Photochemistry and photophysics of copolymers of (−)menthyl acrylate with 4-hydroxystilbene acrylate

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Copolymers of *trans*-4-hydroxystilbene with (−)menthyl acrylate exhibit upon irradiation *trans*→*cis* isomerization of the side-chain stilbene chromophores analogously to *trans*-4-hydroxystilbene-2-methylpropanoate, chosen as low molecular weight model compound. U.v. measurements on polymer samples indicate a deviation from first-order kinetics. In the fluorescence spectra of all-*trans* polymer samples both excimer and monomer emissions are observed. On irradiation the excimeric component is quenched much faster than the monomeric one. Fluorescence polarization experiments indicate a higher conformational rigidity of the stilbene chromophore when inserted in polymeric systems. Comparison of chiroptical properties of both unirradiated and irradiated copolymers suggests that on irradiation a local conformational rearrangement of macromolecules takes place.

Keywords Photochemistry; photophysics; copolymers; menthyl acrylate; 4-hydroxystilbene acrylate; isomerization; chromophores

INTRODUCTION

Polymers containing photoreactive groups are particularly valuable for investigating induced conformational changes[1-3] and for possible practical applications in high-speed compact memory devices[4], in photoconductors[5], and in solar energy conversion[6]. In this respect polymers containing double bonds capable of *trans–cis* photoisomerization appear to be very attractive owing to chemical[7] and/or photochemical reversibility[8,9] of the isomerization process.

The greatest interest devoted to polymeric materials as compared with their low molecular weight analogues arises from the possibility of designing systems which combine the mechanical properties of macromolecules with possible cooperative effects between neighbouring reactive groups.

The use of optically active copolymers containing photoreactive side chains can in principle enhance cooperative effects due to restricted conformational freedom. Moreover the investigation of chiroptical properties should help in detecting primary and secondary structure modifications on irradiation[10].

Previously we have reported the synthesis and characterization of a series of copolymers of (−)menthyl acrylate (MtA) with *trans*-4-hydroxystilbene acrylate (SA), poly(MtA-*co*-SA)[11]. In the present paper we wish to report the results obtained in the investigation of their u.v. absorption and fluorescence emission spectra and their behaviour upon irradiation in the lowest energy $\pi \rightarrow \pi^*$ stilbene absorption band[12].

EXPERIMENTAL

Polymeric samples were prepared and purified as previously reported[11]. In *Table 1* data relevant to polymer composition and distribution of monomeric units are reported.

Trans-4-hydroxystilbene-2-methylpropanoate (SP), m.p. 134°–136°C, was prepared from commercial *trans*-4-hydroxystilbene and 2-methylpropanoyl chloride as previously reported[11].

U.v. spectra in the range 400–240 nm were performed at 25°C in $CHCl_3$ solution by a Cary 14 or Cary 219 spectrophotometer. Concentrations in the range $(3–5)\times 10^{-5}$ mol l^{-1} of stilbene chromophores and cell path length of 1 cm were used. The molar extinction coefficient (ε) in the polymer samples is referred to one SA monomeric unit and is expressed as l mol^{-1} cm^{-1}.

C.d. spectra in the range 400–240 nm were performed at 25°C in $CHCl_3$ solution by a Jobin-Yvon Mark III dichrograph using a cell path length of 0.1 cm. In the case of all-*trans* samples, concentrations in the range $(3–5)\times 10^{-4}$ mol l^{-1} of SA units were used, whereas for irradiated samples concentrations in the range (1–

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Table 1 Composition and distribution of monomeric units of (−)menthyl acrylate (MtA)/*trans*-4-hydroxystilbene acrylate (SA) copolymers

Sample	Units from SA (mol%)	$[\alpha]_D^{25a}$	$X_{SA(n)}{}^b$			$X_{MtA(n)}{}^b$		
			$n = 1$	2	3	$n = 1$	2	3
c1	12.6	−69.0	70.4	22.7	5.5	1.5	2.6	3.4
c2	25.0	−55.4	49.8	29.3	12.9	5.3	8.2	9.4
c3	38.9	−45.8	30.6	27.3	18.3	13.5	17.1	16.2
c4	68.6	−25.1	8.7	12.3	13.0	39.8	29.4	16.3
c5	87.0	−9.9	1.5	2.6	3.5	70.0	22.8	5.6

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

[b] Molar fractions (%) of units from SA and MtA in sequence lengths of *n* units (see ref. 11)

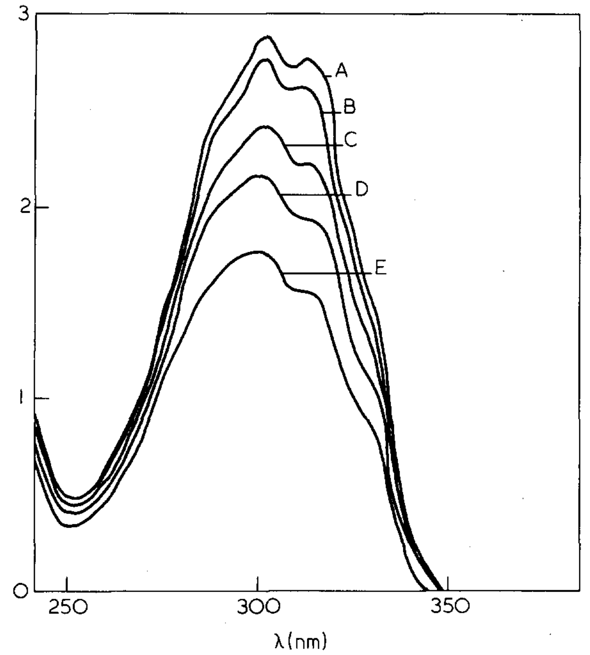

Figure 1 U.v. absorption spectra in $CHCl_3$ solution at 25°C of: (A) *trans*-4-hydroxystilbene-2-methylpropanoate (SP); (B)–(E) poly (MtA-*co*-SA) containing 12.6, 25.0, 68.6 and 100 mol% of units from SA in all-*trans* configuration, respectively

2) $\times 10^{-3}$ mol l^{-1} of SA units were employed. The molar differential dichroic absorption coefficient ($\Delta\varepsilon$) is referred to one monomeric (SA) unit and is expressed as l mol^{-1} cm^{-1}.

Optical rotatory measurements were performed on polymer solution in $CHCl_3$ at 25°C by a Perkin-Elmer 141 spectropolarimeter having sensitivity $\pm 0.003°$ and cell path length 1 dm. Concentrations of 1–3 and 0.1–0.2 g dl^{-1} were used for unirradiated and irradiated polymer samples, respectively.

Fluorescence emission and excitation spectra were recorded by a Perkin-Elmer MPF3 spectrofluorimeter in $CHCl_3$ solution having absorbance lower than 0.1. Experimental spectra were corrected for detector wavelength response.

Irradiation experiments were performed on chloroform solutions having absorbance lower than 0.1 by a 25 W Zn Osram lamp equipped with suitable cut-off filters to select the emission at 334–328 nm.

RESULTS AND DISCUSSION

U.v. absorption

Table 2 U.v. absorption data of high and low molecular weight *trans*-stilbene derivatives[a]

Sample	Units from SA (mol%)	ϵ_{300} (mol l^{-1} cm^{-1})	f^b	$\frac{\epsilon_{288}}{\epsilon_{300}}$	$\frac{\epsilon_{325}}{\epsilon_{300}}$
SP	–	28700	0.617	0.970	0.611
c1	12.6	28500	0.550	0.969	0.607
c2	25.0	27900	0.531	0.950	0.590
c3	38.9	24900	0.476	0.932	0.574
c4	68.6	24300	0.461	0.908	0.561
c5	87.0	21800	0.414	0.886	0.545
c6	100.0	17800	0.350	0.892	0.551

[a] In chloroform at 25°C

[b] f = oscillator strength evaluated as

$$\frac{4.49 \times 10^{-9}}{n} \int \epsilon(\bar{\nu})\, d\bar{\nu}$$

where *n* is the refractive index of the solvent

The u.v. absorption spectra in chloroform solution of poly(MtA-*co*-SA)s and 4-hydroxystilbene-2-methylpropanoate (SP) in all-*trans* configuration in the 350–240 nm spectral region show a broad structured band with two relative maxima at about 300 and 312.5 nm and two shoulders at about 288 and 325 nm (*Figure 1*). In the same region *trans*-stilbene shows a band with relative maxima at 298.3 and 310.4 nm and two shoulders at 291.7 and 322.1 nm assigned to the first $\pi \rightarrow \pi^*$ ($^1B \leftarrow {}^1A$) electronic transition[12]. On increasing the content of units from SA the molar extinction coefficient decreases and the intensity distribution of the Franck–Condon progression[13] changes regularly (*Table 2*); a small bathochromic effect (~1 nm) is also observed. This behaviour, also observed for analogous optically active copolymers of (−)menthyl acrylate with vinyl aromatic monomers[14,15], has been related to interactions between neighbouring chromophores[16,17].

Trans-4-hydroxystilbene-2-methylpropanoate (SP) undergoes *trans*→*cis* photoisomerization upon irradiation in the $\pi \rightarrow \pi^*$ absorption band[9]. With increasing irradiation time the intensity of the absorption band decreases progressively and the maximum shifts to lower wavelength until a photostationary state is eventually reached (*Figure 2a*). The presence of an isosbestic point at 267 nm indicates that only two absorbing species (*trans* and *cis* isomers) are present. However, on prolonged irradiation, a new band appears in the range 265–255 nm, which can be attributed to secondary photochemical products[7,18]. $\mathrm{Ln}[(A_0 - A_\infty)/A_t - A_0)]$, where A_0, A_t and A_∞ are the absorbance of the sample at time 0, *t* and ∞, respectively, shows a linear dependence on irradiation time at low absorbance ($A < 0.1$ at the irradiation wavelength) (*Figure 3*), in accordance with *trans*⇄*cis* first-order equilibrium kinetics (see Appendix).

Poly(MtA-*co*-SA) samples exhibit analogous behaviour on irradiation but, on increasing the content of units from SA, the isosbestic point disappears (*Figure 2b* and *Table 3*) and a progressive deviation from first-order kinetics is observed (*Figure 3*).

Trans→*cis* isomerization has been assumed[19,20] to be the main photochemical process in polymers containing stilbene moieties as in low molecular weight stilbene derivatives[9]. However, cyclodimerization and oxidative cyclization to phenanthrene derivatives[7,8] might occur in polymers, owing to the high local chromophore concentration and relative conformational stiffness.

Owing to the lack of clear experimental evidence on the relevance of possible secondary processes, our data have been interpreted in terms of *trans–cis* photoisomerization, even if the absence of the isosbestic point and the non-monoexponential behaviour can in principle arise at least in part from the above secondary photoreactions. Investigations are in progress in order to clarify the nature of the photochemical products.

A deviation from first-order kinetics has previously been reported in polymers containing either stilbene[19] or azobenzene[21] moieties. Even if this behaviour can be at least partially due to non-ideal irradiation conditions, it has been interpreted in terms of either polarity of the microenvironment[19] or free volume effect[21]. The latter interpretation appears to be more likely in poly(MtA-*co*-SA)s due to the relatively low polarity of both solvent (chloroform) and copolymer units. Besides, in the former case the extent of deviation from monoexponential behaviour should be independent of the content of SA units, contrary to what is observed (*Figure 3*).

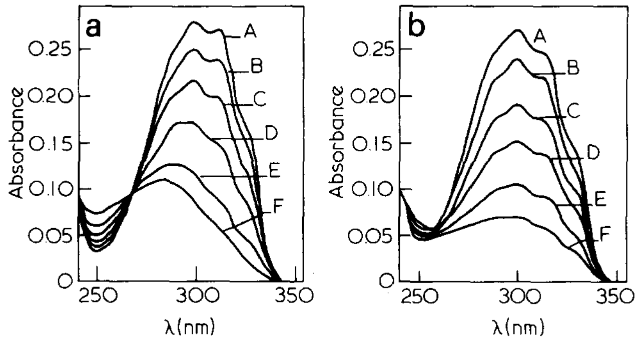

Figure 2 Variation of u.v. absorption spectra of high and low molecular weight stilbene derivatives with irradiation time at 330 nm, in chloroform solution at 25°C: (a) 4-hydroxystilbene-2-methylpropanoate (SP); (b) poly(MtA-*co*-SA) containing 87.0 mol% of SA units. Curves A to F correspond to 0, 3, 8, 15, 30 and 60 min irradiation time, respectively

Fluorescence

The emission spectrum of *trans*-SP consists of a rather well structured band with relative maxima at 342 and 359 nm and a shoulder at about 380 nm (*Figure 4*). All-*trans* poly(MtA-*co*-SA)s containing less than 30 mol% units from SA exhibit emission spectra analogous to SP; at higher content of SA units a long-wavelength emission appears, the intensity of which increases with stilbene chromophore content (*Figure 4* and *Table 4*). This behaviour has already been observed for other polymers having aromatic side chains, and is attributed to fluorescence emission by interacting chromophores (excimers)[15,22]. The excimer emission band evaluated as the difference[23] between the normalized fluorescence spectrum of poly(SA) and that of the low molecular weight model compound SP consists of a broad structureless band centred at about 420 nm (*Figure 4*). The energy

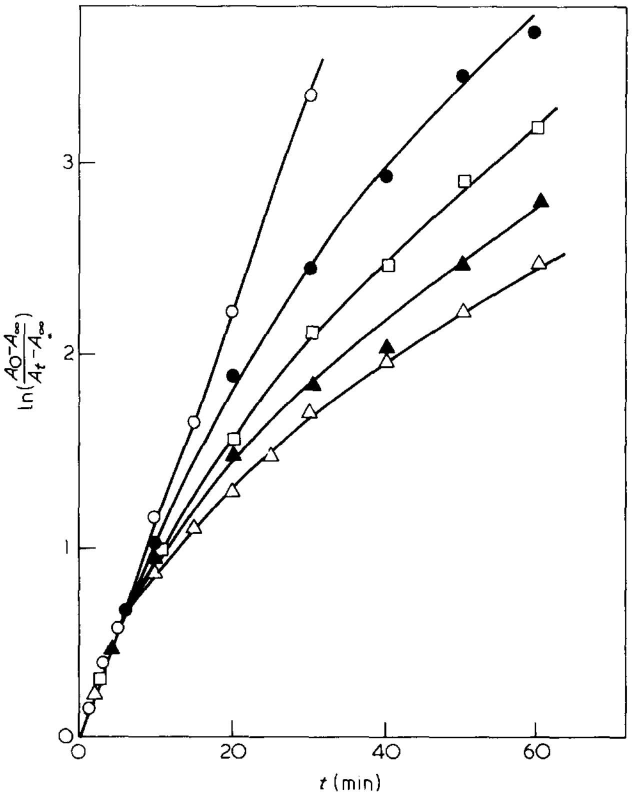

Figure 3 Variation of $\ln[(A_0-A_\infty)/(A_t-A_\infty)]$ with irradiation time: ○, SP; ●, poly(MtA-*co*-SA) containing 12.6 mol% units from SA; □, poly(MtA-*co*-SA) containing 25.0 mol% units from SA; ▲, poly(MtA-*co*-SA) containing 68.6 mol% units from SA; △, poly(SA)

Table 3 Photochromic data of high and low molecular weight stilbene derivatives[a]

Sample	Units from SA (mol%)	λ_{iso}[b] (nm)	ϵ_{trans}[c] (mol l^{-1} cm^{-1})	ϵ_{eq}[c,d] (mol l^{-1} cm^{-1})	α[d,e]
SP	–	267	27100	5700	0.84
c1	12.6	264	27100	5550	0.86
c2	25.0	262	26000	4200	0.83
c3	38.9	260	22600	3900	0.90
c4	68.6	254–258	21200	3900	0.88
c5	87.0	252–256	18500	3400	0.87
c6	100.0	252–255	13100	2250	0.88

[a] In $CHCl_3$ at 25°C, λ_{irr} = 330 nm
[b] At the isosbestic point
[c] At 315 nm
[d] At the photostationary state
[e] Molar fraction of *cis* isomer evaluated according to ref. 27

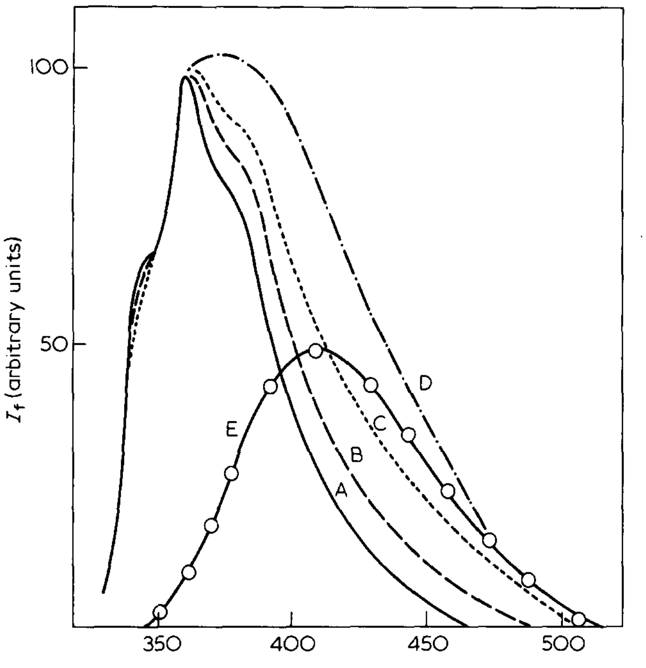

Figure 4 Corrected fluorescence emission spectra of *trans*-stilbene derivatives in chloroform at 25°C (λ_{exc} = 330 nm; normalization at 360 nm): A, ——, SP; B, – – – –, poly(MtA-*co*-SA) containing 25.0 mol% units from SA; C, ······, poly(MtA-*co*-SA) containing 68.6 mol% units from SA; D, –·–·–, poly(SA); E, –○–, difference between the spectra of poly(SA) and SP

Table 4 Fluorescence emission data of high and low molecular weight stilbene derivatives[a]

Sample	Units from SA (mol%)	λ_{max} (nm)	I_{420}/I_{360} Unirradiated[b]	I_{420}/I_{360} After 1 h[b,c] irradiation
SP	–	358	0.14	0.14
c1	12.6	359	0.19	0.18
c2	25.0	360	0.25	0.22
c3	38.9	360	0.27	0.22
c4	68.6	361	0.43	0.22
c5	87.0	362	0.56	0.23
c6	100.0	362	0.62	0.27

[a] In chloroform at 25°C, λ_{exc} = 330 nm, corrected for detector response

[b] I_{360} and I_{420} are the fluorescence intensities at 360 and 420 nm, respectively

[c] Irradiation wavelength = 330 nm

separation between monomer and excimer emission ($\simeq$4000 cm^{-1}) is of the order of magnitude typically observed for excimers of aromatic compounds[24].

Excitation spectra closely resemble the absorption spectra and are independent of fluorescence wavelength, thus confirming the excimeric nature of the long-wavelength emission[15]. All samples show a linear correlation between absorbance and emission intensity in dilute solution (absorbance <0.4).

The degree of fluorescence polarization[25], evaluated as $p=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$, *of poly(MtA-co-*SA) containing 12.6 mol% SA units is significantly higher than that of SP (0.21 and 0.15, respectively), whereas copolymers with a higher content of units from SA exhibit much lower p values, going from 0.11 (25 mol%) to 0.095 (100 mol%).

These data can be interpreted in terms of two opposing effects. The degree of polarization in polymer samples on the one hand increases with respect to the model SP because of higher conformational rigidity of the stilbene chromophores in the polymer matrix and on the other hand decreases because of the exciton migration[25] suggested by the excimer emission.

On irradiation at 330 nm the shape of the fluorescence spectrum of SP does not change, whereas its intensity decreases linearly with decreasing absorbance according to the negligible[26] fluorescence quantum yield of the *cis* form (*Figure 5*). By contrast, in the case of poly(MtA-*co*-SA)s, the long-wavelength emission disappears progressively (*Figure 5*), the difference between fluorescence spectra before and after irradiation giving rise to a broad unstructured band (*Figure 6*) analogous to that reported in *Figure 4E.* Moreover, no linear relationship exists between fluorescence intensity and absorbance. These effects become more evident on increasing the content of units from SA (see I_{420}/I_{360}, *Table 4*).

A possible explanation is that, on irradiation, an increasing fraction of excited SA *trans* monomeric units cannot populate excimeric sites due to the decrease of exciton migration efficiency and of the probability of having two *trans*-stilbene chromophores in suitable orientation. As a consequence, the monomer fluorescence quantum yield increases progressively and a linear correlation between fluorescence intensity at 360 nm and absorbance can be observed only after excimer emission at 420 nm has been completely suppressed (*Figure 5*).

This hypothesis is also supported by the values of the degree of fluorescence polarization p measured after different irradiation times. In fact p is independent of the *trans*/*cis* ratio for the model compound SP, while in the case of poly(MtA-*co*-SA)s it increases monotonically with

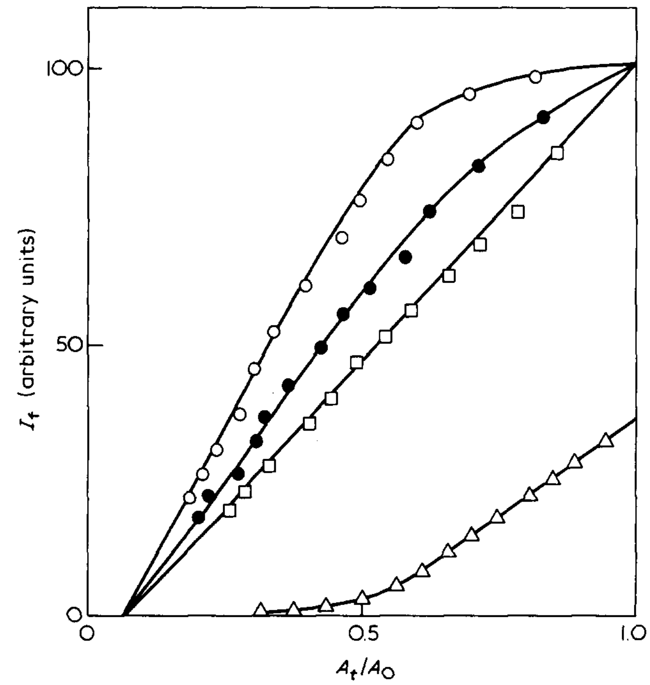

Figure 5 Variation of normalized fluorescence intensity (I_f) (λ_{exc} = 330 nm, λ_{obs} = 360 nm) with respect to relative absorbance at 315 nm at different times (A_t/A_0) in chloroform solution at 25°C of: ○, poly(SA); ●, poly(MtA-*co*-SA) containing 68.6 mol% units from SA; □, SP; △, poly(SA), emission at 420 nm

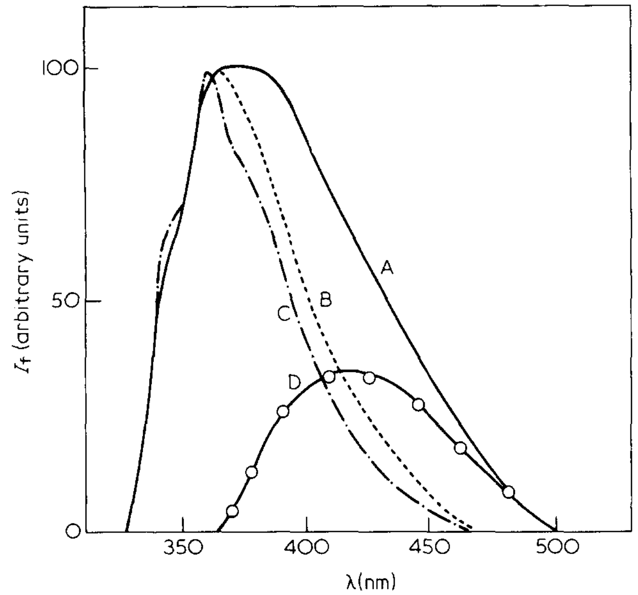

Figure 6 Corrected fluorescence spectra (in chloroform at 25°C, λ_{exc} = 330 nm) normalized at 360 nm of: A, ———, poly(SA) in all-*trans* configuration; B, ······, poly(SA) after 65 min irradiation at 330 nm; C, —·—·—, *trans*-SP; D, —○—, difference between spectra A and B

irradiation time to values higher than that observed for SP (*Figure 7*), in accordance with a decrease of exciton migration efficiency.

In addition, polymer samples at the photostationary state as well as the all-*trans* poly(MtA-*co*-SA) containing 12.6 mol% units from SA, where *trans* chromophores are substantially isolated, display a degree of polarization higher than SP, again indicating a restricted conformational freedom of stilbene chromophores when inserted in macromolecular systems. This has been already shown by ^{1}H n.m.r. spectra of the all-*trans* polymer samples[11].

On the basis of the extrapolated values of absorbance for I_f equal to zero (*Figure 5*) it is possible to evaluate[27] the molar extinction coefficient of the all-*cis* samples and hence the molar fraction α of *cis*-stilbene chromophores in the polymeric samples at the photostationary state (*Table 3*). Within experimental errors, α appears to be, at least in the present case, independent of the polymer matrix.

Chiroptical properties

As reported in a previous paper[11] all-*trans* poly(MtA-*co*-SA)s display optical activity at 589 nm of negative sign. No contribution to optical rotation from SA units was observed, as indicated by the linear correlation between optical activity and composition. The optical rotation of the substantially all-*cis* copolymers (after 1 h of irradiation at 330 nm) is still negative but 15–25% lower in absolute value (*Table 5*). The variation of optical rotation is larger with increasing content of SA units.

C.d. spectra of all-*trans* poly(MtA-*co*-SA)s show[11] a negative structured dichroic band centred at 313 nm in the region of the lowest-energy $\pi \rightarrow \pi^*$ electronic transition of stilbene chromophore[11]. The irradiated samples show in the same spectral region an analogous negative band having much lower ellipticity, in absolute value. However, the observed c.d. corresponds, in the limit of experimental error, to that expected on the basis of the residual content of *trans*-stilbene moieties, thus suggesting that the contribution to c.d. from *cis*-stilbene chromophores is substantially negligible. As the stilbene chromophore itself has a larger molecular dissymmetry in the *cis* form than in the *trans* configuration, this result cannot be explained on the basis of a mere chiral perturbation of isolated photochromic groups. Rather, this behaviour suggests that the observed c.d. band arises from dipole–dipole interactions between *trans*-stilbene units in a particular macromolecular conformation. Indeed, this behaviour is analogous to that reported for polypeptides containing side-chain stilbene or azobenzene chromophores which, on irradiation under suitable conditions, undergo extensive conformational transitions[1–3].

CONCLUSIONS

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

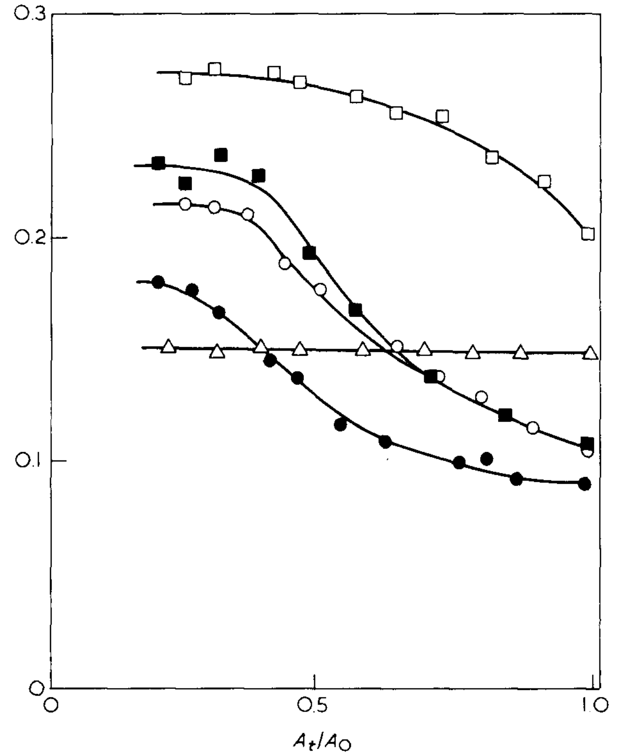

Figure 7 Variation of the polarization degree *p* with the relative absorbance (A_t/A_0) on irradiation time at 330 nm in chloroform at 25°C: □, poly(MtA-*co*-SA) containing 12.6 mol% units from SA; ■, poly(MtA-*co*-SA) containing 25.0 mol% units from SA; ○, poly(MtA-*co*-SA) containing 87.0 mol% units from SA; ●, poly(SA); △–, SP

Table 5 Comparison of optical rotation of poly(MtA-*co*-SA)s before and after irradiation at 330 nm

Sample	Units from SA (mol%)	$[\alpha]^{25}_{436}$ [a] Unirradiated	Irradiated[c]	$\Delta[\alpha]$ [b] (%)
c1	12.6	–136	–115	15.4
c3	38.9	–94	–78	17.0
c4	68.6	–47	–35	25.5

[a] In chloroform solution, *l* = 1 dm

[b] Evaluated as 100 $\{[\alpha]^{25}_{436}\text{ (unirr)} - [\alpha]^{25}_{436}\text{ (irr)}\} / [\alpha]^{25}_{436}\text{ (unirr)}$

[c] In chloroform solution for 60 min

(i) With increasing irradiation time the u.v absorption spectra of poly(MtA-*co*-SA) samples change progressively both in shape and intensity analogously to the low molecular weight model SP, due to *trans–cis* isomerization of side-chain stilbene chromophores. The progressive disappearance of the isosbestic point and deviation from first-order kinetics observed for increasing content of SA units in the copolymers has been attributed to free volume effect.

(ii) Fluorescence spectra are characterized by an excimeric component which increases with increasing content of SA units in the copolymers. The lower emission intensity observed for irradiated samples is attributed to the negligible fluorescence quantum yield of *cis*-stilbene chromophores whereas the progressive disappearance of the excimeric component can be explained by assuming that the *cis* isomers inhibit exciton migration. This is supported by measurements of the degree of fluorescence polarization which also indicate a higher conformational rigidity of the stilbene chromophore when inserted in polymeric systems.

(iii) The observed differences of chiroptical properties between irradiated and unirradiated copolymers seem to indicate that during the *trans→cis* isomerization of stilbene chromophores a local conformational rearrangement of macromolecules takes place.

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APPENDIX

Let us consider a compound S capable of *cis–trans* photoisomerization:

$$S_{trans} \overset{h\nu}{\rightleftarrows} S_{cis} \qquad (A1)$$

In a cell having path length l_1 and containing a c_0 molar solution of S, if equilibrium (1) is the only relevant reaction pathway, under the effect of monochromatic light the amount of S_{trans} which disappears during the time dt in the element dl placed at a distance l from the front of the cell will be:

$$\mathrm{d}x\,\mathrm{d}l = -N_{trans}(l)\Phi_{trans}\,\mathrm{d}t + N_{cis}(l)\Phi_{cis}\,\mathrm{d}t \qquad (A2)$$

where x is the molar concentration of S_{trans}, Φ_{trans} and Φ_{cis} are the quantum yields for *trans→cis* and *cis→trans* photoisomerization, respectively, $N_{trans}(l)$ and $N_{cis}(l)$ are the number of photons (expressed as Einstein $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$) absorbed in the element dl by the *trans* and *cis* isomers, respectively, given by

$$N_{trans}(l) = I(l)(1 - 10^{-\varepsilon_{trans}x\mathrm{d}l}) \qquad (A3)$$

$$N_{cis}(l) = I(l)(1 - 10^{-\varepsilon_{cis}(c_0 - x)\mathrm{d}l}) \qquad (A4)$$

where $I(l)$ is the intensity of the incident light at a distance l from the front of the cell.

When total absorbance is small, i.e. $I(l) \simeq I_0$ and $1 - 10^{-\varepsilon c\mathrm{d}l} \simeq 2.303\varepsilon c\mathrm{d}l$ (the superior terms of the serial expansion are negligible), equations (3) and (4) are transformed to:

$$N_{trans}(l) = 2.303 I_0 \varepsilon_{trans} x\mathrm{d}l \qquad (A5)$$

$$N_{cis}(l) = 2.303 I_0 \varepsilon_{cis}(c_0 - x)\,\mathrm{d}l \qquad (A6)$$

where I_0 is the intensity of incident light, ε_{trans} and ε_{cis} are the molar extinction coefficients of the two isomers at the irradiation wavelength.

From equations (2), (5) and (6) one gets

$$\mathrm{d}x = 2.303 I_0[-\varepsilon_{trans}\Phi_{trans}x + \varepsilon_{cis}\Phi_{cis}(c_0 - x)]\,\mathrm{d}t \qquad (A7)$$

and after integration

$$x = (x_0 - x_\infty)\mathrm{e}^{-kt} + x_\infty \qquad (A8)$$

where x_0 = initial concentration of S_{trans},

$$x_\infty = \varepsilon_{cis}\Phi_{cis}/(\varepsilon_{cis}\Phi_{cis} + \varepsilon_{trans}\Phi_{trans})$$

and

$$k = 2.303 I_0(\varepsilon_{trans}\Phi_{trans} + \varepsilon_{cis}\Phi_{cis})$$

As the total absorbance at the irradiation time t is

$$A_t = \varepsilon_{trans} l_1 x + \varepsilon_{cis} l_1 (c_0 - x) \qquad (A9)$$

from (8) it follows that:

$$A_t = (A_0 - A_\infty)\mathrm{e}^{-kt} + A_\infty \qquad (A10)$$

i.e.

$$\ln[(A_0 - A_\infty)/(A_t - A_\infty)] = kt \qquad (A11)$$

where A_0, A_t and A_∞ are the total absorbance at time 0, t and ∞, respectively.