at 35 °C for polyphosphate triesters **2a–g** and in DMF at 55 °C for polyphosphate diester **2h**.

Acute Toxicity Test. A polymer sample was dissolved in Me_2SO and the solution was intraperitoneally injected into 20 mice (10 male and 10 female). The injected amount of the solution was less than 5 mL/(kg mouse). The LD_{50} value was obtained from the number of surviving mice 14 days after the injection. The dead mice were subjected to dissection analysis and found that they suffered no symptom of anatomical abnormality. As a blank test Me_2SO itself was similarly examined; none of the mice died at a dose rate of 10 mL/(kg mouse) after 14 days.

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Optically Active Vinyl Polymers Containing Fluorescent Groups. 8. Synthesis and Properties of Copolymers of *N*-Vinylcarbazole and (−)-Menthyl Acrylate and (−)-Menthyl Methacrylate

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ABSTRACT: *N*-Vinylcarbazole was free radically copolymerized with (−)-menthyl acrylate and (−)-menthyl methacrylate in benzene at 55 °C to give optically active copolymers characterized by a marked induced optical rotation in the heteroaromatic co-units. Electronic absorption and emission properties, and the estimated reactivity ratios, are entirely consistent with quasi-random copolymerizations with, however, a tendency to alternation, especially for the *N*-vinylcarbazole unit. In contrast to the known behavior of copolymers of chiral monomers with other vinylaromatic monomers, the differential dichroic absorption exhibits a maximum value for copolymers containing approximately 40 mol % *N*-vinylcarbazole units. A similar maximum has been noted previously for copolymers of *N*-vinylcarbazole with (−)-menthyl vinyl ether and confirms the unique value of carbazole units as probes for asymmetric induction in polymer chains.

The investigation of chiroptical properties of stereoregular homopolymers[1-3] and copolymers[4-7] obtained from optically active α-olefins and vinylaromatic monomers led to the discovery of a very powerful tool in the assignment of a secondary structure for such polymers in solution. The scope and applicability of this type of characterization have been adequately reviewed.[8,9]

More recently we extended this method to copolymers of *N*-vinylcarbazole with optically active comonomers,[10,11] as well as to homopolymers of chiral carbazole-containing monomers,[12] with the aim of correlating primary and secondary structure with the complex spectroscopic properties of carbazole-containing macromolecules.[13,14]

At the same time a study of the practical potentiality of preparing macromolecules containing optically active heteroaromatic moieties starting from easily available chiral comonomers was undertaken. Preliminary results[10] obtained from copolymers of *N*-vinylcarbazole (**1**) with (−)-menthyl acrylate (**2**) and (−)-menthyl methacrylate (**3**) stimulated the synthesis of two series of copolymers using conventional free radically initiated polymerizations. A correlation between the physical–optical properties and structural characteristics related to chemical composition and distribution of monomeric units of the reported copolymers is presented.

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Table I
Copolymerization of N-Vinylcarbazole (1) with (–)-Menthyl Acrylate (2) in Benzene at 55 °C

	polymerization conditions[a]			polymeric product			
run	amt of 1, mmol	1/2 molar ratio, mol/mol	convrsn,[b] %	co-units[c] from 1, mol %	[η],[d] dL/g	$[\alpha]^{25}_{D}$,[e] deg	$[\alpha]_0$,[f] deg
A1	0.4	0.11	15.6	17.7	0.50	-61.2	-59.0
A2	1.0	0.25	16.7	29.6	0.65	-62.8	-50.9
A3	1.5	0.43	15.9	35.3	0.88	-55.7	-47.0
A4	2.0	0.67	25.1	40.9	0.83	-57.1	-43.1
A5	2.0	1.00	55.8[g]	46.4	0.65	-53.7	-39.1
A6	3.0	1.55	26.0	50.2	0.91	-52.3	-38.8
A7	3.5	2.33	29.3	47.1	1.24	-54.2	-36.6
A8	4.0	4.00	16.1	54.7	0.95	-52.9	-33.5
A9	50.0	5.68	90.4[h]	66.8[i]		-39.1[i]	-24.9

[a] Total comonomer concentration ([1] + [2]) = 0.8-1 M; comonomers/AIBN molar ratio = 50; polymerization time 30 min. [b] Calculated as [(weight of solid polymer)/(weight of starting comonomers)] × 100. [c] Determined by UV and/or NMR spectroscopy. [d] In chloroform, at 30 °C. [e] In dichloromethane. [f] Evaluated for homopolymer mixtures having the same composition as the corresponding copolymer. [g] Polymerization time 2 h. [h] Polymerization time 4 h. [i] Fraction soluble in boiling diethyl ether.

Table II
Copolymerization of N-Vinylcarbazole (1) with (–)-Menthyl Methacrylate (3) in Benzene at 55 °C

	polymerization conditions[a]			polymeric product			
run	amt of 1, mmol	1/3 molar ratio, mol/mol	convrsn,[b] %	co-units[c] from 1, mol %	[η],[d] dL/g	$[\alpha]^{25}_{D}$,[e] deg	$[\alpha]_0$,[f] deg
MA1	0.5	0.13	15.6	8.8	0.32	-97.8	-88.5
MA2	1.0	0.28	17.1	16.4	0.41	-90.4	-81.9
MA3	1.0	0.33	13.3	18.9		-90.0	-79.5
MA4	1.0	0.38	14.5	20.6		-88.8	-78.1
MA5	1.5	0.48	13.5	23.6	0.45	-88.7	-75.7
MA6	2.0	0.77	14.7	32.3	0.56	-77.2	-67.9
MA7	1.4	1.00	9.5	33.2		-77.3	-63.9
MA8	3.0	1.69	13.5	37.3	0.52	-67.3	-63.2
MA9	3.0	2.14	17.3	43.5	0.43	-63.6	-57.5
MA10	3.5	2.70	8.1	49.2	0.55	-58.6	-52.4
MA11	4.8	5.55	6.2	58.7	0.64	-54.9	-43.2
MA12	50.0	5.68	95.5[g]	63.7[h]	0.24[h]	-46.0[h]	-38.0

[a] Total comonomer concentration ([1] + [3]) = 0.8-1 M; comonomers/AIBN molar ratio = 50; polymerization time 3 h. [b] Calculated as [(weight of solid polymer)/(weight of starting comonomers)] × 100. [c] Determined by UV and/or NMR spectroscopy. [d] In chloroform at 30 °C. [e] In dichloromethane. [f] Evaluated for homopolymer mixtures having the same composition of the corresponding copolymer. [g] Polymerization time 13 h. [h] Fraction soluble in boiling diethyl ether.

Experimental Section

Materials. Commercial 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol.

Commercially available N-vinylcarbazole (1) was purified by three crystallizations from methanol (mp 65 °C).

Commercial (–)-menthol {(1R,3R,4S)-1-methyl-4-isopropylcyclohexan-3-ol} was recrystallized from isooctane {mp 43-45 °C; $[\alpha]^{25}_{D}$ -49.5° (ethanol), optical purity 99.8%[15]}.

(–)-Menthyl acrylate (2) {$[\alpha]^{25}_{D}$ -89.9° (benzene), optical purity 97.0%[16]} was prepared according to the procedure of Frank et al.[17]

(–)-Menthyl methacrylate (3) {$[\alpha]^{25}_{D}$ -91.8° (neat), optical purity 99.0%[18]} was prepared by reacting methacryloyl chloride with (–)-menthol in pyridine in the presence of copper powder.[18]

N-Isopropylcarbazole (4) was prepared according to the method reported by Lopatinskii[19] and twice recrystallized from n-hexane (mp 121-122 °C).

Copolymerization Experiments. All polymerizations were carried out in benzene solution at 55 °C in sealed glass tubes after repeated freeze–pump–thaw cycles, using initial total comonomer concentration in the range 0.8–1.0 M and a comonomers/initiator molar ratio of 50.

Polymerizations were terminated at rather low conversions [30-min and 3-h polymerization time for poly(1-co-2) and poly(1-co-3), respectively] by pouring the reaction mixture into a large excess of methanol. The precipitated copolymers were isolated by filtration, purified by several precipitations from dichloromethane into methanol, and dried in vacuo at 40 °C to a constant weight.

Polymer Characterization. Viscosity measurements were performed by a Desreux-Bischoff dilution viscometer at 30 °C in chloroform. Optical rotatory measurements were performed 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.

Varian T-60 and Varian XL100 spectrometers were used to record 60-MHz and 100-MHz ^{1}H NMR spectra at 37 and 50 °C, respectively, in $CDCl_3$ solution with Me_4Si as an internal standard.

IR spectra were recorded on Perkin-Elmer 225 and 180 spectrophotometers in thin films cast by slow evaporation of the solvent (CH_2Cl_2 or $CHCl_3$) from the polymer solution.

UV measurements were performed in dichloromethane solution in the spectral region 370–220 nm, using a Cary 14 spectrophotometer (path length 0.1–1 cm).

CD spectra in the region 370–220 nm were recorded on a Roussell-Jouan Dichrograph III at 25 °C in dichloromethane with path length 0.1–1 cm.

Fluorescence emission spectra were recorded on a Perkin-Elmer MPF3 spectrofluorimeter at room temperature in dichloromethane solution (10^{-5} M concentration) at the excitation wavelength of 330 nm. All spectra were corrected for the wavelength response of the detection system.

Results and Discussion

Synthesis and Characterization. Copolymers of N-vinylcarbazole (1) with (–)-menthyl acrylate (2) and (–)-menthyl methacrylate (3) were prepared under free-radical conditions in benzene at 55 °C. The polymerization data and some properties of the two copolymer sets are reported in Tables I and II.

Table III
Mean Sequence Length, Distribution $[X_{1(n)}]$, and Related UV Spectral Data of Copolymers of *N*-Vinylcarbazole (1) with (−)-Menthyl Acrylate (2)

run	co-units from 1, mol %	mean sequence length[a] $\bar{I}_1$	$\bar{I}_2$	$X_{1(n)}$[b] $n = 1$	$n = 2$	$n \geqslant 3$	$\epsilon_{231}/\epsilon_{238}$[c]
A1	17.7	1.01	4.90	97.1	2.8	0.1	0.928
A2	29.6	1.03	2.72	93.8	5.9	0.3	0.966
A3	35.3	1.06	2.00	89.7	9.5	0.8	0.991
A4	40.9	1.09	1.65	84.7	13.5	1.8	1.010
A5	46.4	1.13	1.43	78.3	18.0	3.7	1.031
A6	50.2	1.20	1.29	70.0	22.9	7.1	1.031
A7	47.1	1.30	1.18	58.9	27.4	13.7	1.037
A8	54.7	1.52	1.11	43.3	29.6	27.1	1.039

[a] $\bar{I}_1 = r_1([1]/[2]) + 1$ and $\bar{I}_2 = r_2([2]/[1]) + 1$. [b] % fraction of 1 in a sequence of *n*. [c] Molar extinction coefficient ratio of the UV absorption at 231 and 238 nm.

Table IV
Mean Sequence Length, Distribution $[X_{1(n)}]$, and Related UV Spectral Data of Copolymers of *N*-Vinylcarbazole (1) with (−)-Menthyl Methacrylate (3)

run	co-units from 1, mol %	mean sequence length[a] $\bar{I}_1$	$\bar{I}_3$	$X_{1(n)}$[b] $n = 1$	$n = 2$	$n \geqslant 3$	$\epsilon_{231}/\epsilon_{238}$[c]
MA1	8.8	1.01	10.08	97.2	2.7	0.1	0.944
MA2	16.4	1.03	5.21	94.0	5.7	0.3	0.958
MA5	23.6	1.05	3.46	90.2	9.1	0.7	0.964
MA6	32.3	1.08	2.53	84.9	13.3	1.8	0.981
MA8	37.4	1.19	1.70	71.0	22.3	6.7	1.007
MA9	43.5	1.23	1.55	65.5	25.0	9.5	1.013
MA10	49.2	1.30	1.44	60.4	26.9	12.7	1.035
MA11	58.7	1.60	1.22	39.1	29.3	31.6	1.042

[a] $\bar{I}_1 = r_1([1]/[3]) + 1$ and $\bar{I}_3 = r_3([3]/[1]) + 1$. [b] % fraction of 1 in a sequence of *n*. [c] Molar extinction coefficient ratio of the UV absorption at 231 and 238 nm.

In all cases the crude copolymers, isolated as white powders, were soluble in most organic solvents, giving an indirect proof of the formation of copolymer macromolecules instead of mechanical mixtures of parent homopolymers.[11] They were characterized by spectroscopic measurements without any further treatment, except those of runs A9 and M12, where a fractionation by extraction with boiling diethyl ether was carried out. ^{1}H NMR and IR spectra show the occurrence of bands characteristic of both co-units and substantiate a regular head-to-tail structure of monomeric units.

Copolymer compositions were evaluated by UV absorption spectroscopy, assuming the molar extinction coefficient per carbazole residue at 343 nm [$\epsilon = 3.6 \times 10^3$ M^{-1} cm^{-1} for poly(1)] to be independent on the composition. The validity of this method was confirmed by the excellent agreement with the composition data derived from the NMR spectra, even at the lowest (8.8 mol %) content of 1, where the maximum deviation would be expected.

Copolymerization curves relevant to both series of experiments are reported in Figures 1 and 2, respectively. The former system [poly(1-*co*-2)] shows an azeotropic point at 40/60 (1/2) composition, whereas for the latter [poly(1-*co*-3)] the 1/3 molar ratio is always lower in the copolymer than in the feed mixture.

Reactivity ratios, estimated according to the Kelen–Tüdös procedure, were as follows:

$r_1 = 0.13$ $r_2 = 0.43$ [poly(1-*co*-2)]

$r_1 = 0.11$ $r_3 = 1.18$ [poly(1-*co*-3)]

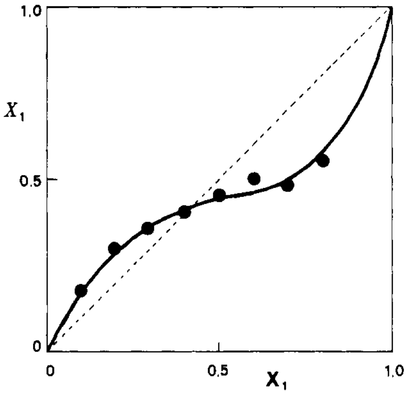

Figure 1. Composition diagram for *N*-vinylcarbazole (1)/(−)-menthyl acrylate (2) copolymerization: X_1 mole fraction of 1 in feed; X_1 mole fraction of 1 in copolymer.

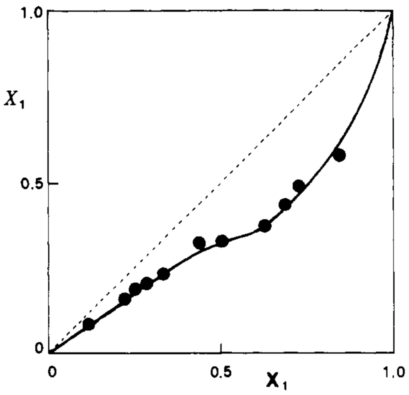

Figure 2. Composition diagram for *N*-vinylcarbazole (1)/(−)-menthyl methacrylate (3) copolymerization: X_1 mole fraction of 1 in feed; X_1 mole fraction of 1 in copolymer.

In both cases the relative reactivity of 1 is lower with respect to the unsaturated ester comonomer, the larger difference being observed for the 1/3 couple. We have to remark that the reported trend is opposite to that observed for copolymerization of 2 and 3 with vinylaromatic monomers such as styrene[20] and 1-vinylnaphthalene.[21] In all cases, however, 3 displays a higher reactivity than 2, thus confirming the general behavior of the two monomers in

Table V
Differential Dichroic Absorption Coefficient ($\Delta\epsilon_{max}$) at Different Wavelengths (λ/nm) of Copolymers of *N*-Vinylcarbazole (1) and (−)-Menthyl Acrylate (2) in CH_2Cl_2 at 25 °C

run	co-units from 1, mol %	$\Delta\epsilon_{max}$ 343	330	294	265	257	250	241	229
A1	17.7	+0.32	+0.17		−0.27	+0.59	+1.04	+1.45	−1.86
A2	29.6	+0.41	+0.18		−0.63	+0.73	+1.08	+1.08	−3.20
A3	35.3	+0.39	+0.23	−0.15	−0.82	+0.93	+1.28	+1.21	−4.10
A4	40.9	+0.41	+0.25	−0.16	−0.76	+1.12	+1.16	+1.36	−4.98
A7	47.1	+0.34	+0.23	−0.28	−0.70	+0.76	+0.84	+1.21	−5.47
A8	54.7	+0.28	+0.17	−0.33	−0.58	+0.83	+0.87	+0.87	−4.30
A9	66.8	+0.18	+0.10		−0.31	+0.58	+0.99	+1.08	−1.59

Table VI
Differential Dichroic Absorption Coefficient ($\Delta\epsilon_{max}$) at Different Wavelengths (λ/nm) of Copolymers of *N*-Vinylcarbazole (1) and (−)-Menthyl Methacrylate (3) in CH_2Cl_2 at 25 °C

run	co-units from 1, mol %	$\Delta\epsilon_{max}$ 345	342	330	295	265	260	246	240	230
MA1	8.8		−0.06	−0.05	−0.32	+0.38	+0.25	−0.51	−1.26	−0.54
MA2	16.4		−0.09	−0.08	−0.13	+0.16	+0.34	−0.39	−1.00	−2.42
MA3	23.6		−0.14	−0.11	−0.66	−0.28	+0.28	−0.58	−2.20	+0.20
MA6	32.3		−0.15	−0.14	−0.84	−0.44	+0.17	−1.64	−2.59	+0.56
MA10	49.2	+0.05	−0.07	−0.11	−1.11	−1.02	−0.81	−1.88	−3.32	+2.44
MA12	63.7	+0.16	−0.05	−0.05	−1.26	−1.29	−1.08	−1.88	−2.63	+1.26

the free-radical polymerization.[22]

The distribution of monomeric units, in terms of mean sequence length and sequence length distribution, as computed on the basis of the reported reactivity ratios[23] is presented in Tables III and IV. As expected, a higher tendency to alternance is observed in poly(**1**-*co*-**2**), as demonstrated by the shorter average length of the sequences of **2** units with respect to **3** units, while in both cases the **1** units are characterized by a smaller tendency to form blocks.

All the copolymers were optically active and the specific optical rotation was consistently of negative sign, as already found for poly(**2**) and poly(**3**)[16,24] (Tables I and II).

Chiroptical Properties. Aromatic chromophores are known to assume a preferentially chiral conformation when inserted, as pendant groups of a vinylaromatic structural unit, in a highly dissymmetric environment[5,6,25] such as that created by the presence of chiral units in isotactic copolymer macromolecules. In many cases this is evidenced by the enhancement of the optical rotation measured at the sodium D line with respect to the value expected on the basis of the content of the monomeric units deriving from the chiral comonomer. An unequivocal proof is, however, provided by the presence of CD absorption bands connected with the $\pi \rightarrow \pi^*$ electronic transitions of the aromatic chromophores which are located in the asymmetric environment generated by the chiral comonomer.

In the copolymers examined a consistent contribution to the optical rotation at long wavelength from **1** monomeric units is detectable in both cases (Tables I and II), the bigger contribution being observable in the poly(**1**-*co*-**2**) series, with a maximum value corresponding to a 50/50 molar composition ratio. Figure 3 indicates a comparison between the experimental trends and those expected for zero contributions. The extent of the induced optical rotation is very similar to that observed in the case of coisotactic copolymers of α-olefins[6,26,27] and alkyl vinyl ethers.[25] In contrast, a linear dependence of the optical rotation on the chemical composition has been found recently for copolymers of **2** and **3** with styrene[20] and 1-vinylnaphthalene,[21] although a marked contribution from achiral monomers has been reported for some methacrylate-based systems, such as triphenylmethyl methacrylate homopolymers[28] and copolymers with (*S*)-α-methylbenzyl methacrylate.[29,30]

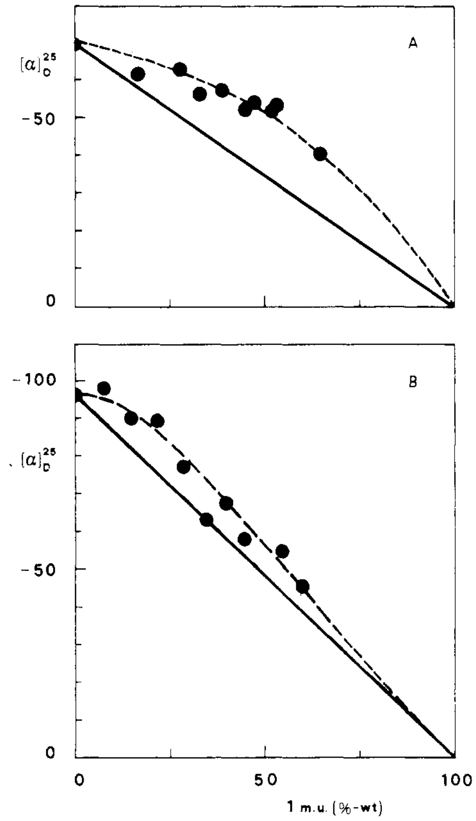

Figure 3. Variation of specific optical rotation ($[\alpha]^{25}_D$) vs. *N*-vinylcarbazole (1) unit content in copolymers of (A) *N*-vinylcarbazole (1)/(−)-menthyl acrylate (2) and (B) *N*-vinylcarbazole (1)/(−)-menthyl methacrylate (3).

Consistent with the optical rotation data noted above, the occurrence of induced asymmetry in the heteroaromatic chromophore is provided by the circular dichroism spectra of copolymer samples in the 360–220-nm region. In fact, both copolymer series show a rather complex set of dichroic bands centered at frequency values which are in close correspondence with the UV absorption

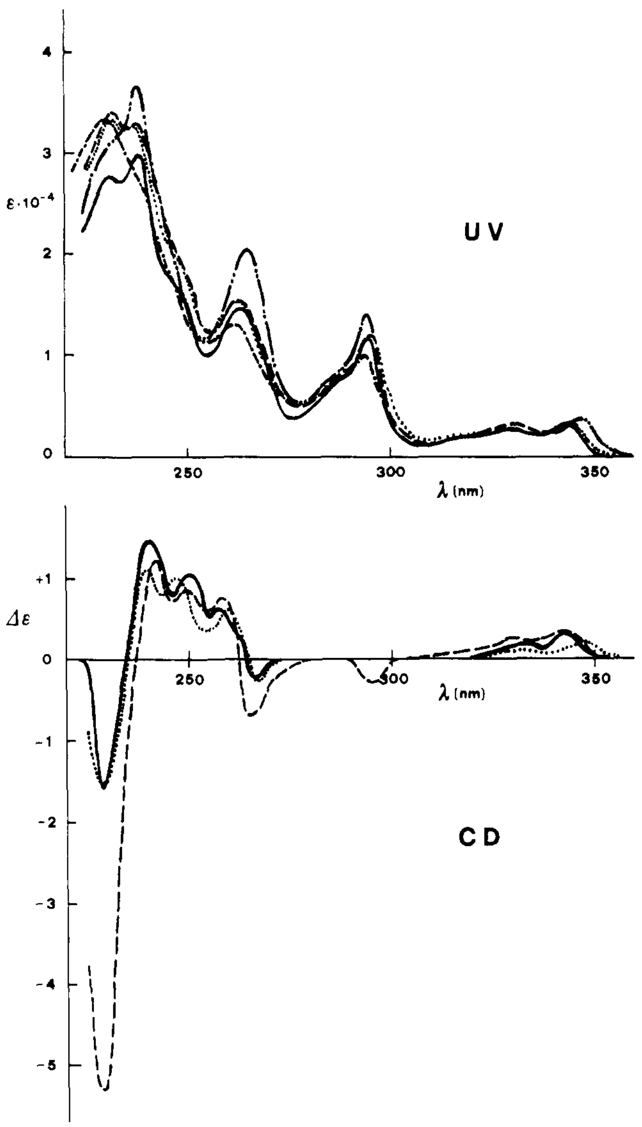

Figure 4. Ultraviolet (UV) and circular dichroism (CD) spectra in CH_2Cl_2 of some typical *N*-vinylcarbazole (1)/(–)-menthyl acrylate (2) copolymer samples having different content (mol %) of 1 units: (—) 17.7; (– – –) 47.1; (···) 66.8; (–··) *N*-isopropylcarbazole (4); (–·–) poly(*N*-vinylcarbazole).

profile of the copolymers which, in turn, reproduces those reported for poly(*N*-vinylcarbazole) and its low molecular weight analogues.[31] A rather detailed picture of dichroic absorption maxima is given in Tables V and VI. Figures 4 and 5 show a comparison of the UV and CD spectra of three samples having, respectively, a low (17.7; 8.8), medium (47.1; 49.2), and reasonably high (66.8; 63.7 mol %) content of heteroaromatic units. Analogous to data reported for copolymers of styrene with α-olefins[8,9] a substantial increment is observed in going from the longer wavelength region to the shorter one. Similar increases in the extent of induced circular dichroism with increasing energies of the corresponding optical transitions have already been reported for isotactic samples of poly[(*S*)-9-(2-methylbutyl)-2-vinylcarbazole],[12] for coisotactic copolymers of 1 with optically active vinyl ethers,[11] and of polypeptides having the carbazolyl group as a side-chain substituent.[32,33]

In the shortest wavelength region (λ <250 nm) the dichroic absorption of the heteroaromatic chromophore is affected at least partially by the tail of the CD band connected with the n → π* electronic transition of the carboxyl group. Nonetheless this contribution is seen to be very small by comparing the observed spectra with the absorption of the corresponding mixtures of homopolymers in the same spectral region.

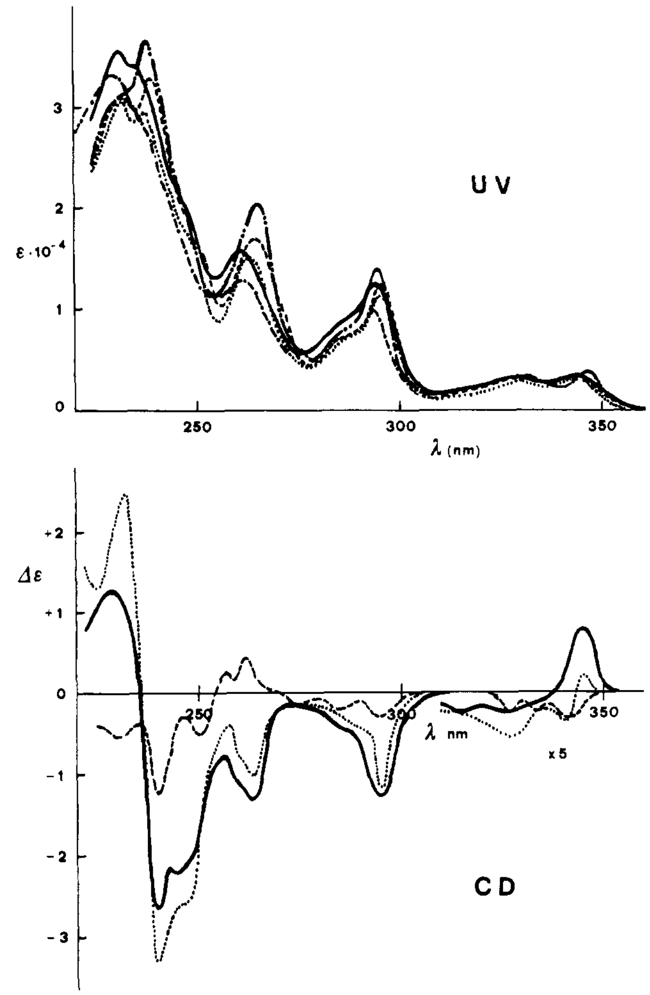

Figure 5. Ultraviolet (UV) and circular dichroism (CD) spectra in CH_2Cl_2 of some typical *N*-vinylcarbazole (1)/(–)-menthyl methacrylate (3) copolymer samples having different content (mol %) of 1 units: (– – –) 8.8; (···) 49.2; (—) 63.7; (–··) *N*-isopropylcarbazole (4); (–·–) poly(*N*-vinylcarbazole).

Poly(1-*co*-2) samples show three negative dichroic bands around 294, 265, and 229 nm and two structured positive bands with maxima centered at 343 and 330 nm and 257, 250, and 241 nm, respectively (Figure 4). Usually in copolymers of a chiral monomer with an achiral one having a chromophore in the side chain the differential dichroic absorption coefficient (Δε) increases with the content of the chiral comonomer up to a saturation value.[6,20] However, in the case of copolymers of *N*-vinylcarbazole with (–)-menthyl vinyl ether it was observed previously that Δε, relative to almost all dichroic bands, increased up to a maximum value at approximately 20 mol % *N*-vinylcarbazole and then decreased, with further increase in the content of the chiral comonomer.[11] A similar behavior seems to be present in the copolymers of 1 with 2, the most marked effect being observed in the 229-nm absorption band (Table V).

Poly(1-*co*-3) samples display an almost identical set of bands, but it is of interest to point out some differences. The structured CD band at the longest wavelength shows two negative peaks of low intensity, while a new peak at 345 nm appears, as the content of 1 reaches 49 mol %. The two positive peaks at 265 and 260 nm gradually change sign and become negative, with increasing content of units from 1 up to about 20 and 35 mol %, respectively. The same behavior is observed for the 230-nm band, which turns from negative to positive within the above-mentioned compositions. A complete understanding of these effects is not yet available but it is clear that cooperative electronic effects of sequences of carbazole units influence the degree of induced circular dichroism. The carbazole chromophore is thus seen to be a particularly sensitive probe for sequence distributions in copolymers, as recently pointed out in other carbazole-containing copolymers.[34,35]

These results indicate that even in radically prepared copolymers of vinylaromatic monomers with optically active acrylic and methacrylic derivatives an appreciable, and even higher than that previously reported for isotactic systems, induced optical activity can be generated. Both ellipticity and the sign of the dichroic bands are very sensitive to composition and sequence length and distribution of copolymer samples, these effects being more markedly present in copolymers with (−)-menthyl methacrylate.

Spectroscopic Properties. The UV absorption spectra in CH_2Cl_2 of copolymer samples are characterized by four bands, centered at about 344, 295, 262, and 230 nm; the first two bands also show vibronic structure. They are similar to the spectra of carbazole-containing polymers and their low molecular weight derivatives, but some differences arise in the comparisons with the UV absorption of *N*-isopropylcarbazole, which can be taken as a reference compound where no intramolecular interaction occurs to affect the electronic transitions of the heteroaromatic chromophore. In fact, in all samples the longest wavelength band, $^1L_b \leftarrow {}^1A$, shows a hypsochromic shift of 3 nm, with respect to *N*-isopropylcarbazole. Moreover, as the content of 1 is increased in the poly(**1**-*co*-**3**) series, the $^1B_2 \leftarrow {}^1A$ band at 265 nm gradually moves toward the blue, thus resembling more and more the corresponding absorption in poly(**1**). More significant and marked differences are, however, detectable in the 240–220-nm region. Two bands are present, with maxima at 238 and 230 nm, respectively. As already reported,[34-37] the latter is related to electronically interacting carbazole chromophores, whereas the former is typical of the isolated carbazole unit. Accordingly, the 230-nm absorption is prominent in poly(*N*-vinylcarbazole), the 238-nm absorption being present only as a slight shoulder. A completely opposite situation is observed in *N*-isopropylcarbazole.

The reported UV data are consistent with the fact that, as the content of **1** and correspondingly the mean sequence length of **1** in the copolymers are increased, the relative intensity of the above-mentioned peaks changes and the shortest wavelength absorption becomes predominant (Tables III and IV).

In this context it was of interest to investigate whether the contribution from the ester comonomers influences the spectrum of poly(**1**). In the 230-nm range poly(menthyl acrylate) and poly(menthyl methacrylate) have maxima at 213 and 217 nm with molar extinction coefficients (ϵ) of 150 and 220 M^{-1} cm^{-1} in *n*-heptane, respectively. These values, at least in the range of compositions examined, indicate that absorbance due to the ester groups can be neglected because of the extinction coefficient (ϵ ~33 000) for poly(*N*-vinylcarbazole) in the same region. Spectra of mixtures of poly(**1**) with poly(**2**) and poly(**3**) do not show any detectable variation, confirming that the copolymer UV absorption of the carbazole group is not significantly influenced by the chiral comonomers.

Fluorescence emission spectra recorded on the two sets of copolymer samples are characterized in both cases by a monomer-type profile[14] up to 40 mol % **1** unit content, whereas for samples with a larger heteroaromatic unit content contribution to the fluorescence spectra by excimer-type emitting species[14] is detectable and, as expected, it increases by increasing **1** unit content in a sequence of two or more. The above trend is therefore consistent with the distribution of monomeric units in the two different copolymers evaluated on the basis of the reported reactivity ratios.

The ^1H NMR spectra of poly(**1**) and block copolymers derived from **1** display in the region of aromatic proton resonance four signals at 7.7, 7.0, 6.3, and 4.8 ppm. The last two peaks have been attributed[38] to strongly interacting protons in adjacent carbazole units, while the first two are typical of the isolated carbazole unit. Only the first two signals are present in the resonance spectra of carbazole and its N-substituted low molecular weight derivatives.

The ^1H NMR spectra of copolymer samples show two resolved peaks at 7.9 and 7.1 ppm, typical of isolated carbazole nuclei, in keeping with their quasi-random, almost alternating, distribution of monomeric units. As the molar content of **1** reaches about 30 and 35 mol % in poly(**1**-*co*-**2**) and poly(**1**-*co*-**3**), respectively, a more or less marked shoulder at around 6.3 ppm becomes appreciable, indicating the occurrence of the above-mentioned interactions between neighboring carbazole nuclei and consistent with a mean sequence length of carbazole units greater than unity.

Conclusions

Polymerization of *N*-vinylcarbazole with chiral monomers such as (−)-menthyl acrylate and (−)-menthyl methacrylate yields, under free-radical initiation, copolymer samples which are characterized by a random distribution of monomeric units with, however, a tendency to alternation.

In all cases the reported copolymers were optically active, the sign of the optical rotation being the same as that of the homopolymers of the appropriate chiral comonomers, and in both series a contribution to the optical rotation measured at the sodium D line by heteroaromatic units is clearly evidenced. Thus the longer (340 nm) and the shorter (230 nm) wavelength $\pi \rightarrow \pi^*$ electronic transitions of the carbazole moieties are optically active and characterized by rotatory strengths which increase, in going from the lowest energy transitions to the highest energy ones. We have to remark that the observed differential dichroic absorption coefficients are comparable in magnitude to those reported for coisotactic copolymers of chiral α-olefins with vinylaromatic monomers (styrene and vinylnaphthalene) and 1 order of magnitude larger than those found for copolymers of the same vinylaromatic monomers with (−)-menthyl acrylate and (−)-menthyl methacrylate.

Moreover, the variation of dichroic absorption with chemical composition of copolymer samples shows the same unusual profile already noted for *N*-vinylcarbazole/(−)-menthyl vinyl ether copolymers with maximum values at a critical composition (about 40 mol % **1**). At this composition there is, therefore, an apparent optimization of the induced optical activity for both types of copolymer. It follows that the carbazole chromophore can be taken as a very sensitive probe for sequence distribution at a given copolymer composition, even though quantitative aspects are not yet rationalized in a simple manner.

UV absorption, fluorescence emission, and ^1H NMR spectra support the existence of only short sequences of interacting carbazolyl groups and agree well with the sequence lengths and distributions evaluated on the basis of the estimated reactivity ratios.

As a final conclusion we have to stress the great potential of the free-radical copolymerization of easily available chiral monomers, such as (−)-menthyl acrylate and (−)-menthyl methacrylate, with *N*-vinylcarbazole to achieve synthetic macromolecules in which the heteroaromatic chromophores strongly contribute to the optical rotation of the polymer as a whole.

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Domain-Boundary Structure of Styrene–Isoprene Block Copolymer Films Cast from Solutions. 5. Molecular-Weight Dependence of Spherical Microdomains

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ABSTRACT: A series of diblock polymers of polystyrene and polyisoprene having nearly equal polyisoprene content (about 15 wt %) but different total molecular weight were synthesized to study the domain size, interdomain distance, and the thickness of the domain-boundary interphase as a function of molecular weight for the spherical microdomain system in the solid state (polyisoprene spheres dispersed in a polystyrene matrix). Quantitative analyses with the small-angle X-ray scattering technique indicated that the size of the spherical domain (radius $\bar{R}$) and interdomain distance $\bar{D}$ vary, respectively, with the molecular weight of the polyisoprene block and that of the entire block polymer to the $^2/_3$ power, while the interfacial thickness is almost independent of the molecular weight covered in this work (about 1.8 nm). The $^2/_3$ power law is consistent with the results predicted from the equilibrium theory of Helfand and Wassermann but the absolute values of $\bar{R}$ and $\bar{D}$ are far below the theoretical values, due to a nonequilibrium effect encountered in the solvent evaporation process. Thus the spherical domain systems in the solid state are in a metastable state with an excess free energy attributed to an excess interfacial area or interfacial volume, which contrasts with the lamellar microdomain systems, where the systems are very close to the equilibrium state.

I. Introduction

In this series of papers[1-4] we have been exploring the microdomain structure and the structure of the polymer–polymer interphase in polystyrene–polyisoprene diblock polymers in relation to the fundamental molecular and thermodynamic variables of the systems by using the small-angle X-ray scattering (SAXS) technique. In part 1 we made a paracrystalline analysis for the block polymer having lamellar microdomains to investigate orientation of the domains, uniformity of the domain size and regularity in their spatial arrangement, and the thickness of the domain-boundary interphase where the incompatible

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