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Synthesis and Characterization of Optically Active Copolymers of Acenaphthylene. 1. Preparation and Characterization

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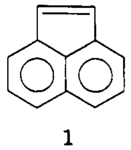
ABSTRACT: Optically active copolymers of acenaphthylene (1) with (−)-menthyl acrylate (2) and (−)-menthyl methacrylate (3) were prepared by free radical initiation in benzene at 70 °C. Reactivity ratios, mean sequence length, and distribution of monomeric units estimated for both copolymer series indicate the formation of quasi-random copolymers, with a higher tendency to blockiness for 1 units. UV and ^{1}H NMR spectra are entirely consistent with these observations and typical signals of strongly interacting aromatic moieties can be identified in the UV short-wavelength region and in the ^{1}H NMR aromatic proton region, respectively. Infrared absorption properties of acenaphthylene homopolymer and copolymers indicate a preferential trans-disyndiotactic configuration of the aromatic unit.

Introduction

Following our interest in the study of optically active vinyl polymers containing side-chain fluorescent groups[1-5] we have undertaken a systematic investigation of chiral copolymers containing acenaphthylene units. Interest in such polymers centers on the fact that the aromatic unit is incorporated in the macromolecular backbone in such a way as to prohibit the coplanar alignment of neighboring chromophores usually invoked to explain excimer formation in vinyl aromatic polymers.[6]

Copolymer systems containing acenaphthylene units have been previously investigated by some other groups;[7-10] however, the use of optically active comonomers affords an additional and powerful tool for further clarification of their unusual properties. It is well established that the chiroptical properties of optically active polymers containing side-chain aromatic chromophores have been extremely useful in assigning a primary and secondary structure to such macromolecules in solution.[11] The peculiarities observed in the fluorescence of acenaphthylene copolymers can be explained only on the basis of distributions of monomeric units and local configurational and conformational order.

In the present paper are reported the synthesis and the structural characterization of two series of copolymers of acenaphthylene (1) with easily accessible chiral comonomers, such as (−)-menthyl acrylate (2) and (−)-menthyl methacrylate (3). Circular dichroism and fluorescence emission properties of these copolymers will be the object of a forthcoming paper.[12]



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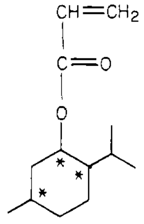

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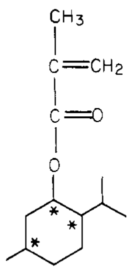

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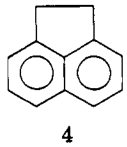

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Experimental Part

Materials. Commercial 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Commercially available acenaphthylene (1) was purified by elution on alumina with petroleum ether and subsequent crystallization from absolute ethanol to give bright yellow needles, mp 92–93 °C. Commercial (−)-menthol [(1*R*,3*R*,4*S*)-1-methyl-4-isopropylcyclohexan-3-ol] was recrystallized from isooctane {mp 43–45 °C; $[\alpha]^{25}_{\mathrm{D}}$ −49.6° (ethanol)}. (−)-Menthyl acrylate (2) {$[\alpha]^{25}_{\mathrm{D}}$ −89.9° (benzene), optical purity 97.0%[13]} was prepared according to the procedure of Frank et al.[14] (−)-Menthyl methacrylate (3) {$[\alpha]^{25}_{\mathrm{D}}$ −91.8° (neat), optical purity

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Table I
Copolymerization of Acenaphthylene (1) with (−)-Menthyl Acrylate (2) in Benzene at 70 °C

	polymerization conditions[a] amount of 1			polymeric product				
run	mmol	mol %	convrsn,[b] %	counits[c] from 1, mol %	$\bar{M}_n$[d] × 10^{-3}	$\bar{M}_w/\bar{M}_n$[d]	$[\alpha]^{25}_D$,[e] deg	$[\alpha]_0$,[f] deg
A1	0.1	1.0	81.3	1.2			−76.1	−76.5
A2	0.5	5.0	12.0	15.1	10.4	1.51	−65.2	−67.0
A3	1.0	10.0	1.0	48.9	7.2	1.36	−47.4	−45.2
A4	2.0	20.0	2.0	69.7	6.5	1.43	−26.6	−28.7
A5	3.0	30.0	4.0	76.3	6.9	1.65	−22.8	−23.0
A6	4.0	40.0	9.4	86.7	6.3	1.83	−14.0	−13.4
A7	6.0	60.0	18.1	93.5	8.4	1.87	−6.9	−6.7
A8	7.0	70.0	23.1	94.1	9.4	1.92	−5.7	−6.1
A9	8.0	80.0	24.3	94.5	14.1	1.79	−5.4	−5.6
A10	9.0	90.0	33.2	95.0	13.6	1.79	−3.9	−5.2

[a] Total comonomer concentration [1] + [2] = 1.0 M; comonomers/AIBN molar ratio = 100; polymerization time 8-25 h. [b] Calculated as [(weight of solid polymer)/(weight of starting comonomers)] × 100. [c] Determined by NMR and UV spectroscopy. [d] By GPC in tetrahydrofuran. [e] In dichloromethane. [f] Evaluated for homopolymer mixtures having the same composition as the corresponding copolymer.

99.0%[15]) was obtained from the reaction of methacryloyl chloride with (−)-menthol in pyridine in the presence of copper powder.[15] Commercially available acenaphthene (4) was twice crystallized from absolute ethanol to give white needles, mp 95.5 °C.

Polymerization Experiments. All polymerizations were carried out in benzene solution at 70 °C in the presence of AIBN in sealed glass tubes after repeated outgassing cycles. Total comonomer concentration of 1.0 M and comonomers/initiator ratio of 100 were used. Polymerizations were stopped after 7–60 h by pouring the reaction mixture into a large excess of methanol. The precipitated polymeric products were isolated by filtration, purified by several precipitations from chloroform into methanol, and dried in vacuo at room temperature.

The copolymer compositions were determined by ^{1}H NMR spectroscopy and for the samples with 1 unit content lower than 30 mol % a UV evaluation was also performed on the basis of the absorption at about 295 nm.

Polymer Characterization. Optical rotatory power measurements were performed at the sodium D line at 25 °C on a Perkin-Elmer 141 spectropolarimeter with a sensitivity of ±0.003°. Dichloromethane solutions having concentrations in the range 2–5 g/dL (path length 1 dm) were used.

100-MHz ^{1}H NMR spectra were recorded at 160 °C on a Jeol PS 100 spectrometer in hexachloro-1,3-butadiene solution with hexamethyldisiloxane (HMDS) as an internal standard.

Infrared spectra were recorded on Perkin-Elmer 180 and 283B spectrometers in thin films of the polymers cast by slow evaporation of the solvent ($CHCl_3$ or CH_2Cl_2) on KBr disks.

Ultraviolet measurements were performed in dichloromethane solution in the spectral region 350–225 nm, using a Cary 14 spectrophotometer (path length 0.1–1 cm).

Gel permeation chromatography (GPC) traces were taken by a Perkin-Elmer 2/2 chromatograph equipped with Shodex S802 and S803 columns and a Perkin-Elmer LC75 UV detector using tetrahydrofuran as an eluent. Monodisperse polystyrene standard samples were employed for molecular weight calibration.

Results and Discussion

Synthesis and Characterization. The copolymerization of acenaphthylene (1) with (−)-menthyl acrylate (2) and (−)-menthyl methacrylate (3) was carried out in benzene solution at 70 °C in the presence of AIBN as a radical initiator. Copolymerization runs were stopped whenever possible at low conversion in order to obtain copolymers having a substantially homogeneous composition and distribution of the monomeric units. In all cases the crude copolymers were isolated as white fine powders and were soluble in most common organic solvents. NMR and IR spectra exhibit the typical signals of both homopolymer mixtures and indicate a regular head-to-tail enchainment of comonomer units through the olefinic double bonds. No appreciable hydrolysis of the menthyl esters occurred during the polymerization process nor in the subsequent purification stages. The actual formation of copolymers with low to medium molecular weights ($\bar{M}_n$ = 6000–35 000) and relatively narrow dispersions ($\bar{M}_w/\bar{M}_n$ = 1.4–1.9) was also proved by GPC measurements in tetrahydrofuran. The polymeric products were found to be slightly degradable in chloroform solution by prolonged exposure to light and heat, whereas no appreciable degradation seemed to occur in the solid state. The copolymer compositions were evaluated by ^{1}H NMR and UV spectroscopy and resulted in accordance, within the limits of the experimental error, throughout all the composition range. Copolymerization data and some properties of poly(1-*co*-2) and poly(1-*co*-3) samples are reported in Tables I and II.

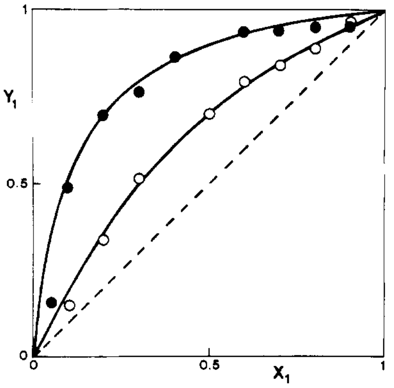

Figure 1. Composition diagram for the copolymerization of acenaphthylene (1) with (●) (−)-menthyl acrylate (2) and (○) (−)-menthyl methacrylate (3). X_1 is the molar fraction of 1 in the feed and Y_1 is the molar fraction of 1 in the copolymer.

In both series, the polymeric products show in all cases a larger content of the units from 1 than the corresponding feed mixture, demonstrating an overall higher reactivity of the aromatic units with respect to the chiral ones (Figure 1). The high reactivity of 1, despite its bulkiness, has been attributed[16] to the strain in the five-membered ring, some of which is relieved on formation of the polymer. Indeed, some conflict is still present in the literature,[8,9,17] especially in the data relevant to the copolymerization of 1 with acrylates and methacrylates. The present results confirm the general trend shown by 1 in the free radical copolymerization. It is, however, fair to mention that the bulkiness of the menthyl group in itself might play some

Table II
Copolymerization of Acenaphthylene (1) with (−)-Menthyl Methacrylate (3) in Benzene at 70 °C

	polymerization conditions[a] amount of 1			polymeric product				
run	mmol	mol %	convrsn[b] %	counits[c] from 1, mol %	$\bar{M}_n$[d] × 10^{-3}	$\bar{M}_w/\bar{M}_n$[d]	$[\alpha]^{25}_D$,[e] deg	$[\alpha]_0$,[f] deg
MA1	1.0	10.0	68.3	14.7	34.9	1.65	−83.2	−85.6
MA2	2.0	20.0	18.2	33.9	24.3	1.69	−63.7	−70.9
MA3	3.0	30.0	35.9	50.1	20.1	1.67	−49.0	−56.9
MA4	5.0	50.0	22.7	70.0	14.0	1.74	−28.8	−37.0
MA5	6.0	60.0	33.7	79.0	12.5	1.82	−21.8	−26.9
MA6	7.0	70.0	36.5	83.7	14.4	1.80	−15.9	−21.3
MA7	8.0	80.0	40.2	88.8	14.3	1.67	−10.2	−15.1
MA8	9.0	90.0	41.7	96.8	12.7	1.85	−5.2	−4.4

[a] Total comonomer concentration [1] + [3] = 1.0 M; comonomers/AIBN molar ratio = 100; polymerization time 20-25 h. [b] Calculated as [(weight of solid polymer)/(weight of starting comonomers)] × 100. [c] Determined by NMR and UV spectroscopy. [d] By GPC in tetrahydrofuran. [e] In dichloromethane. [f] Evaluated for homopolymer mixtures having the same composition as the corresponding copolymer.

Table III
Mean Sequence Length and Sequence Distribution Data of Copolymers of Acenaphthylene (1) with (−)-Menthyl Acrylate (2)

	counits from 1,	mean sequence length[a]		$X_{1(n)}$[b]				$X_{2(n)}$[b]			
run	mol %	$\bar{l}_1$	$\bar{l}_2$	n = 1	n = 2	n = 3	n = 4	n = 1	n = 2	n = 3	n = 4
A2	15.1	1.51	8.00	43.9	29.6	15.0	6.8	1.6	2.7	3.6	4.2
A3	48.9	2.24	3.88	19.9	22.1	18.3	13.5	6.6	9.9	11.0	10.9
A4	69.7	3.79	2.88	7.0	10.2	11.3	11.1	19.2	21.6	18.2	13.6
A6	86.7	7.63	1.54	1.7	3.0	3.9	4.5	42.2	29.6	15.5	7.3
A7	93.5	15.35	1.25	0.4	0.8	1.1	1.4	64.1	25.6	7.6	2.0
A10	95.0	90.72	1.04	0.0	0.0	0.0	0.0	92.5	7.1	0.4	0.0

[a] $\bar{l}_1 = r_1([1]/[2]) + 1$ and $\bar{l}_2 = r_2([2]/[1]) + 1$. [b] Percent fraction of 1 (or 2) units in a closed sequence of *n*.

Table IV
Mean Sequence Length and Sequence Distribution Data of Copolymers of Acenaphthylene (1) with (−)-Menthyl Methacrylate (3)

	counits from 1,	mean sequence length[a]		$X_{1(n)}$[b]				$X_{3(n)}$[b]			
run	mol %	$\bar{l}_1$	$\bar{l}_3$	n = 1	n = 2	n = 3	n = 4	n = 1	n = 2	n = 3	n = 4
MA1	14.7	1.24	6.56	64.9	25.2	7.3	1.9	2.3	3.9	5.0	5.7
MA2	33.9	1.67	3.02	36.1	28.8	17.2	9.2	11.0	14.7	14.7	13.1
MA3	50.1	1.98	2.37	25.5	25.3	18.7	12.4	17.9	20.6	17.9	13.8
MA4	70.0	3.59	1.52	7.8	11.2	12.1	11.7	43.4	29.6	15.2	6.9
MA5	79.0	4.67	1.37	4.6	7.2	8.5	8.9	53.7	28.7	11.5	4.1
MA7	88.8	11.15	1.13	0.8	1.5	2.0	2.4	78.1	18.2	3.2	0.5
MA8	96.8	27.19	1.05	0.1	0.3	0.4	0.5	90.5	8.8	0.6	0.1

[a] $\bar{l}_1 = r_1([1]/[3]) + 1$ and $\bar{l}_3 = r_3([3]/[1]) + 1$. [b] Percent fraction of 1 (or 3) units in a closed sequence of *n*.

special role in controlling the reactivity of the growing polymer chain. We have to remark that a similar relative reactivity of 2 and 3 has been observed in copolymerization with other vinyl aromatic monomers such as styrene[18] and vinylnaphthalene,[19] whereas the opposite trend was found with the heteroaromatic comonomer *N*-vinylcarbazole.[4]

The reactivity ratios were determined by the least-squares treatment of the Kelen–Tüdös parameters[20] derived from the copolymerization data, which were corrected[21] for the relatively high conversions in the poly(1-*co*-3) series and the rather marked difference of reactivity for the poly(1-*co*-2) system. Good linear plots, independent of monomer identity inversion, were obtained in both cases. The values determined are r_1 = 11.2 ± 0.1 and r_2 = 0.32 ± 0.02 and r_1 = 2.91 ± 0.1 and r_3 = 0.46 ± 0.01. These values agree well with an overall higher reactivity of 1 and indicate a substantially statistical distribution with some tendency to form sequences of units from 1 in the case of copolymers with 3, while poly(1-*co*-2) samples essentially have a blocklike structure.

Copolymer microcomposition was evaluated, on the basis of the reported reactivity ratios and corrected monomer concentrations, in terms of mean sequence length ($\bar{l}$) and molar fraction of monomer residues in a closed sequence of *n* units (X_n).[22] In Tables III and IV are collected the statistical data relevant to some poly(1-*co*-2) and poly(1-*co*-3) copolymers, respectively. All the copolymers were optically active and the optical rotation was consistently of negative sign, analogous to the two homopolymers poly(2) and poly(3). The specific optical rotation at the sodium D line ($[\alpha]^{25}_D$) shows practically a linear dependence on the copolymer composition for the poly(1-*co*-2) system (Table I), whereas a small, but definite, contribution by the aromatic chromophore is detected in the poly(1-*co*-3) series (Table II). Figure 2 shows a comparison between the experimental trends and those evaluated for zero contribution from the corresponding homopolymer mixtures. These results indicate the occurrence of induced asymmetry in the acenaphthylene chromophore in the copolymers with 3, even though such induced optical ac-

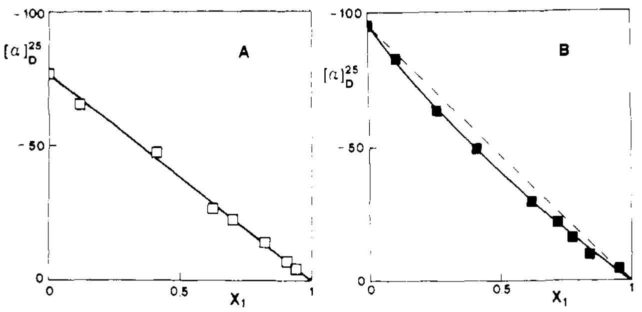

Figure 2. Variation of the specific optical rotation ($[\alpha]^{25}{}_D$) with acenaphthylene (1) weight fraction in copolymers with (A) (–)-menthyl acrylate (2) and (B) (–)-menthyl methacrylate (3).

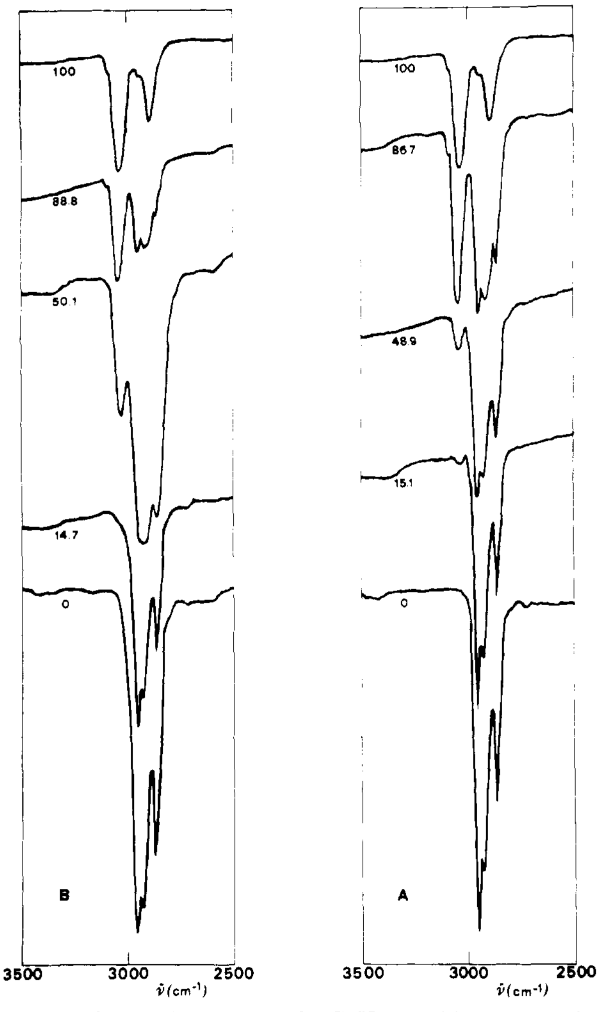

Figure 3. Infrared spectra in the C–H stretching region of copolymers of acenaphthylene (1) with (A) (–)-menthyl acrylate (2) and (B) (–)-menthyl methacrylate (3). Numbers reported on the left side of each spectrum indicate the mol % of 1 units.

tivity cannot be, in principle, ruled out in the series of poly(1-*co*-2).[18,19] An unequivocal proof would be provided by the presence in the circular dichroism spectra of absorption bands related to the transitions of the aromatic moiety inserted in an asymmetrical environment generated by the chiral comonomer.[11,12]

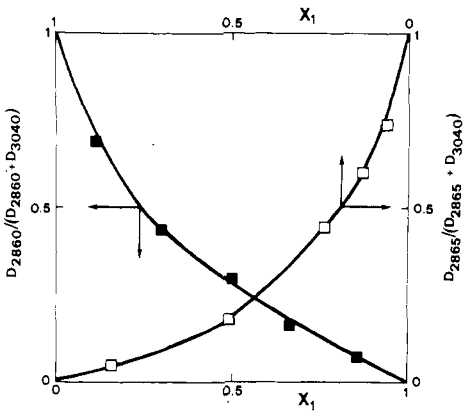

Figure 4. Variation of the optical density ratios $D_{2865}/(D_{2865} + D_{3040})$ and $D_{2860}/(D_{2860} + D_{3040})$ with acenaphthylene (1) molar fraction in copolymers with (□) (–)-menthyl acrylate (2) and (■) (–)-menthyl methacrylate (3).

As anticipated above, the infrared spectra of the copolymers display bands typical of both counits and their relative intensities depend on the chemical composition (Figure 3). In particular, the optical density of the band at 3040 cm^{-1}, in the region of the aromatic C–H stretching, undergoes a marked change with respect to the neighboring bands at 2865 and 2860 cm^{-1}, for poly(1-*co*-2) and poly(1-*co*-3), respectively, in the region of the aliphatic C–H stretching. A plot of the ratio $D_{2865}/(D_{3040} + D_{2865})$ and $D_{2860}/(D_{3040} + D_{2860})$ vs. the content of 1 in the copolymer gives a smooth monotonic curve (Figure 4), and therefore the composition of a given copolymer could also be determined by IR spectroscopy.

Spectroscopic Properties. Infrared spectroscopy provides further information on the configurational organization of acenaphthylene copolymers. In fact, according to Story and Canty,[23] the absorption band at 2887 ± 10 cm^{-1} is attributed to the aliphatic C–H stretching of the aromatic residue in an essentially trans–disyndiotactic configuration of cationically prepared poly(1). Two bands at 2908 and 2840 cm^{-1} are assigned to a prevailing trans–diisotactic configuration. The cis stereoisomers could not be obtained beyond trimer or tetramer.[23]

In the present work, the occurrence of only one band at 2895 cm^{-1} in poly(1) and in copolymers with 1 content higher than 90 mol % would indicate an essentially trans-disyndiotactic configuration also for free radical hompolymer and copolymers. Unfortunately, the IR spectra of copolymers in the same region are complicated by the presence of overlapping bands due to the C–H stretchings of comonomers **2** and **3**, thus not permitting a detailed investigation by this technique.

More detailed information can be obtained by ^{13}C NMR and these studies, which are of rather special interest, will be the subject of a later publication.[24]

The UV absorption spectra in dichloromethane of poly(1-*co*-2) and poly(1-*co*-3) samples are characterized by two bands with relative maxima at about 295 and 230 nm. The former, showing fine vibronic structure, is related to the partial overlapping $^1L_b \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$ transitions of the naphthalene ring, while the latter is due to the $^1B_b \leftarrow {}^1A$ electronic transition of the aromatic chromophore. They are very similar to those of poly(1) and of acenaphthene (**4**), which can be taken as a rather suitable model compound where no intramolecular interactions occur, but distinct differences can be detected in both the position and the intensity of the UV bands. In fact, in both series of copolymers the low-energy maxima are 2–5 nm blue shifted with respect to poly(1) and gradually approach the homopolymer wavelength values, in going from lower to higher 1 content in the copolymers. No evident influence of the chemical composition on the intensity of the band is detectable (Table V). By contrast, more marked and significant differences occur in the high-energy region. The UV spectra of poly(1) show a peak at 225 nm (ϵ = 34 000 M^{-1} cm^{-1}) and a very weak shoulder at 230 nm (ϵ = 32 000 M^{-1} cm^{-1}, whereas for the low molecular weight model compound **4** a distinct peak appears at 230 nm (ϵ

Table V
UV Absorption Data of Copolymers of Acenaphthylene (1) with (−)-Menthyl Acrylate (2) [Poly(1-*co*-2)] and (−)-Menthyl Methacrylate (3) [Poly(1-*co*-3)] and of Acenaphthene (4) in CH_2Cl_2 at 25 °C

sample	run	counits from 1, mol %	λ, nm	$\epsilon \times 10^{-3}$,[a] M^{-1} cm^{-1}	λ, nm	$\epsilon \times 10^{-3}$,[a] M^{-1} cm^{-1}
4			292	6.4	230	70.0
	A2	15.1	293	6.4	230	50.7
poly(1-*co*-2)	A3	48.9	295	6.5	227	48.1
	A5	76.3	296	6.9	226	40.1
	A9	94.5	297	6.9	225	38.1
	MA1	14.7	295	7.0	230	48.2
poly(1-*co*-3)	MA2	33.9	296	7.2	229	43.1
	MA3	50.1	296	7.3	228	41.3
	MA7	88.8	297	7.0	225	38.5
poly(1)	H1	100	297	6.9	225	34.0

[a] Molar extinction coefficient referred to one monomeric unit from acenaphthylene (1).

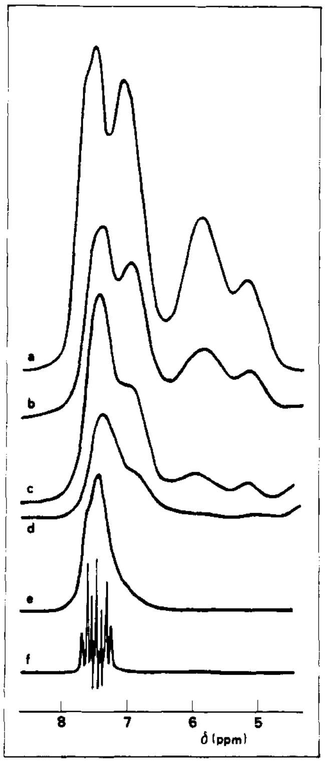

Figure 5. 100-MHz ^1H NMR spectra in hexachloro-1,3-butadiene at 160 °C of (a) poly(acenaphthylene) [poly(1)], poly(acenaphthylene-*co*-(−)-menthyl methacrylate) [poly(1-*co*-3)] containing (b) 88.8, (c) 50.1, (d) 33.9, and (e) 14.5 mol % of 1 units and (f) acenaphthene (4).

= 70 000 M^{-1} cm^{-1}), with only a shoulder at 225 nm (ϵ = 56 000 M^{-1} cm^{-1}). Quite similar spectra have been obtained for the more analogous 1,2-dimethylacenaphthene[25] and for 1,8-dimethylnaphthalene.[26] It is proposed here that the absorption at longer wavelength is characteristic of the isolated aromatic chromophore, while the absorption at 225 nm is due to electronically interacting acenaphthylene nuclei. Analogous assignments have been reported recently for carbazole-containing polymers.[4,27] In accord with this suggestion, the relative intensity of these two peaks changes sharply and the high-energy absorption becomes predominant, as the 1 content increases in the copolymers and leads to marked hypochromic effects[28] (Table V). Any secondary contribution from the ester comonomers in the 240–220 nm region may be ruled out because of the very low extinction coefficients of these chromophores [ϵ = 150 and 220 M^{-1} cm^{-1} for poly(2) and poly(3), respectively].

As already reported by Wang and Morawetz,[7] the ^1H NMR spectrum of poly(1) displays very broad peaks at about 7.4, 7.0, 5.7, 5.0, and 2.8 ppm. These are now known to be better resolved by using higher field NMR apparatus and higher temperature conditions.[7,24] By contrast, acenaphthene (4) shows one multiple peak at about 7.4 ppm and one singlet at 3.2 ppm. On this basis, the signals between 7.0 and 5.0 ppm of the poly(1) spectrum are attributed to aromatic protons which are strongly shielded, due to overlap with adjacent aromatic nuclei, analogous to other vinyl aromatic polymers such as polystyrene[29] and poly(*N*-vinylcarbazole).[27,30] In particular, on decreasing the 1 content and consequently the mean sequence length of 1 units in the copolymer, the relative intensity of the upfield signals diminishes and the resonance peaks resemble the position and the intensity of the lines of acenaphthene. A typical example of the trend of the ^1H NMR signal profile in the examined region is reported in Figure 5.

Concluding Remarks

Copolymers of acenaphthylene with (−)-menthyl acrylate and (−)-menthyl methacrylate can be obtained by free radical initiation (AIBN) in benzene solution at 70 °C. Reactivity ratios determined by the modified Kelen–Tüdös method indicate that acenaphthylene is 1 order of magnitude more reactive than the unsaturated ester comonomer. In all cases the copolymers are optically active and measurements of optical rotatory power at 589 nm show in poly(1-*co*-3) series a small, but definite, contribution from the acenaphthylene unit, indicative of induced asymmetry in such chromophores. Infrared spectra of poly(1) suggest a preferential trans opening of the aromatic double bond to give a trans-disyndiotactic configuration. Such a situation would apparently be present also in copolymers with 2 and 3, although this cannot yet be concluded. Electronic absorption and ^1H NMR properties of the copolymers are consistent with the presence of sequences of 1 units in that typical signals of interacting aromatic nuclei can be identified after comparison with poly(acenaphthylene) and the model compound acenaphthene.

Acknowledgment. We thank SRC (UK) for granting a Visiting Fellowship to G.G. Financial support from CNR (Italy) is also gratefully acknowledged.

Registry No. 1, 208-96-8; 2, 4835-96-5; 3, 2231-91-6; 1–2 copolymer, 81736-89-2; 1–3 copolymer, 81736-88-1.

References and Notes

(1) Chiellini, E.; Solaro, R.; Ledwith A. *Makromol. Chem.* **1978**, *179*, 1929.
(2) Chiellini, E.; Solaro, R.; Colella, O.; Ledwith, A. *Eur. Polym. J.* **1978**, *14*, 489.
(3) Chiellini, E.; Solaro, R.; Ciardelli,. R.; Galli, G.; Ledwith A. *Polym. Bull.* **1980**, *2*, 577.
(4) Chiellini, E.; Solaro, R.; Galli, G.; Ledwith, A. *Macromolecules* **1980**, *13*, 1654.

(5) Galli, G.; Solaro, R.; Chiellini, E.; Ledwith, A. *Polymer* **1981**, *22*, 1088.
(6) Klöpffer, W. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 242.
(7) Wang, Y. C.; Morawetz, H. *Makromol. Chem., Suppl.* **1975**, *1*, 283.
(8) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 457.
(9) Anderson, R. A.; Reid, R. F.; Soutar, I. *Eur. Polym. J.* **1980**, *16*, 945.
(10) David, C.; Baeyens-Volant, D.; Piens, M. *Eur. Polym. J.* **1980**, *16*, 413.
(11) Ciardelli, F.; Chiellini, E.; Carlini, C.; Pieroni, O.; Salvdori, P.; Menicagli, R. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 62*, 143.
(12) Galli, G.; Solaro, R.; Chiellini, E.; Fernyhough, A.; Ledwith, A. *Macromolecules* **1983**, *16*, 502.
(13) Schulz, R. C.; Kaiser, F. *Makromol. Chem.* **1965**, *86*, 80.
(14) Frank, R. L.; Davis, H. R.; Drake, S. S.; McPherson, J. B., Jr. *J. Am. Chem. Soc.* **1944**, *66*, 1509.
(15) Menchini, G. B. Thesis, University of Pisa, 1972.
(16) Ballesteros, J.; Howard, G. J.; Teasdale, L. *J. Macromol. Sci., Chem.* **1977**, *A11*, 29.
(17) Noma, K.; Niwa, M.; Norisada, H. *Doshida Daigaku Rikogaku Kenkyo Hokuku* **1970**, *10*, 349 (*Chem. Abstr.* **1970**, *73*, 77680*m*).
(18) Majumdar, R. N.; Carlini, C. *Makromol. Chem.* **1980**, *181*, 201.
(19) Majumdar, R. N.; Carlini, C.; Rosato, N.; Houben, J. L. *Polymer* **1980**, *21*, 941.
(20) Kelen, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1975**, *9*, 1.
(21) Rao, S. P.; Ponratnam, S.; Kapur, S. L.; Iyer, P. K. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 513.
(22) Mayo, F. R.; Walling, C. *Chem. Rev.* **1950**, *50*, 200.
(23) Story, V. M.; Canty, G. *J. Natl. Bur. Stand. A., Phys. Chem.* **1964**, *68A*, 165.
(24) Solaro, R.; Galli, G.; Chiellini, E.; Ledwith, A., in preparation.
(25) Samori, B., private communication.
(26) Jaffê, H. H.; Orchin, M. "Theory and Application of Ultraviolet Spectroscopy"; Wiley: New York, 1962; p 307.
(27) Chiellini, E.; Solaro, R.; Ledwith, A.; Galli, G. *Eur. Polym. J.* **1980**, *16*, 875.
(28) Tinoco, I., Jr. *J. Am. Chem. Soc.* **1960**, *86*, 80.
(29) Bovey, F. A.; Tiers, G. V. D. *Adv. Polym. Sci.* **1963**, *3*, 139.
(30) Williams, D. J. *Macromolecules* **1970**, *3*, 602.

Synthesis and Characterization of Optically Active Copolymers of Acenaphthylene. 2. Chiroptical and Fluorescence Properties

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ABSTRACT: Chiroptical and fluorescence emission properties of optically active copolymers of acenaphthylene (1) with (−)-menthyl acrylate (2) and (−)-menthyl methacrylate (3) have been investigated and interpreted in terms of copolymer sequence length and distribution as well as of configurational and conformational arrangement. The copolymers with 3 are characterized by a marked induced optical activity in the aromatic counits, and the dichroic absorption coefficient exhibits a maximum value at approximately 50 mol % composition. Surprisingly, no appreciable chiroptical induction was detected in copolymers of 1 with 2. Fluorescence emission spectra of all copolymers display both monomer and excimer emission, whose relative intensity strongly depends on chemical composition. A maximum value of the excimer to monomer intensity ratio was observed in the poly(1-*co*-3) system at 80 mol % content of 1 units, whereas a monotonic trend was shown by poly(1-*co*-2) samples. Fluorescence polarization measurements indicate for all the copolymers, and even for the model compound acenaphthene (4), extensive depolarization. The statistical treatment proposed by some authors for acenaphthylene-containing polymers appears therefore not to be applicable and the extent and mechanism of energy transfer in such systems remain to be better established.

Introduction

Photophysical processes in polymers have been extensively investigated in recent years[1] and intramolecular excimer formation has been recognized in a wide variety of macromolecular systems bearing aromatic chromophores as pendant groups.[2–7] Acenaphthylene (1) homopolymers[8] and copolymers[9–12] have attracted much interest, due to the peculiar way of incorporation of that unit in the polymer backbone, which prohibits the typical sandwichlike conformation between nearest neighbors, widely invoked to explain excimer formation both in polymers[3] and low molecular weight compounds.[13]

It was first reported by Wang and Morawetz[9] that copolymers of 1 with monomers capable of giving a quaternary carbon atom in the polymer main chain (e.g., methyl methacrylate) could, under appropriate conditions, exhibit excimer formation in excess of that of the homopolymer of 1. In contrast, similar copolymers of 1 with methyl acrylate showed a much reduced tendency to form excimers. The apparent difference in ease of excimer formation between copolymers of 1 with methyl acrylate and methyl methacrylate having similar compositions has prompted more detailed studies by Soutar et al.[10,11] and by David et al.[12] In these later works the effects noted by Wang and Morawetz have been confirmed and the question of energy migration in both series of copolymers has been investigated by means of fluorescence depolarization experiments.

Excimer emission intensity is known to depend on both efficiency of energy migration[14] and ability of forming excimer sites,[15] which in turn can be related to the distribution of monomeric units and to the polymer configuration and conformation.[16] It seemed therefore very profitable to investigate two homologous series of copolymers of 1 with optically active monomers whose chiroptical properties could be interpreted in terms of configurational and conformational regularities.[17,18]

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