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

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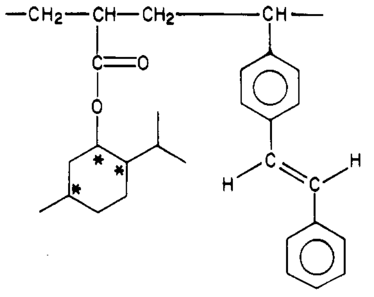
ABSTRACT: Optically active copolymers of (−)-menthyl acrylate (MtA) with *trans*-4-vinylstilbene (VS) were prepared by radical initiation over a wide range of composition. Reactivity ratios, evaluated for both comonomers, indicate that VS exhibits a higher reactivity than MtA. Average sequence lengths of the co-units and their distribution in the macromolecules were also evaluated by statistical calculations. Chiroptical properties of the side-chain *trans*-stilbene chromophores, combined with data of composition and distribution of monomeric units as well as UV and fluorescence measurements, suggest that the copolymer macromolecules assume conformations in solution of a prevailing single chirality due to steric effects.

Introduction

Molecules containing photochromic groups give rise to unique structural changes[1] by their interaction with light. When such photoreactive moieties are inserted in macromolecular systems, materials having the mechanical properties typical of polymers but structurally modifiable by light absorption can be obtained.[1,2] These materials are particularly valuable for possible practical applications in high-speed compact memory devices,[1] in photoconductors,[3] and in solar energy conversion.[3] In addition, the insertion of photochromic moieties in the main or side chain of macromolecules is very attractive for the investigation of their primary and secondary structure, and of the possible conformational changes consequent of light-induced structural modifications.[4-8] In this context, polymers containing side-chain azobenzene[4-6,9] and stilbene[7,8,10] groups, which undergo trans → cis isomerization by light irradiation, were very useful. Furthermore, the insertion of chiral co-units in such polymeric systems opens the possibility for studying the conformation of the above macromolecules in solution by circular dichroism (CD) measurements.[11,12] By this technique poly(L-glutamates) containing side-chain stilbene[7] or azobenzene[4-6] chromophores have been recently shown to undergo an α-helix → random coil conformational transition photoinduced by the trans → cis isomerization of the photochromic groups. Analogous investigations on copolymers of (−)-menthyl acrylate with 4-hydroxystilbene acrylate made it possible to conclude that a local conformational rearrangement of the macromolecules can occur also in this case during the trans → cis isomerization.[10]

The presence of stilbene chromophores directly bound to the main chain of optically active polymers, due to steric requirements, could in principle enhance the side-chain cooperative interactions, which would make the relationships between secondary structure and isomerization phenomena induced by light more evident.

In this paper, the synthesis, structural characterization, and chiroptical properties of optically active copolymers of (−)-menthyl acrylate (MtA) with *trans*-4-vinylstilbene (VS) [poly(MtA-*co*-VS)s] are reported. The investigation of their photochromism will be the subject of a forthcoming paper.



poly(MtA-*co*-VS)

Results and Discussion

Synthesis of *trans*-4-Vinylstilbene (VS). Two slight modifications of known synthetic routes to *trans*-4-vinylstilbene have been investigated (Schemes I and II), as the previously reported procedures[13,14] gave, in our hands, very low overall yields. In the final steps, chlori-

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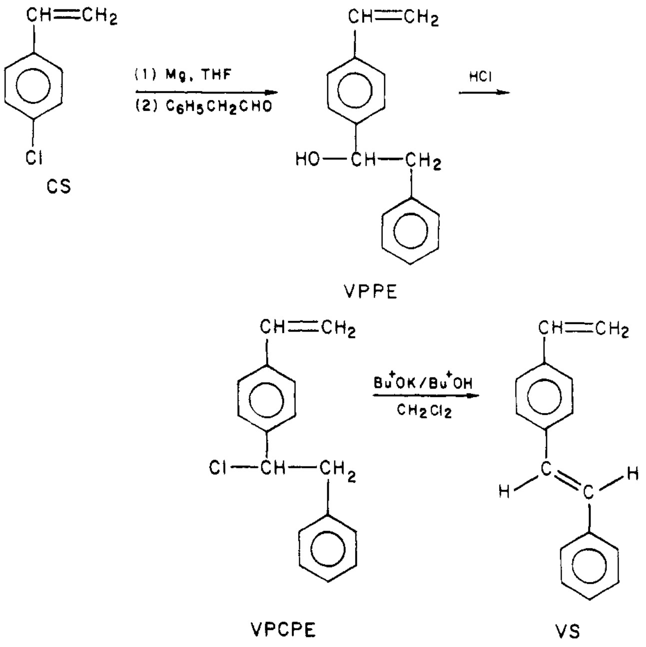
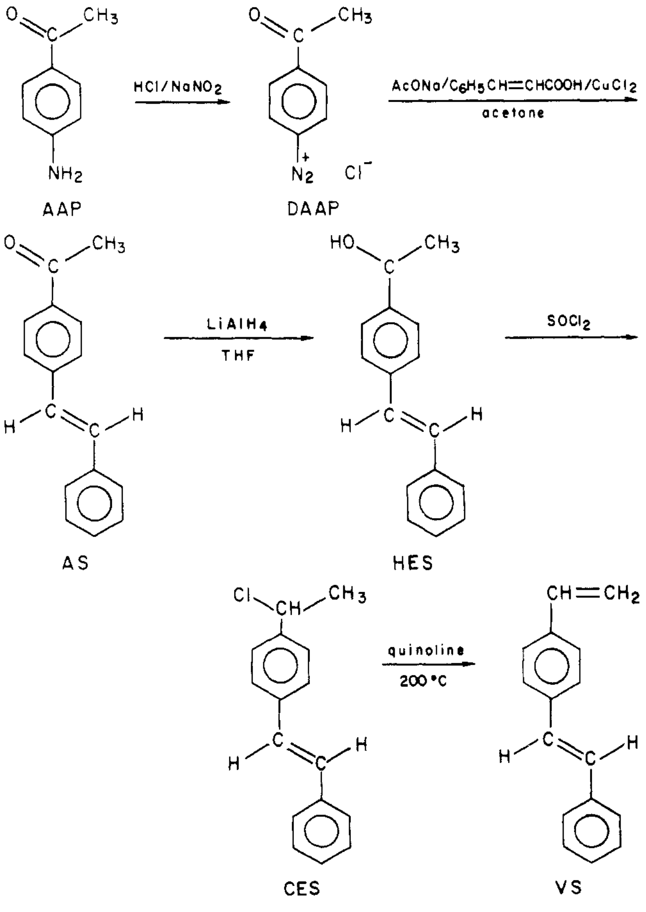
Scheme I



Scheme II



nation and subsequent dehydrochlorination were preferred to direct dehydration of the alcohol, as the latter gave very poor yields when performed on a reasonable scale. The experimental results indicate that the synthetic route of Scheme I is more straightforward and gives larger overall yields (35.0%) as compared to Scheme II (11.7%).

Polymer Synthesis and Characterization. The radical-initiated copolymerization experiments were performed at 60 °C in benzene with AIBN as the initiator. All the runs were stopped at low conversion (<11%) in order to determine reactivity ratios and to obtain polymeric products having a homogeneous composition and distribution of monomeric units (Table I).

^{1}H NMR and IR spectra of poly(MtA-*co*-VS)s show the same bands as the corresponding homopolymer mixtures. The presence in the IR spectra of the copolymers of a strong band at 965 cm^{-1} related to the *trans*-stilbene chromophore and the absence in both the ^{1}H NMR and IR spectra of the signals due to the vinyl group indicate that these polymerizations occur through the reaction of the vinyl group. In particular, the IR spectra show that the bands at 1420 and 695 cm^{-1} and those at 1385 and 1165 cm^{-1}, assignable to VS and MtA units, respectively, can be used for analytical purposes. Accordingly the plots of absorbance ratio R_1 or R_2 [expressed as $A_{1420}/(A_{1420} + A_{1385})$ or $A_{695}/(A_{695} + A_{1165})$, respectively] as a function of composition calculated according to ^{1}H NMR analysis give two smooth monotonic calibration curves (Figure 1) from which

Table I
Synthesis[a] and Structural Properties of Poly(MtA-*co*-VS)s

			copolymer		
feed, mol% VS	duration h	convrsn,[b] %	co-units from VS, mol %[c]	$\bar{M}_w$[d]	$\bar{M}_w/\bar{M}_n$[d]
100.0	49	25.1	100.0	55500	1.78
72.8	8	6.3	89.5	53000	1.61
46.1	8	11.3	78.5	50000	1.67
30.4	7.5	10.7	67.5	35000	1.40
20.9	7.5	8.0	57.8	31000	1.31
11.0	8	3.9	41.0	30500	1.28
5.8	8	3.2	26.0	32000	1.23
3.3	9	4.9	14.9	69000	1.37

[a] In benzene at 60 °C using AIBN [1% (w/w)] as radical initiator. [b] Calculated as (weight of total polymer)/(weight of starting comonomers) × 100. [c] Evaluated by ^{1}H NMR analysis. [d] Determined by GPC measurements.

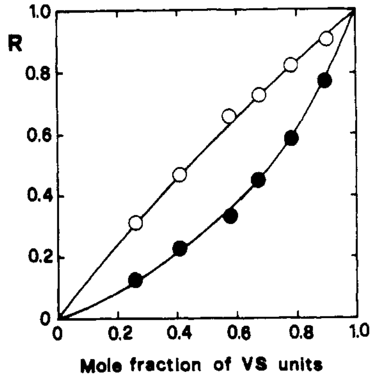


Figure 1. Ratios (R) of IR absorbances vs. copolymer composition: (●) $R_1 = [A_{1420}/(A_{1420} + A_{1385})]$; (○) $R_2 = [A_{695}/(A_{695} + A_{1165})]$.

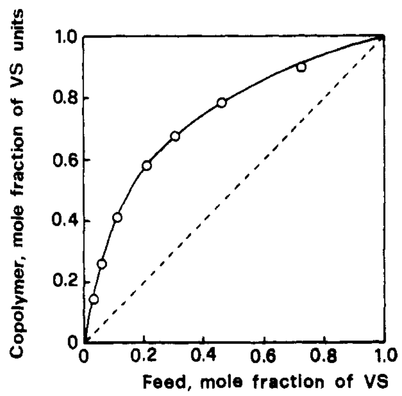


Figure 2. Copolymerization diagram for the (−)-menthyl acrylate (MtA)/*trans*-4-vinylstilbene (VS) system.

Table II
Average Sequence Lengths ($\bar{l}_{VS}$ and $\bar{l}_{MtA}$) and Molar Fractions (%) ($X_{VS(n)}$ and $X_{MtA(n)}$) of Units from VS and MtA in Sequence Lengths of n Units in Poly(MtA-co-VS)s

mole fraction of units from VS, %	$\bar{l}_{VS}$	$\bar{l}_{MtA}$	n											
			$X_{VS(n)}$						$X_{MtA(n)}$					
			1	2	3	4	5	>5	1	2	3	4	5	>5
89.5	10.5	1.1	1.2	2.1	2.8	3.4	3.9	86.8	89.4	9.2	0.8	0.0	0.0	0.0
78.5	4.0	1.2	6.2	9.3	10.4	10.4	9.8	53.9	73.0	21.4	4.6	1.0	0.0	0.0
67.5	2.5	1.3	15.8	19.1	17.4	14.1	10.6	23.0	56.3	28.3	10.6	3.6	1.1	0.1
57.8	1.9	1.6	27.3	26.3	18.9	12.2	7.4	7.9	41.5	29.7	15.9	7.5	3.2	2.2
41.0	1.4	2.2	48.7	29.5	13.4	5.3	2.1	1.0	21.0	22.9	18.7	13.5	9.2	14.7
26.0	1.2	3.4	67.4	23.9	6.4	1.6	0.4	0.3	8.7	12.2	13.0	12.1	10.7	43.3
14.9	1.1	5.3	79.7	17.1	2.7	0.4	0.0	0.0	3.4	5.5	6.6	7.2	7.3	70.0

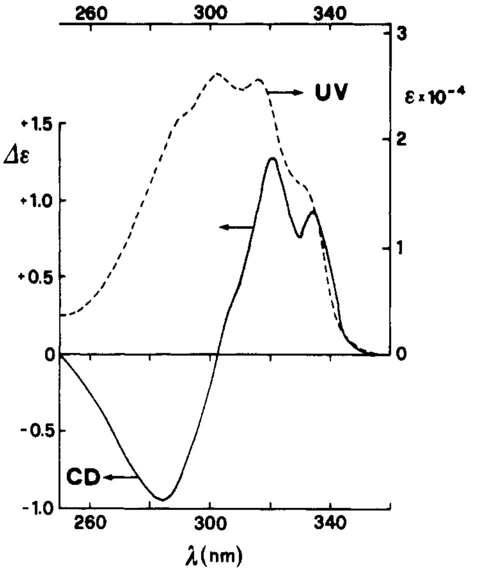


Figure 3. UV (- - -) and CD (—) spectra in the 350–250-nm region of poly(MtA-*co*-VS) with 41.0 mol % VS units in chloroform solution at 25 °C.

the copolymer composition can be directly evaluated.

The copolymerization diagram (Figure 2) shows that, over the entire range of composition, the content of VS units is always larger in the copolymers than in the corresponding feed, suggesting a larger reactivity of VS with respect to MtA. Accordingly, the reactivity ratios, calculated by the least-squares evaluation of the Kelen–Tüdös parameters[15] (r_{VS} = 3.57 and r_{MtA} = 0.15), show that the VS radical greatly favors its own monomer rather than MtA, the opposite occurring for the MtA radical. The product of reactivity ratios is smaller than unity ($r_{VS}r_{MtA}$ = 0.54) and indicates that the distribution of the monomeric units is not approximately random. A certain tendency to alternation occurs, even if the probability of blocks of VS units is on average larger than that of MtA units.

The average sequence lengths of VS and MtA units ($\bar{l}_{VS}$ and $\bar{l}_{MtA}$), calculated according to Mayo and Walling,[17] are reported in Table II. The mole percent of VS and MtA units [$X_{VS(n)}$ and $X_{MtA(n)}$] inserted in sequence lengths of n units derived from VS and MtA, respectively, was also evaluated,[18] with n varying in the range 1–5 (Table II).

UV spectra in $CHCl_3$ solution of poly(MtA-*co*-VS)s in the all-trans configuration show a structured absorption band between 360 and 250 nm with two relative maxima around 303 and 316 nm and two shoulders around 290 and 330 nm (Figure 3), corresponding to the first $\pi \rightarrow \pi^*$ ($^1B \leftarrow {}^1A$) electronic transition of the *trans*-stilbene chromophore,[19] analogous to that observed for the low molecular weight model compounds *trans*-4-methylstilbene (MS). When the content of VS units decreases from 100 to 14.9 mol %, the molar extinction coefficient at 303 nm (ϵ_{303}) linearly increases from 22 800 to 27 700 L mol^{-1} cm^{-1} (Figure 4), the corresponding ϵ_{max} for MS being 30 200. At the same time a variation of the relative intensities of absorption vibrational structure (Frank–Condon progression) and a slight progressive bathochromic effect are observed. A substantially analogous trend was also found for the copolymers of MtA with *trans*-4-hydroxystilbene acrylate (SA)[8,10] and it was reported also to occur in many polymers containing side-chain aromatic chromophores.[20,21] This behavior has been attributed[22,23] to the presence of adjacent aromatic monomeric units, the molar extinction coefficient of interacting chromophores being lower than that of the corresponding isolated units.

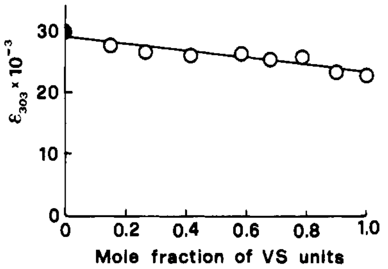


Figure 4. Molar extinction coefficient at 303 nm (ϵ_{303}) in chloroform solution of poly(MtA-*co*-VS)s vs. composition.

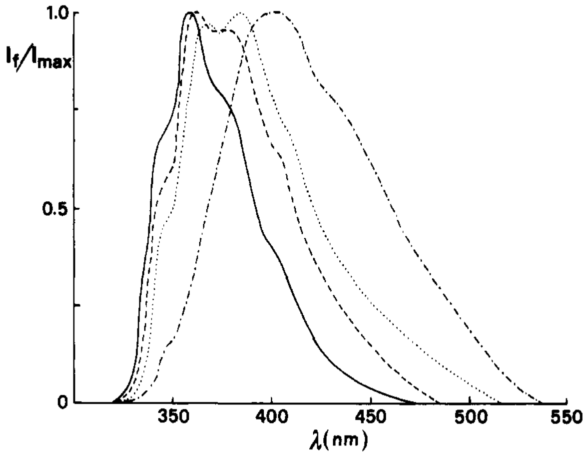


Figure 5. Corrected fluorescence emission spectra of *trans*-stilbene derivatives in chloroform solution at 25 °C (λ_{exc} = 280 nm, normalization at maximum of fluorescence intensity): (—) MS; (- - -) poly(MtA-*co*-VS) with 14.9 mol % VS units; (···) poly(MtA-*co*-VS) with 41.0 mol % VS units; (-·-) poly(VS).

The fluorescence spectrum in $CHCl_3$ solution of the low molecular weight model compound MS shows a structured emission band with a maximum at 360 nm and three shoulders at 345, 375, and 405 nm (Figure 5). As compared with MS, the emission maximum of poly(MtA-*co*-VS)s in the all-trans configuration progressively shifts toward longer wavelengths (from 362 to 405 nm) with increasing content of VS units from 14.9 to 100 mol %

Table III
Optical Activity at 589 nm and Circular Dichroism Data for Poly(MtA-*co*-VS)s in the All-Trans Configuration

copolymer		homopolymer mixture		CD measurements	
mol % VS units	$[\alpha]^{25}{}_{C}$[a]	$[\alpha]^{25}{}_{M}$[b]	$\Delta[\alpha]$[c]	$\Delta\epsilon_{322}$[d]	$\Delta\epsilon_{285}$[d]
89.5	+0.63	-8.2	+8.8	+0.26	-0.16
78.5	+0.97	-16.8	+17.7	+1.22	-0.47
67.5	-2.28	-25.4	+23.1	+1.40	-0.61
57.8	-7.50	-32.9	+25.4	+1.52	-0.86
41.0	-23.41	-45.9	+22.5	+1.48	-0.96
26.0	-42.48	-57.4	+14.9	+1.13	-0.53
14.9	-58.61	-65.8	+7.2	+0.48	-0.35
0.0	-77.20	-77.2	0.0		

[a] In chloroform solution; l = 1 dm. [b] Evaluated as $[\alpha]^{25}{}_{M} = [\alpha]^{25}{}_{0} w_{MtA}$, where $[\alpha]^{25}{}_{0}$ is the specific rotatory power of poly[(−)-menthyl acrylate] and w_{MtA} is the weight fraction of MtA in the homopolymer mixture. [c] Calculated as $[\alpha]^{25}{}_{C} - [\alpha]^{25}{}_{M}$. [d] In $CHCl_3$ solution; l = 1 cm, expressed as L mol^{-1} cm^{-1}.

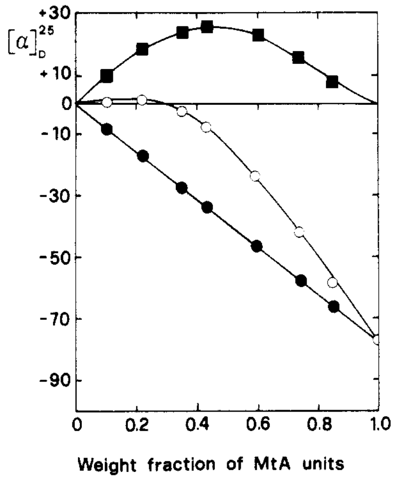


Figure 6. Specific rotatory power at 589 nm in chloroform solution of (○) poly(MtA-*co*-VS)s and (●) homopolymer mixtures, (■) contribution to specific rotatory power from VS units ($\Delta[\alpha]$).

(Figure 5). Such behavior can be attributed to the increasing contribution of excimer emission. However, as suggested by UV spectra, also the distortion of the vibrational modes of excited stilbene chromophores in VS unit sequences could be at least partially responsible for the observed phenomenon.

Chiroptical Properties. All the copolymers in $CHCl_3$ solution are optically active at 589 nm, analogously to other copolymers of MtA with different achiral vinyl aromatic comonomers.[9,10,20,24-26] However, contrary to what was reported for these latter systems, a nonlinear dependence of the specific rotatory power at the sodium D line ($[\alpha]^{25}{}_{D}$) on composition was observed for poly(MtA-*co*-VS)s in the all-trans configuration. In fact $[\alpha]^{25}{}_{D}$ (Table III and Figure 6) shows negative values for contents of MtA units larger than 30 mol %, whereas positive values of optical activity are observed for copolymers containing less than 30 mol % chiral co-units, the maximum value being reached at about 20 mol % MtA units. The above data clearly indicate that the VS units contribute to optical activity at 589 nm depending on copolymer composition. The difference between the specific optical activity of the copolymers and that of the corresponding homopolymer mixtures is the contribution of VS units to the specific rotatory power at the sodium D line ($\Delta[\alpha]$) (Table III). As shown in Figure 6 this contribution, and hence the induced chirality on stilbene chromophores, is maximized in the range of 40–70 mol % VS units. This can be explained by assuming that *trans*-stilbene chromophores in sections of VS units have a mutual geometrical disposition of a prevailing chirality induced by the optically active MtA units. An analogous situation was reported to occur in the case of coisotactic copolymers of trityl methacrylate (TrMA) with (*S*)-α-methylbenzyl methacrylate,[27] which, contrary to what was observed for poly[(*S*)-α-methylbenzyl methacrylate], display a positive optical rotation, probably connected with the existence of isotactic sequences of TrMA units having helical conformations of one prevailing screw sense.

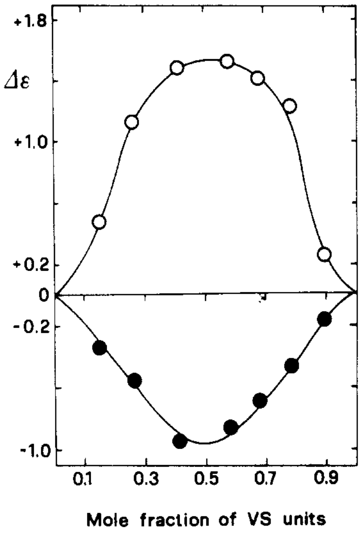


Figure 7. Differential dichroic absorption coefficient at 322 nm (○) and at 285 nm (●) for poly(MtA-*co*-VS) in chloroform solution as a function of composition.

The copolymers containing the stilbene moieties in the all-trans configuration show, in $CHCl_3$ solution between 400 and 250 nm, two CD bands of opposite sign, which could be assigned to the exciton splitting[28] of the lowest energy $\pi \rightarrow \pi^*$ electronic transition of the *trans*-stilbene chromophore, as for poly(L-glutamates) with pendant *trans*-stilbene moieties.[7] The positive CD band displays two relative maxima at 335 and 322 nm and a shoulder around 305 nm (Figure 3), whereas the negative CD band has no definite vibrational structure and is centered at about 285 nm. The former band may be responsible for the positive optical rotation observed at 589 nm in the samples containing a large percentage of VS units. The values of the differential dichroic absorption coefficients around 322 and 285 nm ($\Delta\epsilon_{322}$ and $\Delta\epsilon_{285}$), reported in Table III, are markedly larger than those observed in the case of the copolymers of MtA with 4-hydroxystilbene acrylate (SA).[10] Furthermore, in this latter system no evidence of a couplet occurred, only one negative CD band being observed. The difference in behavior of these two systems may be related to the larger conformational rigidity of the *trans*-stilbene moieties in poly(MtA-*co*-VS)s than in poly(MtA-*co*-SA)s, where the presence of an ester spacer group increases the rotational freedom of side-chain aromatic chromophores. The dependence of the ellipticity of both CD bands on copolymer composition does not show a monotonic trend, a maximum being observed around 50 mol % VS units (Figure 7). Analogous results have been reported in the case of optically active copolymers of MtA with *p*-vinyltrifluoroacetophenone,[25] of 9-vinylcarbazole with (−)-menthyl vinyl ether,[18] (−)-menthyl methacrylate (MtMA),[21] and MtA,[21] and of acenaphthylene with MtMA.[29] In such systems this behavior was tentatively attributed to the overlapping of two opposite contributions: (i) an increase of ellipticity with increasing content of chiral co-units and consequently of the asymmetric induction on the side-chain chromophores and (ii) a decrease of ellipticity due to the reduction of the probability of dipole–dipole interactions involving the pendant chromophores, their distance increasing with decreasing aromatic unit content. It is of interest to mention that the maximum of ellipticity of *trans*-stilbene chromophores is observed for the same copolymer compositions (40–70 mol % VS units) that maximize the content of sequences of 2–4 VS units (Table II). This result is quite reasonable because, due to the low stereoregularity of the polymeric samples, the dissymmetry induced on the *trans*-stilbene chromophores by chiral MtA units can be transmitted only through short sequences of VS units where dipole–dipole interactions between aromatic chromophores, thought to be responsible for most of the observed CD,[30] can still occur. This explanation is supported by the observation that whenever ellipticity is maximized this occurs for sequences lengths of about 2–4 aromatic units, independent of the type of copolymer.[18,21,25,29] It may be concluded therefore that the copolymer macromolecules, due to steric cooperative effects deriving from *trans*-stilbene moieties directly bound to the main chain, can exist, at least for short sections, in a dissymmetric conformation of one prevailing chirality.

Experimental Section

Materials. (−)-Menthyl acrylate (MtA) having $[\alpha]^{25}_{D}$ −89.0° (neat) was prepared and purified as previously reported.[20] 1-(4-Vinylphenyl)-2-phenylethanol (VPPE) was prepared in 81.9% yield from 4-chlorostyrene (CS) as reported elsewhere.[13]

1-(4-Vinylphenyl)-1-chloro-2-phenylethane (VPCPE). A mixture of 60 mL of concentrated aqueous HCl, 14.0 g (62.4 mmol) of VPPE, and some drops of Et_3N was stirred at room temperature for 24 h. The mixture was extracted with chloroform, and the combined extracts were washed with 5% aqueous $NaHCO_3$ and with water. After drying over anhydrous Na_2SO_4 and removal of the solvent under vacuum, 13.3 g of VPCPE, as a yellow-brown oil, was obtained in 87.8% yield; ^1H NMR ($CDCl_3$) δ = 7.4–6.6 (m, aromatic protons and $HC{=}C$, 10 H), 5.8–5.2 (m, $C{=}CH_2$, 2 H), 4.9 (t, $CHCl$, 1 H), 3.3 (d, CCH_2).

***trans*-4-Acetylstilbene (AS)** was obtained in 19.1% yield as a yellow solid, mp 132 °C, starting from 4-aminoacetophenone (AAP) according to the procedure reported[14] for the synthesis of *trans*-4-formylstilbene; ^1H NMR ($CDCl_3$) δ = 8.1–7.1 (m, stilbene protons, 11 H), 2.5 (s, H_3CC, 3 H).

***trans*-4-(1-Hydroxyethyl)stilbene (HES)** was obtained in 91.5% yield by $LiAlH_4$ reduction of AS in THF as an ivory solid (mp 118 °C); ^1H NMR ($CDCl_3$) δ = 7.9–7.1 (m, stilbene protons, 11 H), 4.9 (q, $CHCH_3$, 1 H), 2.1 (s, $HOCH$, 1 H), 1.6 (d, $CHCH_3$, 3 H).

***trans*-4-(1-Chloroethyl)stilbene (CES)** was obtained[31] in 92.3% yield as a yellowish solid, mp 113 °C, by $SOCl_2$ chlorination of HES; ^1H NMR ($CDCl_3$) δ = 7.9–7.1 (m, stilbene protons, 11 H), 5.1 (q, $ClCHCH_3$, 1 H), 1.8 (d, $ClCHCH_3$, 3 H).

***trans*-4-Vinylstilbene (VS). (a) By Dehydrochlorination of VPCPE.** Potassium 60 g (0.153 g atom) was added under dry nitrogen to 100 mL of *tert*-butyl alcohol, the reaction mixture was heated with stirring until the complete dissolution of the metal, and 13.3 g (54.8 mmol) of VPCE dissolved in 100 mL of anhydrous CH_2Cl_2 was added at room temperature. After 48 h the reaction mixture was washed with water, dilute aqueous HCl, water, 5% aqueous $NaHCO_3$, and water, in that order. After drying over anhydrous Na_2SO_4 and removal of the solvent under vacuum, an orange solid product was obtained. This was crystallized from methanol and then eluted over (70–230 mesh ASTM) silica gel using a $CHCl_3$/*n*-heptane eluent [1:4 (v/v)]. This procedure gave 5.5 g of VS (48.7% yield) as white lamellae, mp 160 °C, as reported elsewhere,[2,3] which were stored in the dark at −20 °C.

(b) By Dehydrochlorination of CES. VS was obtained in 72.5% yield by dehydrochlorination of CES in quinoline at 200 °C[31]; ^1H NMR ($CDCl_3$) δ = 7.7–7.1 (m, stilbene protons, 11 H), 6.8 (two d, $HC{=}C$, 1 H), 5.8–5.3 (two d, $C{=}CH_2$, 2 H). The IR spectrum shows the typical bands of the vinyl group (995 and 905 cm^{-1}), the monosubstituted phenyl ring (760 and 690 cm^{-1}), the 1,4-disubstituted phenyl ring (825 cm^{-1}), and the diphenyl-substituted trans double bond (965 cm^{-1}).

***trans*-4-Methylstilbene (MS).** MS was prepared according to the procedure reported for VS in Scheme II. Starting from 8 g (7.5 mmol) of *p*-toluidine and 11 g (7.4 mmol) of cinnamic acid, 3.2 g (22% yield) of MS as an orange solid was obtained after crystallization from *n*-hexane. MS was further purified by elution chromatography on (70–230 mesh ASTM) Al_2O_3 and SiO_2, in that order, using a chloroform/*n*-hexane [1:1 (v/v)] mixture as eluent, to give pure white lamellae, mp 132 °C; ^1H NMR ($CDCl_3$) δ = 7.8–7.0 (m, stilbene protons, 11 H), 2.4 (s, CH_3, 3 H). The IR spectrum shows bands at 2910 and 2850 cm^{-1} connected with asymmetric and symmetric stretching vibrations of carbon–hydrogen bonds of the methyl group, respectively, and bands typical of the monosubstituted phenyl ring (750 and 690 cm^{-1}), the 1,4-disubstituted aromatic nucleus (805 cm^{-1}), and the diphenyl-substituted carbon–carbon double bond of the stilbene system in the trans configuration (970 cm^{-1}).[14]

2,2′-Azobis(isobutyronitrile) (AIBN). The commercial product from Fluka was recrystallized from ethanol.

Copolymerization Experiments. Free radical copolymerizations were performed in benzene at 60 °C in glass vials sealed under high vacuum, using AIBN [1% (v/v)] as initiator. After a suitable time the polymerization was stopped by pouring the reaction mixture into a large excess of methanol. The coagulated polymer was successively purified by repeated precipitations in methanol from chloroform solution. Finally, the polymeric product was filtered, dried under vacuum at room temperature, and stored in the dark at −20 °C.

Polymer Characterization. ^1H NMR spectra were performed in $CDCl_3$ solution with a Varian T-60 or XL100 spectrometer, using Me_4Si as internal standard. The composition of poly(MtA-*co*-VS)s was determined by comparing the area of the broad signals centered at about 7.2 ppm, due to the protons of side-chain stilbene moieties, with that of the signals near 4.6 and 2.8–0.5 ppm, relevant to the saturated aliphatic protons from both monomeric units.

IR spectra of a cast film of the polymer sample or a KBr pellet were recorded on a Perkin-Elmer Model 180 spectrophotometer. The absorbances A_{1420}, A_{1385}, A_{1165}, and A_{695} were calculated, for quantitative determination of copolymer composition, from IR transmission spectra using base lines drawn between 1480 and 1400, 1400 and 1350, 1230 and 1130, and 715 and 650 cm^{-1}, respectively.

UV spectra in the range 400–250 nm were recorded in $CHCl_3$ solution on a Cary 14 or Cary 219 spectrophotometer. Concentrations in the range $(3\text{–}5) \times 10^{-5}$ mol L^{-1} stilbene chromophores and a cell path length of 1 cm were used. The molar extinction coefficient (ϵ) in the polymer sample is referred to one VS monomeric unit and is expressed in L mol^{-1} cm^{-1}.

CD spectral measurements in the range 400–250 nm were carried out at 25 °C in $CHCl_3$ solution, with spectra recorded with a Jasco J500B dichrograph using a cell path length of 1 cm. Concentrations in the range $(3\text{–}5) \times 10^{-5}$ mol L^{-1} VS units were used. The molar differential dichroic absorption coefficient ($\Delta\epsilon$) is referred to one VS unit and is expressed as L mol^{-1} cm^{-1}.

Fluorescence emission spectra were recorded by a Perkin-Elmer MPF3 spectrofluorimeter on chloroform solutions having an absorbance lower than 0.4. Experimental spectra were corrected for the detector wavelength response.

Optical rotatory measurements were performed on polymer solutions in $CHCl_3$ at 25 °C by a Perkin-Elmer 141 spectropolarimeter having a sensitivity of ±0.003°. A cell path length of 1 dm and concentrations of 1–5 g/dL were used.

Average molecular weights of polymers were determined by GPC measurements on a Perkin-Elmer Model 2/2 HPLC, equipped with A 802/S and A 803/S Shodex columns connected in series and a variable-wavelength Perkin-Elmer LC75 UV detector. Polystyrene standards were used for calibration curve.

Melting point measurements were performed on a hot-plate Köfler microscope at a 3 °C/min heating rate.

Registry No. VS, 23602-48-4; MtA, 4835-96-5; VPPE, 91742-23-3; VPCPE, 91742-24-4; AS, 20488-42-0; AAP, 99-92-3;

HES, 91742-25-5; CES, 91742-26-6; MS, 1860-17-9; poly(MtA-*co*-VS), 90168-61-9.

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Optically Active Hydrocarbon Polymers with Aromatic Side Chains. 12. Synthesis and Characterization of Coisotactic Copolymers of (*S*)-4-Methyl-1-hexene with Styrene

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ABSTRACT: The preparation of five styrene/(*S*)-4-methyl-1-hexene copolymer samples in the presence of a stereospecific catalyst [$TiCl_4/Al(i\text{-}C_4H_9)_3$] is reported, and reactivity ratios $r_{St} = 0.76$ and $r_{4MH} = 1.65$ have been evaluated for styrene and (*S*)-4-methyl-1-hexene, respectively. The fractionation of the crude copolymerization products by extraction with boiling solvents led to fractions whose chemical composition and relevant spectroscopic characteristics provided qualitative and quantitative information on the distribution of monomer units. This turned out to be completely different from the quasi-random distribution expected from the reported values of the reactivity ratios.

Introduction

Early studies of the copolymerization of a prochiral monomer such as styrene, with an optically active α-olefin by anionic coordinate stereospecific catalysis, led to the synthesis of copolymers characterized by marked induced optical rotation detectable at the level of the aromatic co-units.[1] Accordingly, the potential of this copolymerization method was stressed both with respect to the synthesis of a wide variety of new optically active polymeric materials[2,3] and to the investigation of the chain conformation in solution, by chiroptical techniques.[4,5] To gain a better understanding of the correlation between the circular dichroism of aromatic chromophores and the extent of conformational homogeneity, accurate knowledge of chemical composition, distribution of monomer units, and tacticity are prerequisites to any further speculation on the usefulness of the copolymerization technique and on the polymerization mechanism. While information relevant to the chemical composition of copolymers can be easily achieved by chemical and spectroscopic analysis, only a qualitative measure of the microstructure has been gained by fractionation of the crude polymers with boiling solvents.[2]

The copolymerization of styrene with α-olefins other than propylene has been rather extensively studied since the early sixties and noteworthy are the contributions given in a series of papers by Anderson et al.,[6–9] Overberger and Miyamichi,[10] and Baker and Tait.[11] As a general comment we may stress that the apparent reactivity ratios, reported for copolymerization experiments carried out under different conditions, are affected, other things being equal, by the nature of the catalyst. Moreover, styrene appears to be generally less reactive than linear and far branched α-olefins, whereas with respect to 3-substituted α-olefins styrene displays a marked higher reactivity.

In a previous study[12] on the monomer sequence distribution in copolymers of styrene with chiral α-olefins [(*R*)-3,7-dimethyl-1-octene and (*S*)-4-methyl-1-hexene] prepared in the presence of a $VCl_4/Al(i\text{-}C_4H_9)_3$ Ziegler–Natta catalyst, a random distribution with some tendency

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