Synthesis, fluorescence emission spectra and chiroptical properties of copolymers of *N*-vinylcarbazole and optically active fumarates

Giancarlo Galli, Roberto Solaro and Emo Chiellini*
Istituto Chimica Organica Industriale, University of Pisa, Centro CNR Macromolecole Stereordinate Otticamente Attive, Via Risorgimento 35, 56100 *Pisa, Italy*

and Anthony Ledwith
*Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, Liverpool L*69 3*BX, UK*
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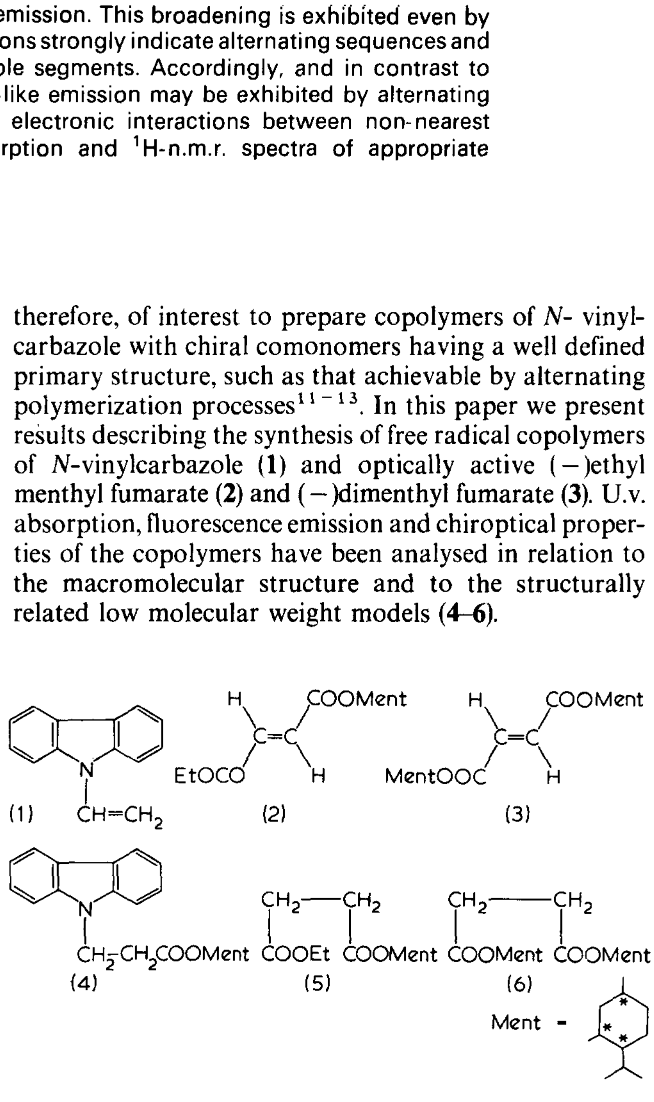
Optically active (−)menthylethylfumarate (**2**) and (−)dimenthylfumarate (**3**) have been synthesised and free radically copolymerized with *N*-vinylcarbazole (**1**). Copolymers of (**1**) and (**2**) exhibit a strong tendency to alternation in agreement with earlier conclusions from studies of copolymerization of (**1**) with diethylfumarate. Surprisingly the much more hindered, but symmetrical fumarate, (**3**) yields copolymers which always have carbazole monomer contents in excess of the 1:1 alternating ratio. Chiroptical measurements indicate significant induced optical activity in the carbazole chromophores of all the copolymers obtained but, in accord with the predominance of alternating structures, there is no real evidence for any sequence-determined maximum in induced circular dichroism. Fluorescence emission spectra of all copolymer samples exhibit significant asymmetric broadening on the long wavelength (low energy) side of the normal carbazole monomeric emission. This broadening is exhibited even by poly (**1**-co-**2**) samples for which the monomer compositions strongly indicate alternating sequences and must, therefore, represent interaction between carbazole segments. Accordingly, and in contrast to widely held assumptions, it is concluded that excimer-like emission may be exhibited by alternating copolymers of *N*-vinylcarbazole. Further evidence for electronic interactions between non-nearest neighbour carbazole units is provided by u.v. absorption and ^{1}H-n.m.r. spectra of appropriate copolymers.

INTRODUCTION

N-vinylcarbazole is an extremely reactive monomer, easily polymerized by free radical[1] and cationic[2] processes. Its polymerization has been initiated thermally[3] and photochemically[4] as well as by Ziegler–Natta catalysts[5]. Copolymers of *N*-vinylcarbazole with a wide variety of comonomers are known[6,7] and recent reports have been concerned with alternating copolymerization[8–10] with electron-acceptor comonomers, such as fumaronitrile[11], diethyl fumarate[12], and diethyl maleate[13]. Aspects of both homopolymerization, copolymerization and practical application of carbazole-containing polymers have been extensively reviewed[14]. In the framework of our investigations into the configurational and conformational organisation of optically active vinyl polymers[15–17], we have characterized optically active homopolymers and copolymers containing the carbazole nucleus[18], with the aim of gaining further insight into the correlations between primary and secondary polymer structures and photophysical properties of the attached carbazole units[19].

As a result of these studies we recently pointed out the rather special properties of the carbazolyl chromophore as a valuable conformational probe in the assignment of a secondary structure[20–22], even in systems characterized by a very low conformational homogeneity[23]. It became, therefore, of interest to prepare copolymers of *N*- vinylcarbazole with chiral comonomers having a well defined primary structure, such as that achievable by alternating polymerization processes[11–13]. In this paper we present results describing the synthesis of free radical copolymers of *N*-vinylcarbazole (**1**) and optically active (−)ethyl menthyl fumarate (**2**) and (−)dimenthyl fumarate (**3**). U.v. absorption, fluorescence emission and chiroptical properties of the copolymers have been analysed in relation to the macromolecular structure and to the structurally related low molecular weight models (**4**–**6**).



(1) (2) (3)

(4) (5) (6)

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EXPERIMENTAL

Materials

Commercial 2,2′-azobisisobutyronitrile (AIBN) was recrystallized from ethanol.

Commercially available *N*-vinylcarbazole (**1**) was purified by 3 recrystallizations from methanol (m.p. 65°C).

(−)Menthol [(1R,3R,4S)-1-methyl-4-isopropylcyclohexan-3-ol] was crystallized from isoctane {m.p. 43-45°C; $[\alpha]_D^{25}-49.5$ (ethanol)]. (−)Ethylmenthyl fumarate (2) was synthesised according to the general procedure of Barnett *et al.*[24] 15.6 g (0.1 mol) of menthol was dissolved in 7.9 g (0.1 mol) of dry pyridine and 125 ml of anhydrous diethyl ether. A solution of 16.2 g (0.1 mol) of fumaric acid monoethyl ester chloride[25] in 25ml of ether was added dropwise at room temperature over a period of 1 h. The reaction mixture was heated under reflux for 10 h, then 100ml of water was added. The organic layer was washed respectively with water, 5% $NaHCO_3$, water, dried over $MgSO_4$, and evaporated *in vacuo*. The dark-brown liquid obtained was decolourised with activated charcoal using n-hexane as a solvent. Subsequent distillation gave 20.5g (72.9% yield) of a slightly viscous oil {b.p. 130-132°C/2mmHg; $[\alpha]_D^{25}-72.3$ (benzene)] which could not be crystallized.

^{1}H-n.m.r. (CCl_4) $\delta=6.8$ (*s*, 2H, =CH), 4.8 (*m*, 1H, COOCH), 4.3 (*q*, 2H, CH_2) and 2.3-0.6 ppm (*m*, 21H, other aliphatic protons).

The i.r. spectrum displayed the typical set of bands diagnostic of alkyl fumarates: 1720, 1645, 1385 and 1365 (δ isopropyl), 1290, 1255, 1175, 1150 and 770 cm^{-1}. M.s.: m/e 282 (M^+, 1%), 254, (5), 237 (5), 155 (4), 139 (41), 138 (95), 127 (19), 123 (34), 99 (34), 95 ($M^+-C_9H_{17}O_4$, 100), 83 (63), 82 (33), 81 (88), 51 (83).

(−)Dimenthyl fumarate (**3**) {$[\alpha]_D^{25}-91.6$ (benzene)} was prepared by reacting fumaroyl chloride[26] with menthol in chloroform in the presence of dry quinoline.

(−)Menthyl 3-(9-carbazolyl)-propionate (**4**) {$[\alpha]_D^{25}-43.5$ (chloroform)} was synthesised as will be reported elsewhere[27].

(−)Ethyl menthyl succinate (**5**) was prepared according to the conventional esterification procedure. To a solution of 14.1g (0.09 mol) of menthol in 20.9ml (0.27 mol) of dry pyridine 14.8g (0.09 mol) of succinic acid monoethyl ester chloride[28] was added dropwise at 0°C over a period of 1 h. The reaction mixture was kept stirred overnight at room temperature, poured into iced 10% HCl, then extracted with n-pentane. The organic layer was washed with 5% $NaHCO_3$, water, dried over $MgSO_4$ and evaporated *in vacuo*. The viscous oil obtained, after purification by elution with dichloromethane on a column of silica gel, gave 21.1 g (82.7% yield) of a colourless oil having $[\alpha]_D^{25}-55.9$ (n-heptane).

^{1}H-n.m.r. (CCl_4) $\delta=4.4$ (*m*, 1H, COOCH), 3.8 (*q*, 2H, CH_2), 2.3 (*s*, 4H, CH_2COO) and 2.0-0.6 ppm (*m*, 21H, other aliphatic protons).

I.r. (liquid film) = 1745, 1395 and 1375 (δ isopropyl), 1165 (broad), 1100, 1030 and 985 cm^{-1}.

M.s. = m/e 155 (12%), 147 (45), 139 (43), 138 (93), 129 (100), 123 (34), 101 (86), 95 (56), 83 (28), 82 (17), 81 (42), 55 (42).

(−)Dimenthyl succinate (**6**) {$[\alpha]_D^{25}-83.0$ (n-heptane)} was prepared by reacting succinic acid with menthol in benzene in the presence of *p*-toluensulphonic acid.

Polymerization experiments

The copolymerizations were carried out in benzene solution at 65°-70°C using AIBN as a free-radical initiator. Total comonomer concentrations in the range 0.8-1.0M and a molar ratio, comonomer/initiator = 100 were used. All runs were performed after several freeze-pump-thaw cycles in sealed glass tubes, wrapped in aluminium foil to avoid exposure to light[29]. The polymerizations were stopped by pouring the homogeneous mixture into a large excess of methanol. The coagulated polymer was filtered, purified by repeated precipitations from dichloromethane solution into methanol, dried and weighed. Crude copolymers were twice fractionated at room temperature with carbon tetrachloride, in which *N*-vinylcarbazole homopolymer is insoluble. Attempted homopolymerizations of the two chiral monomers (**2**) and (**3**) in the same experimental conditions did not yield any amount of methanol-precipitable polymeric product.

Polymer characterization

Viscosity measurements were performed by a Desreux-Bischoff dilution viscometer at 25°C in chloroform.

Optical rotatory measurements were carried out at 25°C on a Perkin-Elmer 141 Spectropolarimeter, using solutions having concentrations in the range 1-3g/dl (path length 1dm).

I.r. spectra were recorded by a Perkin-Elmer 180 Spectrometer either on thin films cast by slow evaporation of the solvent from the polymer solution or on KBr pellets.

60 MHz and 100 MHz ^{1}H-n.m.r. spectra were recorded on Varian T60 and XL100 Spectrometers at 37°C in $CDCl_3$ solution, using TMS as an internal standard. M.s. spectra were recorded by a Varian MAT Mod. CH7 Spectrometer.

Gel permeation chromatography (g.p.c.) spectra were taken in toluene solution using a Waters 200 Instrument, and also in tetrahydrofuran solution by means of a Du Pont 860 Instrument.

U.v. measurements were carried out on either dichloromethane or n-heptane solutions in the spectral region 370-200nm by using a Cary 14 Spectrometer (path length 0.1-1cm).

C.d. spectra in the same spectral region were recorded on a Roussell-Jouan Dichrograph III at 25°C.

Fluorescence emission spectra were recorded on a Perkin-Elmer MPF3 Spectrofluorimeter in concentration conditions to avoid any correction for the self-absorption ($c=10^{-5}$mol/l), at the excitation wavelength of 330nm in dichloromethane solution. All spectra were corrected for the wavelength response of the detection system.

RESULTS AND DISCUSSION

Synthesis and characterization of copolymers

Copolymers of *N*-vinylcarbazole (**1**) with electron-accepting monomers, such as (−)ethyl menthyl fumarate (**2**) and (−)dimenthyl fumarate (**3**) were prepared by free-radical initiation (AIBN) in benzene at 65°C. The polymerization data and some properties of the two copolymer series are summarized in *Table 1*.

In both systems the copolymers were preferentially obtained with concurrent formation of small amounts of homopoly(**1**) (10-15% of the total), which was easily removed by fractionation with carbon tetrachloride at room temperature. Attempted homopolymerizations of (**2**) and (**3**) in the same experimental conditions did not

Table 1 Copolymerization of *N*-vinylcarbazole (**1**) with (–)ethyl menthyl fumarate (**2**) or (–)dimenthyl fumarate (**3**) in benzene at 65°C

	Polymerization conditions[a]			Polymeric product[c]		
Run	Amount of (1) (mmol)	Molar ratio (1)/(2) or (1)/(3)	Conversion[b] %	(1) units[d] (% mol)	$[\eta]$[e] (dl/g)	$[\alpha]_D^{25}$[e]
E1	1.0	0.33 (2)	9.3	49.9	0.56	–38.1
E2	2.0	0.66 (2)	17.3	52.1	0.66	–38.0
E3[f]	3.0	1.00 (2)	4.3	53.0	0.85	–40.5
E4	4.0	4.00 (2)	94.5	59.8	1.13	–35.4
D1	2.0	0.66 (3)	9.6	57.9	0.56	–49.4
D2[f]	3.0	1.00 (3)	2.6	68.5	0.82	–37.7
D3	4.0	4.00 (3)	77.1	73.7	1.02	–46.0

[a] Total comonomer concentration 0.8–1.0M; molar ratio comonomers/AIBN = 100; polymerization time 24 h
[b] Calculated as (weight of solid polymer/total weight of starting comonomers) x 100
[c] Fraction soluble in CCl_4 at room temperature
[d] Determined by ^{1}H-n.m.r. spectroscopy
[e] In chloroform, at 25°C
[f] At 70°C; polymerization time 4 h

give any solid polymer, contrasting with a report of the homopolymerization of diethyl fumarate[30]. G.p.c. traces of the prepared samples in different solvents were found to be monomodal, supporting the formation of copolymer macromolecules and this was also unambiguously confirmed by solubility, n.m.r., u.v. and c.d. measurements. The copolymers, isolated as white powders, were characterized by a rather high molecular weight[31] $\{[\eta] = 0.5–1.2$ dl/g$\}$, the value of the intrinsic viscosity depending upon the molar fraction of (**1**) in the feed mixture.

The i.r. spectra are characterized by a profile which can be considered as derived from combinations of absorbances typical of poly(**1**) and of the succinic diester type structural units. No band typical of C–H bending of the double bond between 1000 and 800 cm^{-1} or of C–O stretching of carboxylic acid groups is observed, thus confirming that the polymerization process occurs at the olefinic double bond, with no cleavage of the ester groups under the adopted polymerization conditions and the subsequent manipulation of the polymeric materials. Copolymer compositions were easily evaluated by n.m.r. spectroscopy, because of the good separation between the resonance signals of the heteroaromatic and aliphatic protons.

In all cases the copolymers were optically active, the value of the optical rotation $[\alpha]_D^{25}$ being dependent on the content of chiral comonomer, although a clear correlation between copolymer composition and optical rotation cannot be detected. The composition data of poly (**1**-co-**2**) samples show that they are constituted by approximately equimolar amounts of the two comonomers for monomer feeds where the *N*-vinylcarbazole molar fraction is either equal to, or less than 0.5. Deviation from alternation occurs on increasing (**1**) content in the initial mixture, as previously reported for copolymerization of (**1**) with dimethyl and diethyl maleates[13]. However, regardless of feed composition poly(**1**-co-**3**) samples are always richer in *N*-vinylcarbazole units than in the chiral comonomer, in contrast to the report by Mikawa and co-workers[11,12] of the formation of strictly 1:1 alternating copolymers of (**1**) with other symmetrical fumaric acid derivatives. The Japanese authors propose a generalized mechanism for alternating radical copolymerization, which involves the participation of both monomer charge-transfer (*CT*) complexes and free monomers in the propagating steps of the copolymerization[12,32,33]. They have been able to separate and to quantify the individual contributions to the overall process, although the relative degree of participation of the *CT* complex and the free monomers is conceived to depend greatly on the polymerization system[33]. The present data indicate that apparent alternating copolymerizations may exhibit features which vary on changing the nature of parameters such as polarity and steric hindrance in the monomeric species involved.

Chiroptical properties

Aromatic chromophores are known to give an appreciable contribution to molar optical rotation when inserted in a highly dissymmetric environment[34,35], such as that generated by the presence of chiral units in isotactic polymers. For the copolymers under investigation, the magnitude of enhancement, if any, of the optical rotation at the sodium *D* line can not be directly evaluated, due to the lack of the homopolymers of the corresponding chiral comonomers. Nevertheless, the occurrence of such an asymmetric perturbation of the heteroaromatic chromophore is clearly evidenced by the circular dichroism (c.d.) spectra of the samples in the 360–220nm region. In fact, both systems display a rather complex set of bands at frequency values closely related to the u.v. absorption bands of the carbazolyl moiety in the copolymers (*Figures 1* and *2*). A substantial increase of the induced circular dichroism effects is observed in going from the long wavelength region to the short one, analogous to our previous observations for copolymers of (**1**) with optically active vinyl ethers[20], acrylates and methacrylates[22], and of polypeptides having the carbazolyl chromophore as pendant group[36].

All the copolymer samples show three negative dichroic bands centred at about 297, 262 and 231nm and two structured positive dichroic bands with relative maxima at about 337, 325 and 250, 242nm respectively. The c.d. spectrum of menthyl 3-(9-carbazolyl)-propionate (**4**), taken as low molecular weight analogue, displays positive dichroic absorptions at 342, 329, 297 and 225nm and negative ones at 292, 260, 250 and 239nm. The differences both in sign and relative intensity between the c.d. bands of the copolymer samples and those of (**4**) unequivocally demonstrate the occurrence of a well defined polymer chain effect on the conformational properties of the heteroaromatic units. However, the c.d. spectra of (–)ethyl menthyl succinate (**5**) and (–)dimenthyl suc-

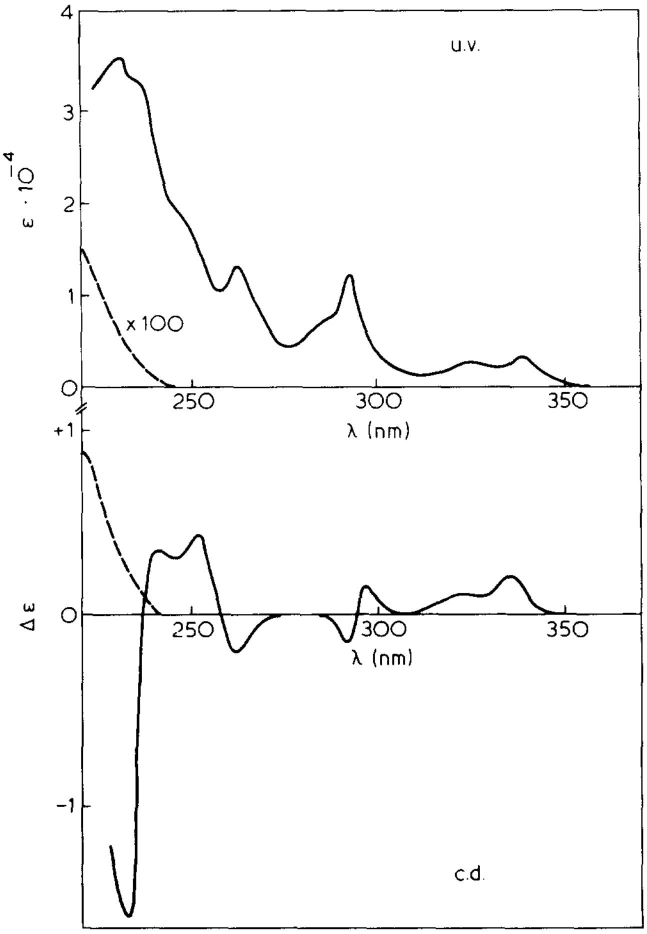

Figure 1 U.v. and c.d. spectra of: (——) Poly(*N*-vinylcarbazole-co-ethyl menthyl fumarate) [Poly(1-co-2)] Run E1 in CH_2Cl_2; – – – –(–)Ethyl menthyl succinate (**5**) in n-heptane

cinate (**6**), taken as model compounds for the chiral units in the two copolymer series, show only a positive band with maximum at 215nm, thus ruling out any significant contribution of the chiral co-unit to the observed spectra in the 230–350nm region.

In poly(**1**-co-**2**) samples the absolute values of molar dichroic absorption coefficient (Δε) decrease with increasing (**1**) content (*Table 2*), this trend being typical for copolymers of a chiral monomer with an achiral one having an aromatic chromophore in the side chain[35,37]. On the contrary, for the poly(**1**-co-**3**) series the absolute values of Δε increase with (**1**) content in the range 59–73 mol% (**1**) unit (*Table 3*). An analogous trend has already been observed in the case of copolymers (**1**) with (–)menthyl vinyl ether[20] and (–)menthyl acrylate and methacrylate[22], where Δε is maximized for (**1**) contents of about 20 and 40%-mol respectively. This anomalous behaviour has been tentatively explained by assuming the existence of a critical sequence length of (**1**) units, which is reached at different (**1**) contents, depending on reactivity ratios. The maximum Δε is observed in block-like menthyl vinyl ether-(**1**) copolymers at 20%(**1**) unit content, whereas in more statistical copolymers of (**1**) with menthyl acrylate and menthyl methacrylate the maximum in Δε occurs at 40% (**1**) units. Therefore, considering the strong tendency to alternation in the investigated copolymers of alkyl fumarates it is possible that the critical (**1**) unit sequence length required to maximise Δε is only reached when the content of monomer (**1**) reaches at least 73 mol%.

Electronic absorption spectra

The u.v. absorption spectra in dichloromethane solution of the copolymers investigated are characterized by four main bands centred at about 339, 294, 262 and 230nm; the first two bands also show vibronic structure. These are very similar to the spectra of other carbazole-containing polymers but some interesting differences are detectable both in profile and absorption intensities when compared to u.v. absorption behaviour displayed by poly(**1**) and the model compound (**4**). In fact, in all the samples the positions of the low energy maxima at 339 and 325nm, due to $^1L_b \leftarrow {}^1A_1$ transition of the carbazolyl moiety, are 3–5nm blue shifted with respect to poly(**1**) (*Figure 3*). The extent of this hypsochromic effect is almost certainly[38] related to the electron-attracting effect of the structural unit deriving from the disubstituted olefinic comonomer and seems to be sensitive to composition[13]. Accordingly, the absorption maxima wavelengths gradually increase and approach the value of poly(**1**), on increasing (**1**) content in poly(**1**-co-**3**). More significant features are, however, detectable in the 240–220nm region (*Figure 3*). In this range the model compound (**4**) is characterized, as expected, by an absorption band with a maximum at 238nm and a slight shoulder at 230nm, whereas in the present series of copolymers a maximum at 230nm and a shoulder at 238nm are observed.

Previous studies[22,39,40] have shown that poly(**1**) and random copolymers of (**1**) with methylmethacrylate exhibit absorbtion maxima at 230nm with a weak shoulder at 238nm, provided that the amount of (**1**) present in

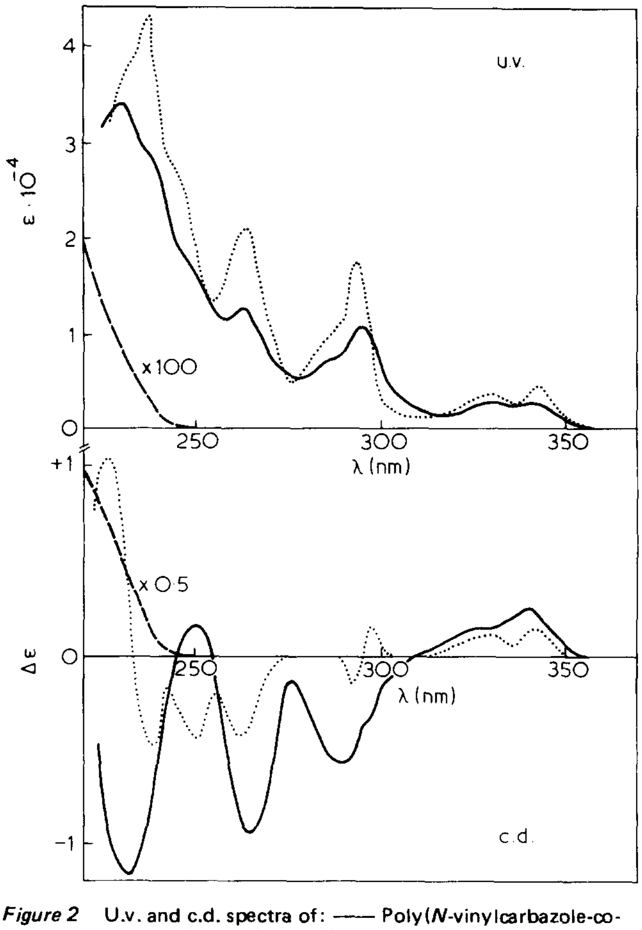

Figure 2 U.v. and c.d. spectra of: —— Poly(*N*-vinylcarbazole-co-dimenthyl fumarate) [Poly(1-co-3)] Run D3 in CH_2Cl_2. – – –(–) Dimenthyl succinate (**6**) in n-heptane. · · · · (–)menthyl-3-(9-carbazolyl) propionate (**4**) in CH_2Cl_2

Table 2 Differential dichroic absorption coefficient ($\Delta\epsilon_{max}$) at different wavelengths of copolymers of *N*-vinylcarbazole (**1**) and (−)ethyl menthyl fumarate (**2**) in CH_2Cl_2 at 25°C

Run	1 Units (%-mol)	$\Delta\epsilon_{max}/\lambda$ (nm)							
		337	325	297	292	262	250	242	231
E1	49.9	+0.41	+0.24	+0.34	−0.26	−0.38	+0.87	+0.67	−3.2
E2	52.1	+0.40	+0.22	+0.15	−0.34	−0.42	+0.93	+0.84	−3.1
E3	53.0	+0.42	+0.24	+0.23	−0.30	−0.27	+0.89	+0.89	−2.8
E4	59.8	+0.26	+0.10	−0.35	−0.49	−0.56	+0.49	+0.49	−2.0

Table 3 Differential dichroic absorption coefficient ($\Delta\epsilon_{max}$) at different wavelengths of copolymers of *N*-vinylcarbazole (**1**) and (−)dimenthyl fumarate (**3**) in CH_2Cl_2 at 25°C

Run	1 Units (%-mol)	$\Delta\epsilon_{max}//\lambda$ (nm)						
		340	325	297	292	264	252	232
D1	57.9	+0.15	+0.08	+0.15	−0.16	−0.53	+0.53	n.d.
D2	68.5	+0.17	+0.09	+0.15	−0.15	−0.40	+0.56	−1.26
D3	73.7	+0.25	+0.13	−0.33	−0.58	−0.94	+0.15	−1.16

the copolymers is greater than 60–70%. In addition, block copolymers of (**1**) with (−)menthylvinylether exhibit a maximum at 230nm and a shoulder at 238nm[21]. It must be concluded, therefore, that electronic interactions in extended sequences of carbazole units in poly(**1**) and appropriate copolymers of (**1**) are responsible for the absorption maximum at 230nm and that isolated carbazole units are responsible for the absorption at 238nm. As a consequence it can be assumed that even in copolymers with apparent alternating structures (Runs E1–E3), there are strong electronic interactions among the carbazole nuclei, comparable in magnitude to those of poly(**1**) and significantly higher than those observed in statistical carbazole-containing copolymers[22,40], and contributing to an appreciable observed hypsochromic effects with increasing (**1**) unit content. Any secondary contribution to this trend by ester chromophore absorption in the same spectral region can be ruled out because of the two orders of magnitude difference in molar extinction coefficients of (**4**) when compared with (**5**) and (**6**) which are taken as representative models of co-units (**1**), (**2**), and (**3**) respectively.

Fluorescence emission spectra

The fluorescence emission spectra display a broad profile with little vibronic structure and a maximum centred in the range 360–375nm depending on composition (*Figure 4*). In comparison with the model compound (**4**) however, all samples are characterized by a long wavelength tail with maximized relative intensity at highest (**1**) content, thus suggesting that an excimer emission[19] is present. It is worth noting that in previous reports of alternating copolymers of vinylaromatic monomers[41] and apparently of *N*-vinylcarbazole[42] no excimer component was observed. Taking into account that in the case of carbazole containing polymers any excimer formation reported to date seems to be confined to 1,3 interacting chromophores[43,44], it is conceivable that the observed excimer emission should be attributed to the presence, even in the 50/50 copolymer samples, of a reasonably small amount of short sequences of (**1**) units, which are populated by exciton migration[42]. Alternatively it may be that there are weak interchromophoric interactions between carbazole nuclei separated by more than three carbon atoms of the polymer backbone. The occurrence of excimer emission from interacting nuclei separated by more than three carbon atoms has already been reported in the case of homopolymers of acenaphthylene[45], 1-naphthyl acrylate[46], 2-naphthylalkyl methacrylates[47] and of alternating copolymers of maleic anhydride with stilbene[48], 1-vinylpyrene[42] and acenaphthylene[49]. In some helical polymers the naphthalene rings, separated from each other by one pitch of the helical array can also generate emitting excimer species[50].

Examination of the spectra for poly(**1**-co-**2**) samples given in *Figure 4*, and especially the comparison of an assumed 1:1 copolymer with the model (**4**) indicated in *Figure 5*, leave little room for doubt that a long wavelength emitting species ($\lambda \simeq 420$nm) is present—even for the copolymers whose composition best approximates to the alternating sequence. Furthermore the copolymer emission monitored separately at 360, 370, and 420nm has an excitation spectrum which is identical to the usual carbazole absorption. These results contrast markedly with the absence of any related long wavelength emission in other types of copolymer containing carbazole units pendant to the main chain[51], including random copolymers of (**1**) with methyl methacrylate in which the molar proportion of carbazole units is less than 60–70%[40].

It is reasonable to question whether the observed long wavelength asymmetry in the emission spectra (*Figures 4*, *5*) is sufficient in magnitude to merit assignment as emission from a species other than isolated carbazole units. In fact, the spectra are not unlike those reported for intramolecular excimer formation in 1,3-bis(*N*-carbazolyl)propane[52] and of homopolymers of vinylcarbazoles in which the vinyl group is attached to various ring positions of the carbazole nucleus[53]. It is necessary to conclude, therefore, that the long wavelength tailing of emission spectra of 1:1 alternating copolymers of (**1**) and (**2**) arises from the usual long wavelength type of carbazole excimer. This conclusion, intimating a significant degree of interaction between non-nearest neighbour carbazole

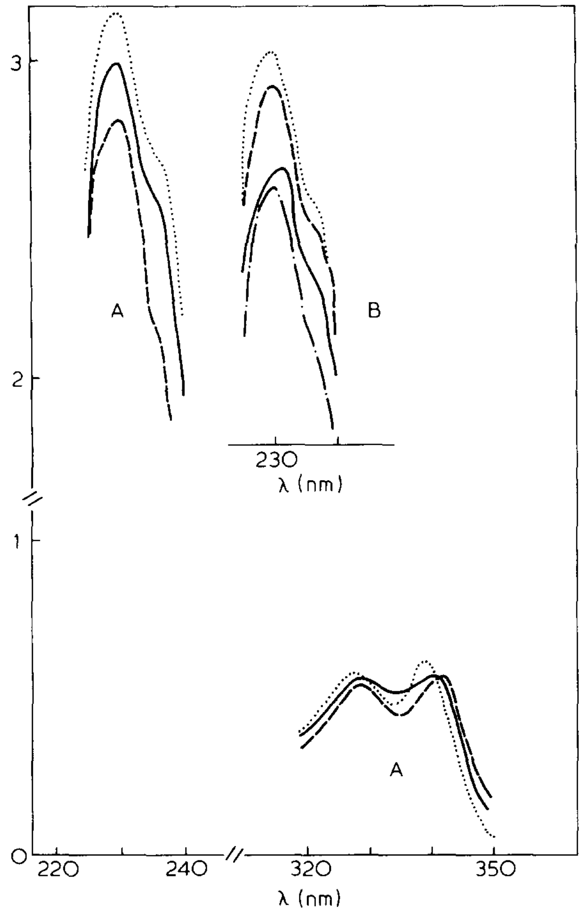

Figure 3 U.v. spectra in CH_2Cl_2: (A), Poly(*N*-vinylcarbazole-co-dimenthyl fumarate) [Poly(**1**-co-**3**)f having different content (% mol) of (**1**) units: (· · · ·) 57.9, (——) 68.5, and (– – – –) 73.7. (B), Poly(*N*-vinylcarbazole-co-ethyl menthyl fumarate) [Poly (**1**-co-**2**)] having different content (% mol) of (**1**) units: (· · · ·) 49.9, (– – – –) 52.1, (——) 53.0, and (– · – · –) 59.8

groups, is strongly supported by the absorption spectra referred to previously. Additionally, examination of the ^{1}H-n.m.r. spectra (*Figure 6*) in the region of aromatic proton resonance, indicates the presence of an extra shoulder at 6.3 ppm. The presence of this signal is related to the existence of strongly interacting carbazole nuclei[21,54,55]. Both these observations are similar to those made for poly(**1**) where excimer formation is manifest.

Earlier work by Mikawa *et al.*[42] had shown that very similar alternating copolymers of *N*-vinylcarbazole with diethyl maleate, and diethyl fumarate did not, exhibit excimer emission although the same alternating copolymers gave almost perfect depolarization of fluorescence in rigid glasses at 77K, indicative of highly efficient energy migration. This absence of long wavelength emission in the copolymers reported by Mikawa *et al.*[42] has been much quoted as evidence of the requirement for nearest neighbour participation in excimer formation, even in a most recent and enlightened review article[56]. Conclusions from the present results would, therefore, appear to be at variance with widespread assumption and require further comment.

Examination of the actual emission spectra published for copolymers of *N*-vinylcarbazole with diethyl fumarate and diethyl maleate (see *Figures, 3, 4* in reference 42) reveals a marked similarity to those reported in the present work for equivalent copolymers of *N*-vinylcarbazole with ethylmenthylfumarate. In particular, a similar type and extent of long wavelength broadening may be observed, implying weakly emitting excimer formation even in copolymers of (**1**) with diethyl maleate and diethyl fumarate.

We suggest, therefore, that the widely held conclusion that alternating copolymers of *N*-vinylcarbazole do not exhibit excimer formation be treated with reserve until further evidence is available. There is no reason to assume that non-nearest neighbour carbazole groups bound to the main chain would have greater difficulty in interacting than equivalent emitting groups in alternating copolymers of maleic anhydride with acenaphthylene, stilbene, and 1-vinylpyrene, where excimer formation is known to occur[42,48,49].

CONCLUSIONS

Free radical copolymerizations of *N*-vinylcarbazole (**1**) with (–)menthylethylfumarate (**2**) and (–)dimenthylfumarate (**3**) yield products with a strong tendency to alternation, especially in the case of the first named

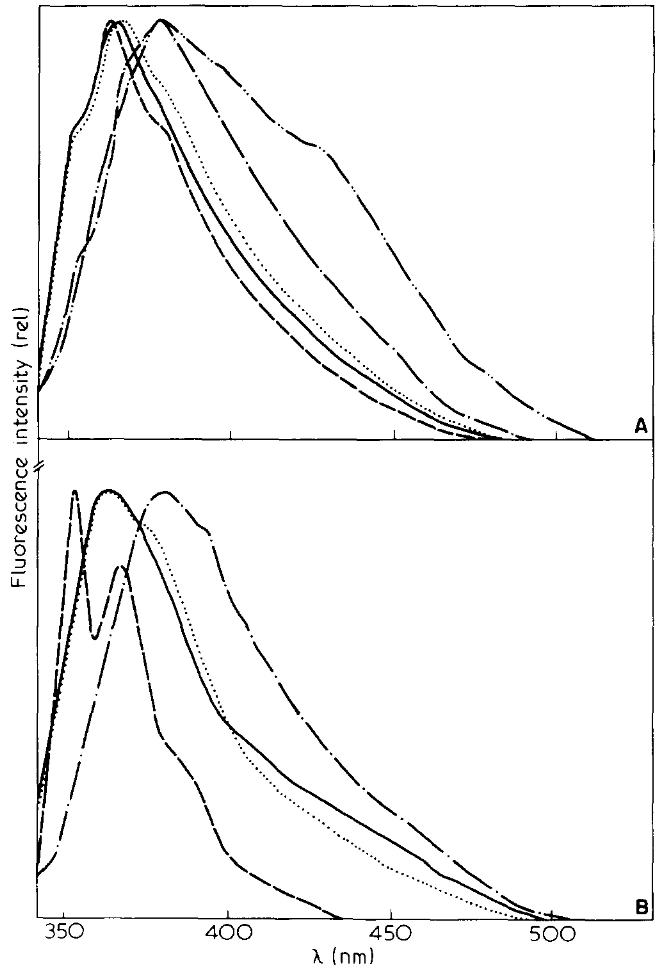

Figure 4 Corrected fluorescence emission spectra (λ_{exc} = 330 nm) normalized at the maximum intensity of: (A), Poly(*N*-vinylcarbazole-co-ethyl menthyl fumarate) [Poly(**1**-co-**2**)] containing: (– – – –) 49.9, (———) 52.1, (· · · ·) 53.0, and (– · – · –) 59.8 % mol of (**1**) units, and (– · · –) poly(**1**) (free radical). (B), Poly(*N*-vinylcarbazole-co-dimenthyl fumarate) [Poly(**1**-co-**3**)] containing: (· · ·) 57.9, (———) 68.5, and (– · – · –) 73.7 % mol of (**1**) units, and (– – –) (–)menthyl 3-(9-carbazolyl)propionate (**4**)

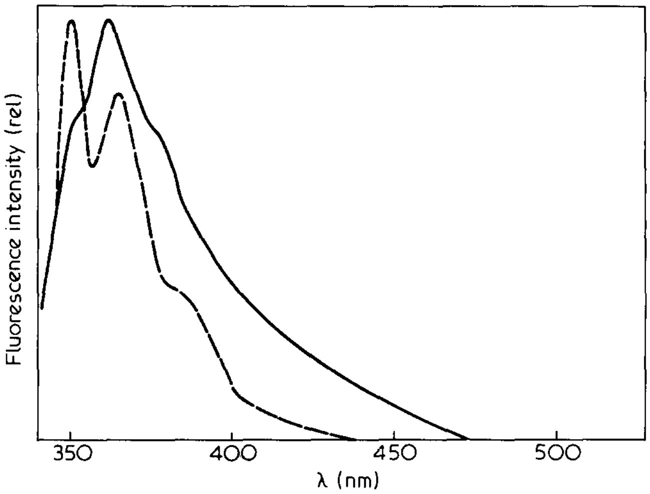

Figure 5 Corrected fluorescence emission spectra (λ_{exc} = 330 nm) of poly(*N*-vinylcarbazole-co-ethyl menthylfumarate) containing 49.9 mol % (**1**) units (——) and model compound (**4**) (— — —)

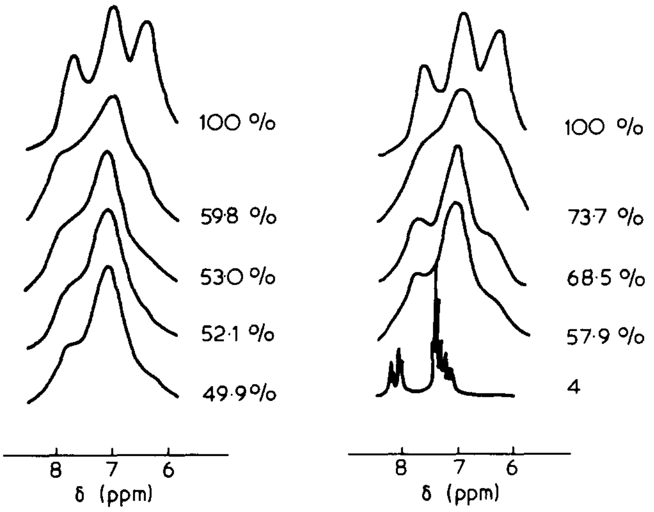

Figure 6 ^{1}H-n.m.r. spectra in the aromatic proton region of: (A), Poly(*N*-vinylcarbazole-co-ethyl menthyl fumarate) [Poly (**1**-co-**2**)] at different content (% mol) of (**1**) units. (B), Poly(*N*-vinylcarbazole-co-dimenthyl fumarate) [Poly(**1**-co-**3**)] at different content (% mol) of (**1**) units and model compound (**4**)

fumarate. The di-menthylester (**3**) is apparently too hindered to permit strictly alternating copolymers; all products being enriched in the carbazole monomer.

Circular dichroism studies indicate significant induced optical activity in the carbazole chromophores of both series of copolymers. There is no evidence of a sequence induced maximization of induced optical activity in poly(**1**-co-**2**) samples in accord with their essentially alternating structures. For poly(**1**-co-**3**) materials it is possible that a maximum value of induced optical activity could arise but only when the copolymers have carbazole contents in excess of about 70 mol %.

Fluorescence emission spectra for all the copolymers exhibit a significant asymmetric broadening on the long wavelength side of the usual isolated carbazole chromophore emission. It is concluded that, even in essentially alternating copolymers of (**1**) and (**2**), excimer formation occurs. Excimer formation in these cases can not involve nearest neighbour carbazole groups and further support for interaction between remote carbazole groups is provided by u.v. absorption and ^{1}H-n.m.r. spectroscopy.

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