Optically Active Polymers Containing Side-Chain *trans*-Stilbene Chromophores Directly Bound to the Backbone: Photochemistry and Photophysics of Copolymers of (–)-Menthyl Acrylate with *trans*-4-Vinylstilbene

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ABSTRACT: Radical-initiated copolymers of (–)-menthyl acrylate (MtA) with *trans*-4-vinylstilbene (VS) exhibit trans → cis photoisomerization of the side-chain stilbene chromophores which, contrary to the low molecular weight structural model *trans*-4-methylstilbene (MS), does not obey first-order kinetics. UV absorption, fluorescence emission, degree of fluorescence polarization, and induced circular dichroism have been measured as a function of irradiation time and composition. The obtained results have been interpreted in terms of interactions between *trans*-stilbene side chains along the macromolecular backbone. In particular, chiroptical properties of the polymers suggest the existence of locally ordered "trans" polymer segments which are disrupted by trans → cis photoisomerization.

Introduction

In a previous article[1] the synthesis of optically active copolymers of (–)-menthyl acrylate (MtA) with *trans*-4-vinylstilbene (VS) [poly(MtA-*co*-VS)s] has been reported. Spectroscopic and chiroptical measurements evidenced interactions between aromatic chromophores and a nonlinear dependence of chiroptical properties on copolymer composition. This behavior was tentatively attributed to the presence in solution of at least locally ordered conformations of one prevailing chirality, due to the cooperative effect of the chiral side chains. A rather different behavior had been observed in analogous copolymers containing stilbene groups separated from the main chain,[2,3] where interactions between side chains should be less relevant.

It has been reported that, upon UV irradiation, conformational transitions occur in conformationally homogeneous, rigid polypeptides containing side-chain photochromic groups.[4-7] Therefore, in the present article the photophysics and photochemistry of poly(MtA-*co*-VS)s are investigated and the chiroptical properties of the resulting irradiated samples examined in order to gain information about the possible conformational reorganization of the copolymer macromolecules in solution.

Results and Discussion

Data relevant to the polymer samples obtained by radical-initiated copolymerization[1] of MtA with VS (r_{MtA} = 0.15 and r_{VS} = 3.57) are summarized in Table I.

UV Absorption. UV spectra in $CHCl_3$ solution of poly(MtA-*co*-VS)s in the all-trans configuration show in the 350–250-nm region a broad structured absorption band, having two relative maxima at about 316 and 303 nm and two shoulders at 330 and 290 nm (Figure 1). Maxima position, molar extinction coefficient, and intensity distribution of the Frank–Condon progression of this band regularly change with the copolymer chemical composition (Table II).

Upon irradiation in the $\pi \rightarrow \pi^*$ absorption band, the low molecular weight analogue *trans*-4-methylstilbene (MS) undergoes trans → cis photoisomerization.[8] With increasing irradiation time the intensity of this band progressively decreases with a shift of the absorption maximum to lower wavelengths, until the photostationary state is reached (Figure 2). The presence of an isosbestic point at 268 nm demonstrates that only two absorbing species (trans and cis isomers) are present. The linear dependence of ln $[(A_0 - A_\infty)/(A_t - A_\infty)]$, where A_0, A_∞, and A_t represent the absorbance of the sample at time 0, ∞, and *t*, respectively, vs. irradiation time (Figure 3) indicates that the photoisomerization process obeys first-order kinetics.[3]

Poly(MtA-*co*-VS) samples exhibit a similar behavior, but when the content of VS units is increased, the isosbestic point broadens (Table II). As an example the UV spectra at different irradiation times are reported in Figure 4 for poly(MtA-*co*-VS) containing 67.5 mol % of VS units.

Trans → cis isomerization is the main photochemical process in low molecular weight stilbene derivatives;[8] however, cyclodimerization and oxidative cyclization to phenanthrene derivatives[9,10] may also occur, the former process being more probable in polymers owing to the high local chromophore concentration. The broadening of the isosbestic point in the UV spectra of copolymer samples can be attributed to secondary photoreactions and indeed this phenomenon is more evident with increasing the content of VS units. However, these secondary processes are not relevant under the adopted irradiation conditions.[8] Therefore, our data have been interpreted in terms of trans → cis photoisomerization only, analogously to what has been previously reported for copolymers containing either stilbene[3,5,11] or azobenzene[12,13] moieties.

In the case of copolymer samples the photoisomerization process does not obey first-order kinetics and in fact the dependence of ln $[A_0 - A_\infty)/(A_t - A_\infty)]$ on irradiation time is not linear (Figure 3). In similar copolymers of MtA with 4-hydroxystilbene acrylate, where the stilbene chromophore is separated from the main chain by an ester group, the isomerization rate decreases on increasing the stilbene content and is always lower than for the low molecular weight model compound.[3] On the contrary, in poly(MtA-*co*-VS)s, where the stilbene moieties are directly bound to the polymer backbone, the initial isomerization rate is always larger than that observed for MS, this effect being more pronounced the higher the content of VS units. As expected from this trend the cationic VS homopolymer exhibits the highest initial isomerization rate. However, the radical initiated poly(VS) is characterized by a much lower photoisomerization rate (Figure 3). At present this anomalous behavior cannot be entirely explained and it can be only tentatively attributed either to significant

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Table I
Composition and Distribution of Monomeric Units of Poly(MtA-*co*-VS)s in the All-Trans Configuration[1]

sample	counits from VS,[a] mol %	$10^{-3}\bar{M}_w$[b]	CD[c]		$X_{VS(n)}$[d]			$X_{MtA(n)}$[d]		
			$\Delta\epsilon_{322}$	$\Delta\epsilon_{285}$	$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$
RC1	89.5	53.0	+0.26	−0.16	1.2	2.1	2.8	89.4	9.2	0.8
RC2	78.5	50.0	+1.22	−0.47	6.2	9.3	10.4	73.0	21.4	4.6
RC3	67.5	35.0	+1.40	−0.61	15.8	19.1	17.4	56.3	28.3	10.6
RC4	57.8	31.0	+1.52	−0.86	27.3	26.3	18.9	41.5	29.7	15.9
RC5	41.0	30.5	+1.48	−0.96	48.7	29.5	13.4	21.0	22.9	18.7
RC6	26.0	32.0	+1.13	−0.53	67.4	23.9	6.4	8.7	12.2	13.0
RC7	14.9	69.0	+0.48	−0.35	79.7	17.1	2.7	3.4	5.5	6.6

[a] Evaluated by ^1H NMR. [b] Determined by GPC measurements. [c] In $CHCl_3$ solution, $l = 1$ cm. [d] Percent fraction of VS (or MtA) units in a closed sequence of n.

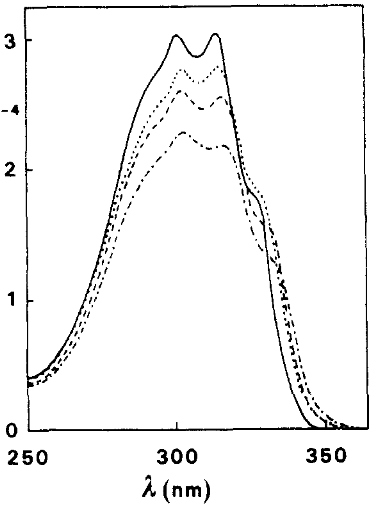

Figure 1. UV absorption spectra, in chloroform solution at 25 °C, of stilbene derivatives in all-trans configuration: (—) MS, poly(MtA-*co*-VS)s containing (···) 14.9 and (- - -) 41.0 mol % of VS units, and (-·-) poly(VS).

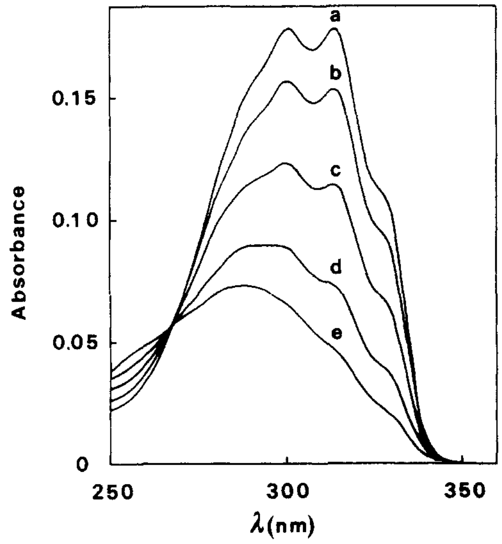

Figure 2. Variation of the UV absorption spectrum of MS vs. time of irradiation at 330 nm, in chloroform solution at 25 °C. Curves a–e correspond to 0, 2, 6, 14, and 40 min of irradiation time, respectively.

differences in the main-chain tacticity or to possible side reactions occurring in the radical homopolymer during the long polymerization time.[1]

On increasing the irradiation time however in all the samples the isomerization rate progressively decreases and levels off to a value approximately 2 times smaller than that reported for the low molecular weight model compound MS.

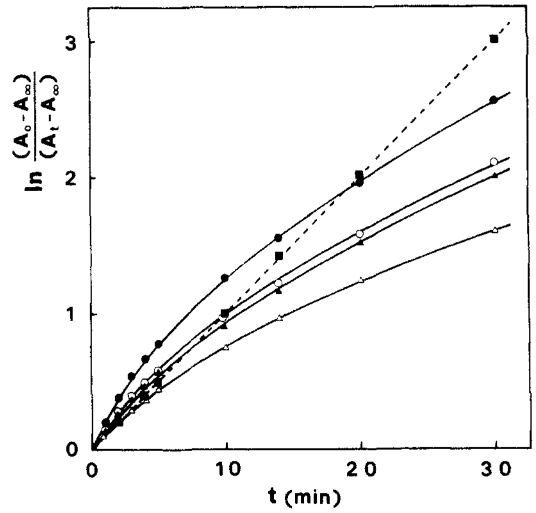

Figure 3. Variation of ln $[(A_0 - A_\infty)/(A_t - A_\infty)]$ with the time of irradiation at 330 nm, in chloroform at 25 °C: (■) MS, poly(MtA-*co*-VS)s containing (△) 14.9, (▲) 41.0, and (●) 89.5 mol % of VS units, (○) radical- and (●) cationic initiated poly(VS).

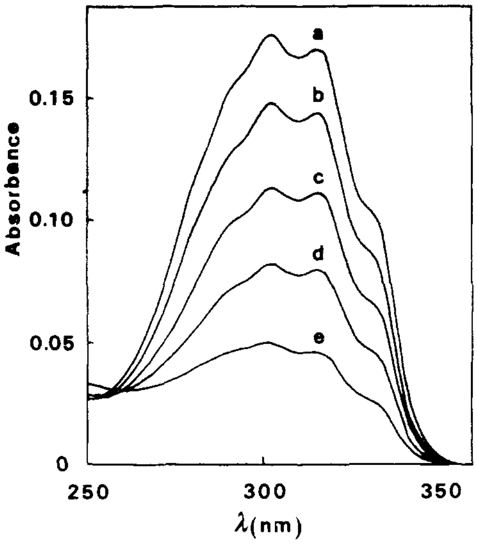

Figure 4. Variation of the UV absorption spectrum of poly(MtA-*co*-VS) containing 67.5 mol % of VS units vs. time of irradiation at 330 nm, in chloroform solution at 25 °C. Curves a–e correspond to 0, 1, 4, 10, and 30 min of irradiation time, respectively.

Steric and electronic effects can be claimed to explain this behavior by assuming that either *trans*-VS units inserted into sequences photoisomerize more effectively than isolated ones or, owing to energy-transfer processes, the excitation is not confined to the light-absorbing chromophore but can migrate along the polymer chain up to stilbene groups more prone to isomerization that act as

Table II
UV Absorption Data on Poly(MtA-*co*-VS)s in the All-Trans Configuration and in the Photostationary State[a]

		before irradiation							after irradiation[b]		
sample	counits from VS, mol %	λ_{max}', nm	λ_{max}'', nm	$\epsilon_{max}'^{c}$	$\epsilon_{max}''/\epsilon_{max}'$	$\epsilon_{290}/\epsilon_{max}'$	$\epsilon_{330}/\epsilon_{max}'$	$\epsilon_{trans}^{c,d}$	isosbestic point, nm	ϵ_{cis}^{c-e}	$\alpha_{trans}^{e,f}$
RH[g]	100.0	303.0	317.0	22 800	0.958	0.859	0.586	21 700	250–266	600	0.27
RC1	89.5	302.5	316.5	23 500	0.954	0.873	0.589	22 200	250–260	600	0.19
RC2	78.5	302.5	316.5	25 800	0.964	0.852	0.592	24 400	252–262	800	0.13
RC3	67.5	302.5	316.5	25 500	0.964	0.861	0.595	24 200	252–263	800	0.15
RC4	57.8	302.5	316.5	26 500	0.971	0.867	0.590	25 200	258–265	1000	0.14
RC5	41.0	302.5	316.5	26 000	0.988	0.847	0.600	24 600	260–265	1000	0.11
RC6	26.0	302.5	316.5	26 600	1.066	0.833	0.633	25 400	260–265	2200	0.15
RC7	14.9	302.5	316.0	27 700	1.010	0.837	0.642	26 900	266	3500	0.20
MS[h]		301.0	314.0	30 200	1.005	0.838	0.626	28 900	268	3800	0.09

[a] In $CHCl_3$ solution. [b] At 330 nm. [c] Referred to one VS unit and expressed as L mol^{-1} cm^{-1}. [d] Evaluated at 313 nm. [e] Evaluated according to ref 3. [f] Mole fraction of the residue trans isomer, present at the photostationary state. [g] Radical-initiated homopolymer. [h] 4-Methylstilbene.

Table III
Fluorescence Data of Poly(MtA-*co*-VS)s in the All-Trans Configuration (Unirradiated) and in the Photostationary State (Irradiated)[a]

		λ_{max},[b] nm		I_{360}/I_{420}[b,d]		p[e]	
sample	counits from VS, mol %	unirr	irr[c]	unirr	irr[c]	unirr (p_0)	irr[c] (p_∞)
RH	100.0	405	380	0.33	0.93	0.015	0.151
RC1	89.5	390	370	0.74	2.00	0.021	0.148
RC2	78.5	390	370	0.75	2.08	0.033	0.151
RC3	67.5	390	370	1.07	2.31	0.054	0.149
RC4	57.8	390	370	1.33	2.53	0.053	0.148
RC5	41.0	385	370	1.65	3.10	0.075	0.150
RC6	26.0	365	365	2.38	3.26	0.110	0.175
RC7	14.9	362	360	2.55	2.60	0.167	0.190
MS		360	360	5.63	5.63	0.147	0.147

[a] In $CHCl_3$ solution, λ_{exc} = 280 nm. [b] Corrected for detector response. [c] Irradiation wavelength = 330 nm. [d] I_{360} and I_{420} are the fluorescence intensities at 360 and 420 nm, respectively. [e] Degree of fluorescence polarization evaluated at 360 nm as $p = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$.

traps. When the content of *cis*-VS units is increased, the extent of both interactions among *trans*-VS units and energy migration should become less significant. Correspondingly the isomerization rate should decrease to a value lower than that observed for MS, due to the restricted mobility and the steric crowding around stilbene chromophores linked to a polymer chain.

This interpretation completely accounts for the reported phenomenology. However, we have to stress that close inspection of the equation relating absorbance with irradiation time (see Appendix in ref 3) reveals that both preexponential and exponential factors depend on the molar extinction coefficients of *trans*- and *cis*-VS units. These coefficients are connected with chemical composition and distribution of aromatic units (Tables I and II) and it is possible that under irradiation their values change because of the decreasing (increasing) content and mean sequence length of *trans*-(*cis*)-VS units. As a consequence the reported dependence of isomerization rate on irradiation time may not reflect a real variation of the isomerization quantum yields and can be at least partially attributed to variation of the molar extinction coefficients.

Fluorescence. Fluorescence spectra of poly(MtA-*co*-VS)s in the all-trans configuration show in the 350–500-nm region a structured broad band, the emission maximum of which progressively shifts toward longer wavelengths with increasing content of VS units (Table III). Excitation spectra closely resemble the absorption spectra and are independent of emission wavelength, thus excluding the possibility that the observed fluorescence arises from more than one light-absorbing species. The observed shift of the emission band can be attributed to an increasing contribution of the emission of interacting chromophores (excimers),[1,3] as evidenced by the trend of I_{360}/I_{420} intensity ratios (Table III). However, this effect could be partially attributed to the distortion of *trans*-stilbene moieties when inserted into sequences.[1] This distortion may also account for the reported dependence of copolymer UV spectra on chemical composition. Fluorescence quenching experiments, in principle capable of discriminating between two hypotheses, are not feasible because of the too short fluorescence lifetime of the stilbene chromophore.[14]

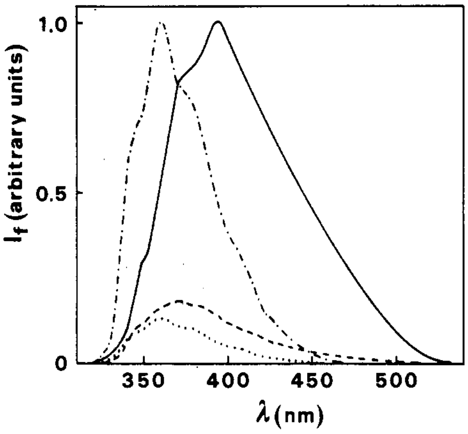

Figure 5. Corrected fluorescence spectra (in chloroform at 25 °C, λ_{exc} = 280 nm) of MS (-·-) trans and (···) after 30-min irradiation at 330 nm and of poly(MtA-*co*-VS) containing 89.5 mol % of VS units (—) in all-trans configuration and (---) after 30-min irradiation at 330 nm. Spectra of all-trans samples have been normalized at the maximum emission intensity.

The shape of the emission band of MS does not change (Figure 5) on irradiation at 330 nm whereas its intensity decreases linearly with decreasing the relative absorbance (Figure 6), according to the negligible fluorescence quantum yield of the cis form.[15] By contrast, when the irradiation time is increased, in copolymer samples the

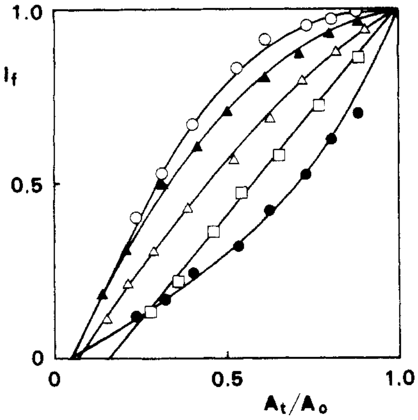

Figure 6. Variation of the normalized fluorescence intensity (I_f) (λ_{exc} = 280 nm, λ_{obsd} = 360 nm) vs. relative absorbance at 313 nm (A_t/A_0) at different irradiation times of (□) MS, poly(MtA-*co*-VS)s containing (△) 41.0 and (▲) 78.5 mol % of VS units, and (○) radical and cationic poly(VS). (●) Poly(VS), emission at 420 nm.

emission maximum progressively shifts toward shorter wavelengths (Table III) owing to the higher depletion rate of the longer wavelength fluorescence emission (Figure 5). Moreover, the dependence of emission intensity at 360 nm on the relative absorbance (A_t/A_0) deviates from linearity (Figure 6). These effects are more pronounced the greater the content of VS units in the copolymers. It is possible that on irradiation an increasing fraction of excited *trans*-stilbene moieties cannot populate excimeric sites, because of the decrease of both the probability of having two aromatic trans chromophores in suitable orientation and the exciton migration efficiency. In this way the quantum yield of the monomeric emission progressively increases and contemporarily the long-wavelength excimer fluorescence decreases. As a consequence a linear correlation between fluorescence intensity at 360 nm and the relative absorbance (A_0/A_∞) can be observed only after the excimer emission has been completely suppressed (Figure 6). However, after irradiation, the I_{360}/I_{420} ratio of all copolymer samples is still markedly lower than that of MS (Table III), even in the sample containing 14.9 mol % of VS units where at the photostationary state excimer formation can be completely ruled out. Therefore, the reported differences between the fluorescence properties of copolymers and the model MS must be at least partially ascribed to the distortion of the stilbene chromophore directly bonded to the polymer backbone.

If one takes into account that *cis*-stilbene emission is negligible,[15] the molar extinction coefficient of *cis*-VS units can be evaluated[16] from the extrapolated value of absorbance at I_f equal to zero (Figure 6). Even if these values are affected by rather large experimental errors, their marked dependence on copolymer chemical composition is however remarkable (Table II). This can be attributed either to the steric crowding of neighboring bulky *cis*-VS units or to hypochromism, as generally observed in copolymers of vinylaromatic monomers.[17,18] Also a possible hypsochromic shift could be particularly effective, as the extinction coefficients have been determined on the tail of the *cis*-stilbene absorption band. The mole fraction (α) of residual *trans*-VS units at the photostationary state has been evaluated from the reported absorption data (Table II). Values in the 0.2–0.1 range are found, but no specific relation between α and content of VS units can be evidenced.

Owing to the very short fluorescence lifetime of the stilbene chromophore (~100 ps),[14] its degree of fluorescence polarization (p) can be determined also in liquid solution at room temperature. The p values measured on chloroform solutions of poly(MtA-*co*-VS)s in the all-trans configuration are lower than that of the model MS, the only exception being the sample containing 14.9 mol % of VS units (Table III). However, in all the polymer samples p increases with increasing irradiation time (Figure 7) to values greater than that of MS which remain constant on irradiation.

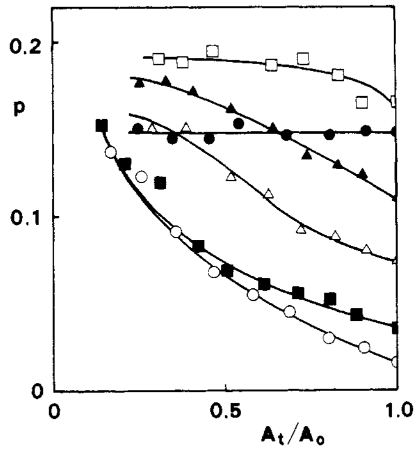

Figure 7. Variation of the degree of fluorescence polarization (p) (in chloroform solution at 25 °C, λ_{exc} = 280 nm, λ_{obsd} = 360 nm) vs. the relative absorbance (A_t/A_0) under irradiation at 330 nm of poly(MtA-*co*-VS)s containing (□) 14.9, (▲) 26.0, (△) 41.0, and (■) 78.5 mol % of VS units; (○) poly(VS); (●) MS.

An analogous trend has been reported[3] for the related copolymers of MtA with 4-hydroxystilbene acrylate (SA) [poly(MtA)-*co*-SA)s]. The higher p values observed in the sample containing 14.9 mol % of VS units in the all-trans configuration can be attributed to lower rotational freedom of stilbene chromophores linked to a polymer chain as compared to low molecular weight derivatives, the *trans*-stilbene chromophores being on average too far from each other for giving rise to a significant energy migration. However, when the content of VS units in the all-trans configuration in the polymer sample is increased, the energy migration becomes more and more efficient, thus becoming responsible for the observed extensive depolarization of fluorescence emission. This last effect is progressively lost with photoisomerization as *cis*-VS units do not participate in energy migration, an increase of p values being observed on irradiation for all the copolymer samples.

Lower p values are observed in poly(MtA-*co*-VS)s than in poly(MtA-*co*-SA)s both in the all-trans configuration and in the photostationary state,[3] in spite of the greater conformational freedom of the latter system. This behavior can be explained by considering that poly(MtA-*co*-VS)s are reasonably characterized by a higher energy migration efficiency, as expected from the larger mean sequence length of aromatic units, as compared to that of poly(MtA-*co*-SA)s having similar composition.[1,2]

Chiroptical Properties. CD spectra of *all-trans*-poly(MtA-*co*-VS)s are characterized, in the 250–400-nm region, by the presence of two structured dichroic bands having opposite sign, which have been tentatively assigned[1] to the exciton splitting[19] of the lowest energy $\pi \rightarrow \pi^*$ electronic transition of the *trans*-stilbene chromophore. The dependence of the ellipticity of both bands on copolymer composition exhibits a maximum around 50 mol % of *trans*-VS units[1] (Table I).

On irradiation at 330 nm the intensity of both bands progressively decreases whereas their profile remains practically unchanged (Figure 8), thus indicating that no

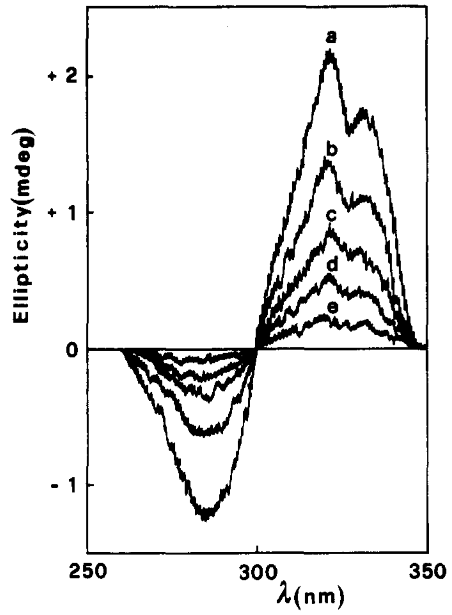

Figure 8. Ellipticity of poly(MtA-*co*-VS) containing 57.8 mol % of VS units, at different irradiation times. Curves a–e correspond to 0, 2, 8, 15, and 45 min of irradiation at 330 nm, respectively (in chloroform at 25 °C, $c = 4.30 \times 10^{-5}$ mol L^{-1} of VS units, $l = 1.0$ cm, sensitivity = 0.2 mdeg cm^{-1}).

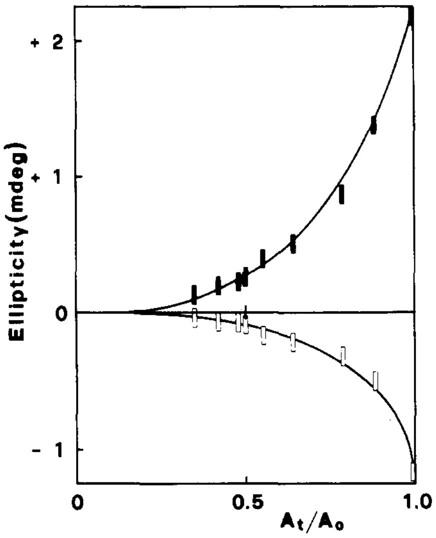

Figure 9. Ellipticity at (upper curve) 322 and (lower curve) 285 nm vs. the relative absorbance (A_t/A_0) under irradiation at 330 nm of poly(MtA-*co*-VS) containing 57.8 mol % of VS units (in chloroform at 25 °C, $c = 4.30 \times 10^{-5}$ mol L^{-1} of VS units, $l = 1.0$ cm, sensitivity = 0.2 mdeg cm^{-1}).

new dichroic absorption relevant to VS units in the cis configuration occurs. Because of the unfavorable anisotropic factor ($\Delta\epsilon/\epsilon$) the dependence of CD on the extent of trans-to-cis isomerization has been investigated only in the RC4 sample, the one having the largest $\Delta\epsilon$ value (Table I).

A plot of the experimental differential dichroic absorption (Θ_0) vs. relative absorbance (A_t/A_0) extrapolates to zero for both bands at an absorbance value closely corresponding to a complete trans-to-cis isomerization (Figure 9). This result and the absence of new dichroic absorption due to *cis*-VS units unequivocally indicate that the contribution of the *cis*-stilbene chromophore to the observed CD is negligible, analogous to what was already reported for other stilbene-containing polymers.[3,5,7]

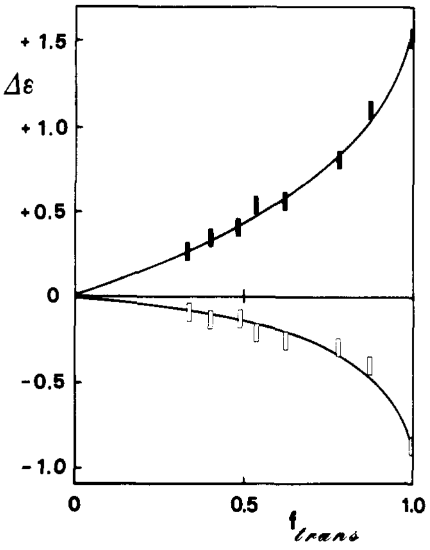

Figure 10. Variation on irradiation of the molar dichroic extinction coefficient ($\Delta\epsilon$) at (upper curve) 322 and (lower curve) 285 nm (in chloroform at 25 °C) vs. the mole fraction of stilbene chromophores in trans configuration (f_{trans}) of poly(MtA-*co*-VS) containing 57.8 mol % of VS units.

It is worth noting that when the content of residual VS units in the trans form (f_{trans}) is decreased, the molar dichroic absorption coefficient ($\Delta\epsilon$) referred to one *trans*-VS unit decreases monotonically up to negligible values for both bands (Figure 10) and fits a linear regression in f_{trans}^2.[6] Therefore, it must be concluded that significant dichroic absorption originates only from interacting *trans*-stilbene moieties, whereas isolated chromophores do not give rise to measurable effects. Analogous indications can be derived also from the reported dependence of $\Delta\epsilon$ on the content of VS units in *all-trans*-poly(MtA-*co*-VS) samples. In fact, when the content of VS units is decreased, i.e., when the percentage of isolated *trans*-stilbene chromophores (Table I) is increased, the molar differential extinction coefficient of both dichroic bands extrapolates to zero.[1]

Conclusions

Trans → cis photoisomerization of stilbene side chains in poly(MtA-*co*-VS)s does not obey first-order kinetics and shows a lower final isomerization rate than the corresponding low molecular weight structural analogue MS. This result is in accordance with the restricted mobility of stilbene chromophores attached to a polymer chain. However, the greater is the content of VS units in the copolymers, the greater is the initial photoisomerization rate, as compared to MS, probably due to steric and electronic interactions and/or energy-transfer processes occurring among *trans*-VS units in sequence. Accordingly the fluorescence properties of poly(MtA-*co*-VS)s, both in the all-trans configuration and after irradiation, are consistent with the occurrence of interactions among *trans*-stilbene chromophores.

All these observations strongly suggest that, despite the probable low degree of main-chain stereoregularity, sections of the copolymer macromolecules containing *trans*-VS units adopt in solution conformations of a predominant chirality which is disrupted by trans → cis isomerization. The presence of stilbene moieties directly bonded to the polymer backbone may be responsible for the observed effects which are much less evident in analogous copolymers containing stilbene chromophores separated from the main chain.[3]

The progressive variation of both isomerization rate and chiroptical properties demonstrates that no sharp conformational transition is promoted in the macromolecules by the light-induced isomerization process, but rather continuous rearrangements occur on a local scale.

Experimental Section

Polymer samples, obtained by radical initiation, were prepared and purified as previously reported.[1] Poly(*trans*-4-vinylstilbene) (poly-VS) was also prepared by cationic polymerization (CH sample) under dry nitrogen at −40 °C in CH$_2$Cl$_2$ solution using BF$_3$·Et$_2$O as initiator (molar ratio VS/BF$_3$·Et$_2$O = 30). The polymerization was stopped by pouring the reaction mixture into a large excess of methanol. The coagulated polymer was dissolved in CHCl$_3$ and reprecipitated into methanol several times in the dark. After drying, the polymer samples were stored in the dark at −30 °C.

trans-4-Methylstilbene (MS), mp 132 °C, was prepared as previously reported.[1] UV spectra in the range of 400–250 nm were performed at 25 °C in CHCl$_3$ solution with a Cary 219 or a Jasco UVIDEC-710 spectrophotometer. Concentrations in the range $(3–5) \times 10^{-5}$ mol L^{-1} of stilbene chromophores and a cell path length of 1 cm were used. The molar extinction coefficient (ϵ) in the polymeric samples is referred to one VS monomeric unit and is expressed as L mol^{-1} cm^{-1}. CD spectra in the range of 400–250 nm were recorded at 25 °C in CHCl$_3$ solution by a Jasco J500B dichrograph using a cell path length of 1.0 cm. In the case of all-trans samples concentrations in the range of $(3–5) \times 10^{-5}$ mol L^{-1} of VS units were employed, whereas for irradiated samples concentrations in the range $(1–2) \times 10^{-4}$ mol L^{-1} of VS units were generally used. The molar differential dichroic absorption coefficient ($\Delta\epsilon$), expressed as L mol^{-1} cm^{-1}, is referred to one VS monomeric unit and has been calculated as $\Delta\epsilon = (Es)/(3300cl)$ where E is the measured elongation in centimeters, s is the sensitivity in mdeg cm^{-1}, c is the chromophore concentration in dmol L^{-1}, and l is the cell path length in centimeters. Fluorescence emission and excitation spectra were recorded with a Perkin-Elmer MPF3 spectrofluorimeter for CHCl$_3$ solutions of the samples having absorbance lower than 0.4. In the case of emission spectra a 280-nm excitation wavelength was used. Experimental spectra were corrected for detector response. The degree of fluorescence polarization (p) was measured at 360 nm by using an excitation wavelength of 280 nm. Irradiation experiments were carried out on CHCl$_3$ solutions having absorbance at 330 nm lower than 0.1 with a 25-W Zn Osram lamp equipped with suitable cutoff filters to select the emission at 334–328 nm. Photoisomerization reactions were followed by measuring the absorbance of the sample at 313 nm at different irradiation times.

Registry No. Poly(MtA-*co*-VS) (copolymer), 90168-61-9; MS, 1860-17-9; poly(*trans*-4-vinylstilbene) (homopolymer), 25067-52-1.

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Water-Soluble Photon-Harvesting Polymers: Intracoil Energy Transfer in Anthryl- and Fluorescein-Tagged Poly(vinylpyrrolidinone)

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ABSTRACT: Poly(vinylpyrrolidinone) containing small mole fractions of pendent 9,10-diphenylanthracene (DPA) and fluorescein (F) was prepared. These copolymers are soluble in polar solvents such as methanol and water. Absorption of light by DPA results in efficient intracoil sensitization of the ^{1}(F)* state. The quantum efficiency (χ) of this process was determined to be 0.4 in methanol and 0.8 in water. It is demonstrated that this increase in χ corresponds to a decrease in polymer coil size in water. Analysis of the fluorescence decay also demonstrates (1) the intracoil energy-transfer process is essentially a static process and (2) anthryl aggregation can result in nonexponential fluorescence decay, which is interpreted as a dynamic equilibrium between ^{1}(DPA)* and a nonfluorescent dimer state. Fluorescence quenching demonstrates that these polymers are not homogeneous and apparently self-organize into hydrophobic and hydrophilic regions.

Introduction

In polymer photophysics it has been recognized that there are at least two "polymer effects" that differentiate this field from small-molecule photophysics: (1) solvent effects on both the polymer-bound chromophore and the polymer coil itself and (2) intracoil energy transfer and/or excited-state annihilation. In the former case the polymer can be used to direct photochemical processes via hydrophobic or electrostatic interactions (i.e., polyelectrolytes). In the latter case the polymer can be used as a photon-harvesting agent, either providing for intracoil multiphoton processes or extending the "action spectrum" of some polymer-bound energy trap.[1] The present study has an element of both of these features. Copolymers have been prepared in which water-soluble poly(vinylpyrrolidinone)

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