Majumdar, R. N., Carlini, C., Rosato, N. and Houben, J. L. *Polymer* 1980, **21**, 941

11 Carlini, C., Cheng, C. H., Ciardelli, F., Majumdar, R. N. and Pearce, E. M. *Preprints IUPAC Symposium on Macromolecules*, Florence, 1980, vol. 2, p. 455

12 Chiellini, E., Solaro, R., Ciardelli, F., Galli, G. and Ledwith, A. *Polym. Bull.* 1980, **2**, 577

13 Chiellini, E., Solaro, R., Galli, G. and Ledwith, A. *Macromolecules* 1980, **13**, 1654

14 Chiellini, E., Solaro, R. and Ciardelli, F. *Makromol. Chem.* 1982, **183**, 103

15 Majumdar, R. N., Carlini, C. and Bertucci, C. submitted to *Makromol. Chem.* in press

16 Kelen, T. and Tüdös, F. *J. Macromol. Sci. Chem.* 1975, **9**, 1

17 Mayo, F. R. and Walling, C. *Chem. Rev.* 1950, 200

18 Chiellini, E., Solaro, R., Colella, O. and Ledwith, A. *Eur. Polym. J.* 1978, **14**, 489

19 Chiellini, E., Solaro, R., Ledwith, A. and Galli, G. *Eur. Polym. J.* 1980, **16**, 875

20 Jaffè, H. H. and Orchin, M. in 'Theory and Application of Ultraviolet Spectroscopy', Wiley, New York, 1962, p. 276

21 Tinoco, I. Jr. *J. Am. Chem. Soc.* 1960, **82**, 4785

22 Okamoto, K., Itaya, A. and Kusabayashi, S. *Chem. Lett.* 1974, 1167