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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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Table I
Properties of the Investigated Samples of Poly[acenaphthylene-*co*-(−)-menthyl acrylate] [Poly(1-*co*-2)]

run	counits from 1, mol %	$\bar{M}_n{}^b \times 10^{-3}$	$[\alpha]^{25}{}_D$,^{c} deg	$X_{1(n)}{}^a$ $n = 1$	$n = 2$	$n = 3$	$X_{2(n)}{}^a$ $n = 1$	$n = 2$	$n = 3$
A2	15.1	10.4	−65.2	43.9	29.6	15.0	1.6	2.7	3.6
A3	48.9	7.2	−47.4	19.9	22.1	18.3	6.6	9.9	11.0
A4	69.7	6.5	−26.6	7.0	10.2	11.3	19.2	21.6	18.2
A6	86.7	6.3	−14.0	1.7	3.0	3.9	42.2	29.6	15.5
A10	95.0	13.6	−3.9	0.0	0.0	0.0	92.5	7.1	0.4

[a] Percent fraction of 1 (or 2) units in a closed sequence of *n*. [b] By gel permeation chromatography in THF. [c] In dichloromethane.

Table II
Properties of the Investigated Samples of Poly[acenaphthylene-*co*-(−)-menthyl methacrylate] [Poly(1-*co*-3)]

run	counits from 1, mol %	$\bar{M}_n{}^b \times 10^{-3}$	$[\alpha]^{25}{}_D$,^{c} deg	$X_{1(n)}{}^a$ $n = 1$	$n = 2$	$n = 3$	$X_{3(n)}{}^a$ $n = 1$	$n = 2$	$n = 3$
MA1	14.7	34.9	−83.2	64.9	25.2	7.3	2.3	3.9	5.0
MA2	33.9	24.3	−63.7	36.1	28.8	17.2	11.0	14.7	14.7
MA3	50.1	20.1	−49.0	25.5	25.3	18.7	17.9	20.6	17.9
MA4	70.0	14.0	−28.8	7.8	11.2	12.1	43.4	29.6	15.2
MA5	79.0	12.5	−21.8	4.6	7.2	8.5	53.7	28.7	11.5
MA7	88.8	14.3	−10.2	0.8	1.5	2.0	78.1	18.2	3.2
MA8	96.8	12.7	−5.2	0.1	0.3	0.4	90.5	8.8	0.6

[a] Percent fraction of 1 (or 3) units in a closed sequence of *n*. [b] By gel permeation chromatography in THF. [c] In dichloromethane.

In the present paper are reported the results obtained in the investigation of the chiroptical and fluorescence emission properties of two series of copolymers of acenaphthylene (**1**) with (−)-menthyl acrylate (**2**) and (−)-menthyl methacrylate (**3**), whose preparation has been already described in a previous paper.[19] The investigated properties are related to chemical composition and distribution of monomeric units in the copolymer.

Experimental Part

Preparation of the polymer samples was described in part 1.[19] The same notation is maintained here, and in Tables I and II some pertaining data are collected.

Circular dichroism (CD) spectra in the 350–220-nm region were recorded on a Roussell-Jouan Dichrograph III at room temperature in dichloromethane solution with path length 0.1–1 cm. The spectra in the higher energy region (λ <220nm) were run in *n*-heptane solution with 0.1-cm cells.

Fluorescence emission spectra were recorded on a Perkin-Elmer MPF43 spectrofluorimeter at room temperature in dichloromethane and 2-methyltetrahydrofuran (2-MeTHF) at the excitation wavelength of 300 nm. Dilute solutions (10^{-5} M concentration) were used in all cases to avoid any self-absorption correction. All spectra were not corrected for the nonlinear response of the detection system. Excimer to monomer emission ratio was evaluated from the corresponding areas obtained by deconvolution of the overall fluorescence spectrum.

Fluorescence polarization experiments were carried out in 2-MeTHF glassy solution at 77 K at excitation and emission wavelengths of 300 and 340 nm, respectively. Polarization measurements in poly(methyl methacrylate) film dispersions were performed at room temperature by using excitation and emission wavelengths in the ranges 270–310 and 320–340 nm, respectively. The degree of polarization *P* was evaluated from the relation[20]

$$P = (I_{\parallel} - GI_{\perp})/(I_{\parallel} + GI_{\perp})$$

where $I_{\parallel}$ and $I_{\perp}$ are the components of emitted radiation parallel and perpendicular to the plane of polarized excitation. $G = I_{\perp}/I_{\parallel}$ is a correction factor due to instrumental anisotropy.

Results and Discussion

Chiroptical Properties. The copolymers of acenaphthylene with (−)-menthyl methacrylate exhibit in the CD spectrum in CH_2Cl_2 solution a negative band at 235 nm and a structured positive band with relative maxima at 285, 298, 310, and 321 nm, in close correspondence respectively with the $^1B_b \leftarrow {}^1A$ and the overlapping $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ electronic transitions of the aromatic chromophore (Figure 1). In the short-wavelength region (λ <250 nm) the dichroic absorption of the aromatic group is partially affected by the tail of the CD band connected with the n → π* transition of the carboxyl group. Nevertheless, this contribution is found to be very small by comparing the observed spectra with the absorption of the corresponding mixtures of homopolymers in the same region. In the far end of the CD spectrum (λ <230 nm) a

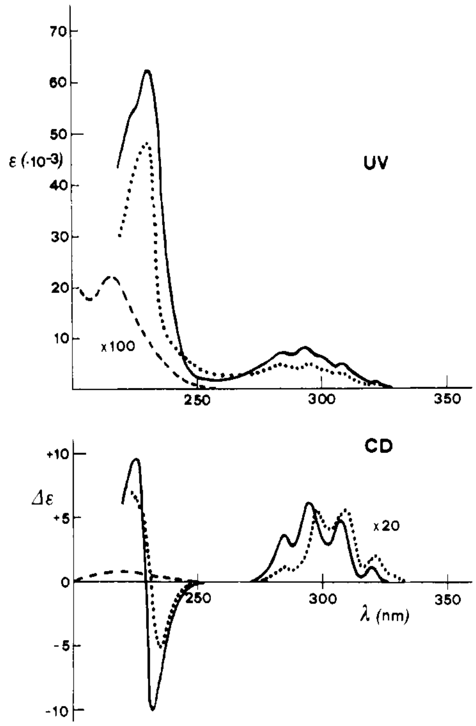

Figure 1. Ultraviolet (UV) spectra and circular dichroism (CD) spectra of poly[acenaphthylene-*co*-(−)-menthyl methacrylate] [poly(**1**-*co*-**3**)] (14.7 1 mol %) in (—) *n*-heptane and (···) dichloromethane and of poly(**3**) (- - -) in *n*-heptane. CD spectra were corrected for the contribution of the methacrylate units.

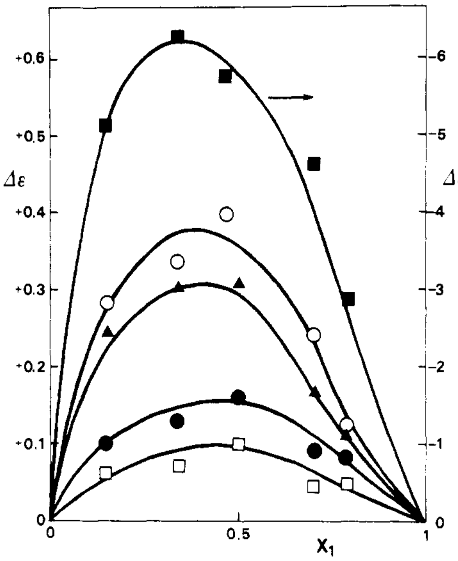

Figure 2. Variation of the dichroic molar absorption coefficient ($\Delta\epsilon$) with acenaphthylene (1) molar fraction (X_1) of copolymers of 1 with (−)-menthyl methacrylate (3) in dichloromethane at different wavelengths: (●) 321, (▲) 310, (○) 298, (□) 285, and (■) 235 nm.

positive band starts to appear, which cannot be fully investigated due to the strong absorption of the halogenated solvent in that spectral region. However, the copolymer with the lowest 1 content (run MA1) is soluble also in transparent hydrocarbon solvents, and the spectrum in *n*-heptane (Figure 1) shows two strong dichroic bands of opposite sign having maxima at 232 nm ($\Delta\epsilon$ −10) and 225 nm ($\Delta\epsilon$ +10), respectively, attributable to exciton splitting arising from dipole–dipole interactions of chirally perturbed chromophores.[21]

For all the CD bands, whose intensities incidentally are of the same order of magnitude as those observed for coisotactic copolymers of vinyl aromatic monomers with chiral α-olefins[18,22] and alkyl vinyl ethers,[23] the molar differential extinction coefficient ($\Delta\epsilon$) increases up to a maximum value at approximately 50 mol % of 1 in the copolymer and then decreases with further increase in the content of the achiral comonomer (Figure 2). In earlier works[23-25] we have given the first reports that an unusual maximum in the intensity of the induced CD may be observed in optically active copolymers of *N*-vinylcarbazole at an intermediate chemical composition. For example, in copolymers with (−)-menthyl vinyl ether and (−)-menthyl methacrylate, maximum induced CD was observed respectively at 20 and 40 mol % *N*-vinylcarbazole, while for copolymers with optically active fumarates that maximum was not yet reached at *N*-vinylcarbazole contents as high as 70 mol %.

The present data clearly indicate that the conformational effects responsible for the origin of such maxima are not restricted to carbazole-containing copolymers, although they are not generally observed with many other vinyl aromatic monomers.[26-29] It is generally assumed that large induced circular dichroism is generated by dipolar interactions among aromatic chromophores located in a chirally homogeneous conformational environment. The presence of a maximum value suggests that those interactions are maximized not for the isolated chromophore, but rather for appropriate sequences of units derived from the relatively rigid achiral monomer adjacent to sequences of intrinsically chiral counits.

The occurrence of a maximum in the present series of copolymers at a composition of about 50 mol % 1 can be tentatively explained by examining the sequence distribution of the two counits, as evaluated on the basis of the reported reactivity ratios[19] (Table II). It can be seen that for runs MA2 and MA3 the fraction of 1 residues in closed sequences of two or three units is maximized. Concurrently, more than 80 mol % of chiral units is inserted in sequences of two units or more. Therefore, it is reasonable to assume that cooperative effects from sequences of two or three 1 units adjacent to sequences of 3 units give rise to a maximum induced circular dichroism.

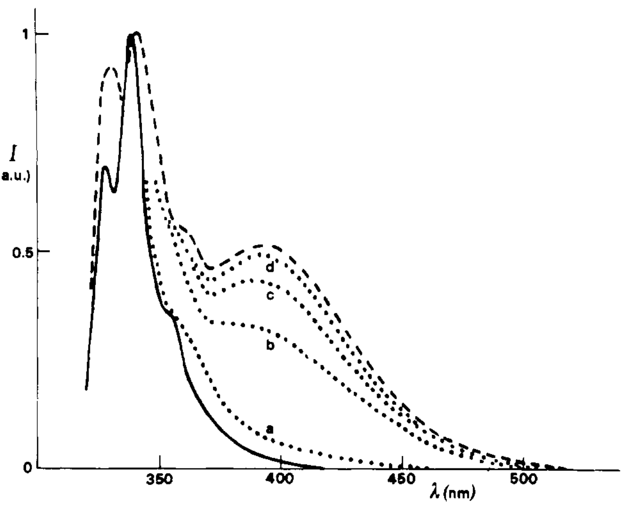

Figure 3. Uncorrected fluorescence emission spectra (dichloromethane, λ_{exc} = 300 nm) normalized at the maximum intensity of (—) acenaphthene (4), (- - -) poly(acenaphthylene) [poly(1)], and (a–d) copolymers of 1 with (−)-menthyl acrylate (2) [poly(1-*co*-2)] containing 15.1, 48.9, 69.7, and 86.7 1 mol %, respectively.

To account for this ability to transmit the chiral perturbation over some distance from the optically active groups, we have to assume that neighboring aromatic chromophores can strongly interact, as clearly evidenced by the exciton splitting observed in the shorter wavelength region of the CD spectrum. The copolymers of 1 with (−)-menthyl acrylate (2) do not exhibit any appreciable induced circular dichroism in the 1 chromophore, despite the fact that 2 is known to produce significant induced CD effects in a wide variety of vinyl aromatic counits.[24,27,30]

At the present, no conclusive explanation of the different behavior between acrylate and methacrylate copolymers can be put forward. However, both different distribution of monomeric units in the two copolymer systems and lower flexibility of the main chain in methacrylate copolymers must play a significant role in determining the asymmetry of the local environment in which the acenaphthylene units are embedded.

Fluorescence Properties. Fluorescence emission spectra of copolymers of 1 with 2 and 3 are characterized by a structured band centered at about 340 nm, whose position is almost independent of the chemical composition, and a broad band centered at about 400 nm, whose intensity and profile strongly depend on copolymer composition. In particular, the intensity of the latter emission increases in a monotonic fashion on increasing the 1 content in poly(1-*co*-2) samples (Figure 3), whereas it reaches a value in excess of that of poly(1) in the poly(1-*co*-3) series (Figure 4). The two bands can be attributed to a monomer and excimer emission, respectively, but it should be noted that, due to the structural peculiarity of the aromatic unit in acenaphthylene homopolymer[8] and copolymers,[9-12] emitting excimer species cannot be formed through the interaction of two nearest-neighbor chromophores.[8] Excimer to monomer emission ratios (I_E/I_M) exhibit a clear

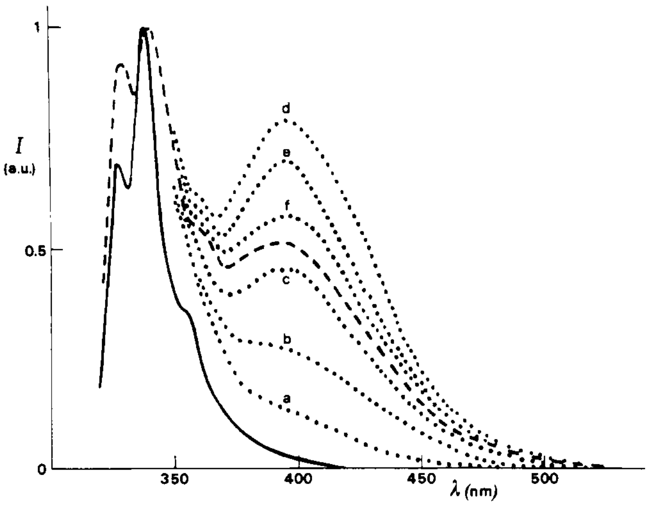

Figure 4. Uncorrected fluorescence emission spectra (dichloromethane, λ_{exc} = 300 nm) normalized at the maximum intensity of (—) acenaphthene (4), (- - -) poly(acenaphthylene) [poly(1)] and (a–f) copolymers of 1 with (−)-menthyl methacrylate (3) [poly(1-*co*-3)] containing 14.7, 33.9, 50.1, 79.0, 88.8, and 96.8 1 mol %, respectively.

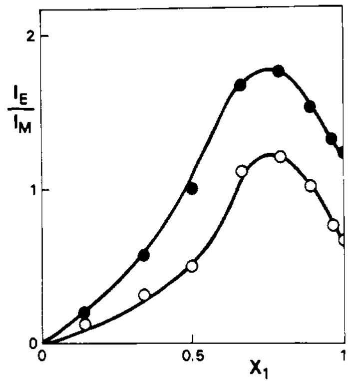

Figure 5. Variation of the excimer to monomer emission intensity ratio (I_E/I_M) with acenaphthylene (1) molar fraction in copolymers of 1 with (−)-menthyl methacrylate (3) in (●) dichloromethane and (○) 2-methyltetrahydrofuran.

maximum for the methacrylate series at approximately 80 mol % 1 content, in both CH_2Cl_2 and 2-MeTHF solvents (Figure 5). However, an overall reduction of the capability of excimer formation takes place in the latter solvent, probably due to differences in chain conformations and/or changes in quenching efficiencies. On the contrary, the I_E/I_M ratio decreases monotonously with decreasing 1 content for the acrylate series (Figure 6). This trend is similar to that previously reported in analogous copolymer systems of 1 containing achiral comonomers.[10,11] The different behavior of the two series of copolymers can be interpreted assuming that in the methacrylate copolymers there is a structural effect of the comonomer that serves to enforce the alignment of two 1 units required for excimer formation, whereas this effect is apparently not present in the much more flexible acrylate copolymers.

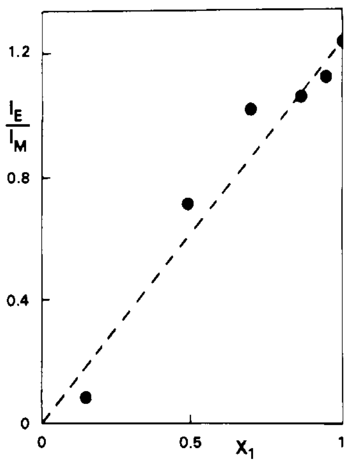

Figure 6. Variation of the excimer to monomer emission intensity ratio (I_E/I_M) with acenaphthylene (1) molar fraction in copolymers of 1 with (−)-menthyl acrylate (2) in dichloromethane.

Table III
Fluorescence Emission and Fluorescence Polarization Data of the Investigated Samples of Poly[acenaphthylene-*co*-(−)-menthyl acrylate] [Poly(1-*co*-2)]

run	counits from 1, mol %	I_E/I_M[a]	P[b]
A2	15.1	0.07	0.014
A3	48.9	0.71	0.010
A4	69.7	1.02	0.009
A6	86.7	1.05	−0.005
A10	95.0	1.11	−0.006
H1	100	1.23	−0.029

[a] Excimer to monomer emission intensity ratio, in CH_2Cl_2 at room temperature (λ_{exc} = 300 nm). [b] Degree of fluorescence polarization, in 2-MeTHF glassy solution at 77 K (λ_{exc} = 300 nm, λ_{em} = 340 nm).

Table IV
Fluorescence Emission and Fluorescence Polarization Data of the Investigated Samples of Poly[acenaphthylene-*co*-(−)-menthyl methacrylate] [Poly(1-*co*-3)]

run	counits from 1, mol %	I_E/I_M[a]	P[b]
MA1	14.7	0.18	0.022
MA2	33.9	0.54	0.017
MA3	50.1	0.98	0.015
MA4	70.0	1.68	0.012
MA5	79.0	1.75	0.008
MA7	88.8	1.53	0.002
MA8	96.8	1.30	0.008
H1	100	1.23	−0.029

[a] Excimer to monomer emission intensity ratio, in CH_2Cl_2 at room temperature (λ_{exc} = 300 nm). [b] Degree of fluorescence polarization in 2-MeTHF glassy solution at 77 K (λ_{exc} = 300 nm, λ_{em} = 340 nm).

It is generally assumed that polymerization of 1 involves overall trans addition to the double bond,[31] but any preference for cis addition would yield an obvious configurational difference, which might be reflected in enhanced excimer formation. Alternatively, it is also possible that enhanced excimer formation in the methacrylate copolymers is caused by conformational effects arising from the presence of quaternary carbon atoms in the polymer backbone, as originally proposed by Wang and Morawetz.[9] These would have the obvious effect of reducing segmental mobility in the poly(1-*co*-3) series.

Depolarization of fluorescence of copolymers of 1 has been investigated in an attempt to understand the mechanism and extent of energy migration in such systems. It may be envisaged that energy migration occurs by two distinct processes:[32] one involving the usual down-chain hopping along sequences of 1 units, and the other involving energy transfer between remote units randomly interacting within individual polymer coils. In principle, a choice between these two alternatives could be made by comparison of depolarization data with copolymer compositions and sequence distributions. Such an analysis has been attempted by various authors.[10–12]

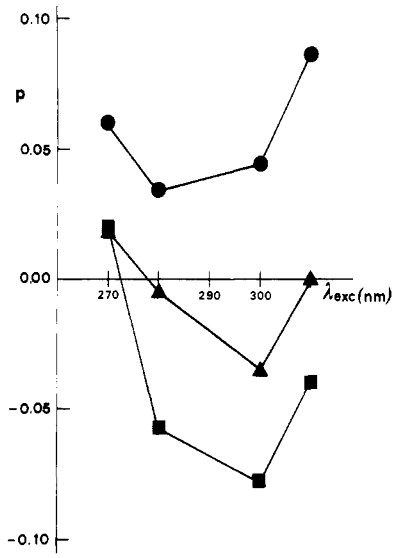

Figure 7. Variation with the excitation wavelength of the degree of polarization (P) of acenaphthene (4) fluorescence emission at (■) 322, (●) 327, and (▲) 337 nm in poly(methyl methacrylate) glass at room temperature.

In the present work (Tables III and IV), we have noted that depolarization is extensive not only for all the polymers but even for the model compound acenaphthene (4) (P = 0.045). This could arise in part as a result of the mixed polarization of the vibrational levels in the long-wavelength absorption band of the acenaphthene chromophore, as first reported by David et al.[12] on the basis of a study on the dependence of the degree of polarization on the excitation wavelength in the model compound.

In the present work the results of David et al.[12] were perfectly duplicated, yet the very low degrees of polarization observed might be, at least in principle, attributed to the separation of acenaphthene microcrystals on freezing. However, an analogous experiment carried out in a poly(methyl methacrylate) glass at room temperature gave very similar results (Figure 7). It follows therefore that, due to the even lower values of P observed in copolymers with 2 and 3, it is not reasonable to attempt any quantitative correlation of fluorescence polarization with copolymer structure. Not surprisingly, the statistical treatment of the experimental data according to Soutar et al.[10,11] did not give the expected linear trend, but rather only scattered points (Figure 8). This implies that, for the moment, the extent and mechanism of energy transfer in polymers of acenaphthylene remain to be better established.

Concluding Remarks

Optically active copolymers of acenaphthylene (1) with (−)-menthyl methacrylate (3) are characterized by a marked induced optical activity in the aromatic chromophore, as evidenced by CD measurements. In the high-energy region of the CD spectra, exciton splitting bands are detectable, which are known to arise from dipole–dipole interactions of chirally perturbed chromophores. For all the CD bands the dichroic absorption coefficient increases on increasing the 1 content in the copolymer and exhibits a maximum value for samples containing about 50 mol % 1 units. Such a behavior, previously reported only for copolymers of N-vinylcarbazole, indicates that interactions among chromophores located in a chirally homogeneous environment are maximized for appropriate sequences of aromatic units. In the present case, cooperative effects from sequences of two or three acenaphthylene units adjacent to sequences of 3 units appeared to give rise to a maximum induced CD. By contrast, optically active copolymers of 1 with 2, which are expected to have more flexible backbones, do not exhibit any appreciable induced CD.

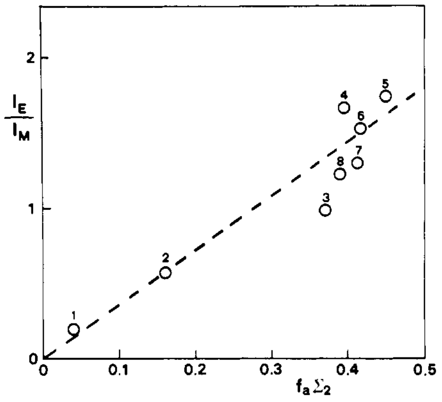

Figure 8. Variation of the excimer to monomer emission intensity ratio (I_E/I_M) with $f_a\sum_2$ (see ref 10 and 11) in copolymers of acenaphthylene (1) with (−)-menthyl methacrylate (3): 14.7, 33.9, 50.1, 70.0, 79.0, 88.8, 96.8, and 100 mol % 1 (circles 1–8, respectively).

Both monomer and excimer fluorescence emission are detected in the two copolymer systems. While in the poly(1-*co*-2) series the excimer to monomer intensity ratio regularly increases on increasing the aromatic content in the copolymer, in poly(1-*co*-3) samples that ratio displays a maximum value at approximately 80 mol % 1 units. These results confirm previous conclusions that in acenaphthylene-containing polymers excimer formation does not take place through the interaction between two nearest-neighbor chromophores. The different behavior displayed by the two copolymer series can be most likely imputed to the higher overall main-chain flexibility and conformational freedom in acrylate copolymers with respect to methacrylate ones. Fluorescence polarization measurements yield very low degrees of polarization for both copolymer series, indicative of efficient energy migration. However, extensive depolarization was found to occur even in the model compound acenaphthene, probably due to the mixed polarization of the vibrational levels of the long-wavelength absorption of the aromatic chromophore. Therefore, the statistical treatment proposed by others to elucidate energy transfer and excimer formation in acenaphthylene polymers seems not to be fully applicable to such systems.

Registry No. 1–2 copolymer, 81736-89-2; 1–3 copolymer, 81736-88-1.

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Far-Ultraviolet Circular Dichroism Spectra of Isotactic Optically Active Poly(alkyl vinyl ethers) and Their Low Molecular Weight Models

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Received May 25, 1982

ABSTRACT: Vacuum-UV circular dichroism (CD) (210–140 nm) spectra of optically active poly(alkyl vinyl ethers) are reported and compared with those of low molecular weight analogues. In spite of the ordered structure of the macromolecules, no particular CD feature connected with the polymer conformation is evident. However, the CD is sensitive to even subtle differences in the isotacticity degree of the polymeric samples.

Introduction

The stereochemical properties of isotactic chiral synthetic polymers have been widely investigated by chiroptical techniques, and the relationship between the conformation in solution of the macromolecules and their optical activity has been established by experimental and theoretical studies.[1] As far as optically active poly(alkyl vinyl ethers) are concerned, the aforementioned relationship has not been properly investigated because of the instrumental difficulty in measuring far-UV optical rotatory dispersion (ORD) and circular dichroism (CD) spectra. In fact, the chiroptical properties of poly(alkyl vinyl ethers) were investigated down to 185 nm and only the lowest energy band related to the ethereal chromophore was detected.[2] The same occurred for optically active poly(oxiranes), in which the ethereal oxygen is located in the main chain.[3] The data reported on the chiroptical properties of the poly(alkyl vinyl ethers) indicate that in solution the macromolecules assume a helical conformation with a predominant screw sense, as proposed for poly(α-olefins).[4]

More recently, the CD of the ether chromophore was reconsidered, thanks to the availability of special far–UV CD spectrometers. Some papers appeared in the literature concerning the far-UV CD of poly[(*R*)-oxypropylene][5] and of low molecular weight ethers.[6-8] Therefore, it appeared interesting to investigate the vacuum-ultraviolet spectral region also for the poly(alkyl vinyl ethers), with the aim of more properly establishing the relationship between optical activity and conformation in solution.

Experimental Section

Synthesis of Polymers. Poly(menthyl vinyl ether) (IA-C) samples were obtained by polymerization of (−)-menthyl vinyl ether by using different catalytic systems and experimental conditions that have been described elsewhere.[9,10] The polymers were purified by several reprecipitations with methanol from hydrocarbon or chloroform solutions (Table I). Poly[(*S*)-1-methylheptyl vinyl ether] (IIA,B) samples were obtained by polymerization of the corresponding monomer in the presence of a catalyst based on the $Al(O\text{-}i\text{-}C_3H_7)_3/H_2SO_4$ system and $BF_3{\cdot}OEt_2$, respectively, according to the procedure previously described.[10]

The model compounds for the isolated chromophore, (−)-menthyl ethyl ether and (−)-(*S*)-1-methylheptyl ethyl ether, were prepared by hydrogenation of the corresponding vinyl ethers in the presence of Raney Ni according to a procedure described elsewhere.[11]

^{13}C NMR Spectra. NMR spectra were recorded on a Bruker HF-90 and the evaluation of the isotacticity degree was done for polymer I samples on the basis of the signal at 48.5 ppm (Me_4Si),[12] whereas for polymer II samples no definitive attribution has been so far performed.

CD Measurements. CD spectra were recorded with a vacuum-ultraviolet spectrometer[13] by using standard cylindrical quartz cells of 50- and 100-μm path length for the bulk of the measurements. Sandwich-type cells with aluminum foil spacers were