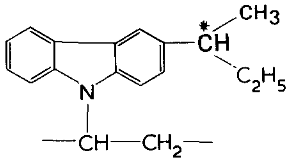
Optically active vinyl polymers containing fluorescent groups:
5. Fluorescence properties of poly(9-vinyl carbazole) and optically active polymers containing carbazole units

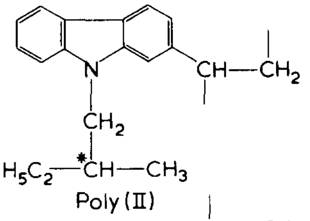
Julien L. Houben and Barbara Natucci
Laboratorio per lo Studio delle Proprietà Fisiche di Biomolecole e Cellule, Via Buonarroti 9 Pisa 56100, Italy
and Roberto Solaro, Orlando Colella and Emo Chiellini
Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica e Chimica Organica Industriale, Via Risorgimento 21, Pisa 56100 Italy
and Anthony Ledwith
Donnan Laboratories, University of Liverpool, Liverpool L69 3BX, UK
(Received 7 December 1977)

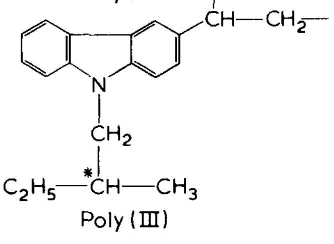
The optically active homopolymers polyI, polyII, and polyIII and copolymers of 9-vinyl carbazole with (−) menthyl vinyl ether all exhibit fluorescence related to that of cationically and free radically prepared poly(9-vinyl carbazole). The fluorescence is interpreted for all polymers as arising from three components: monomeric carbazole emission, high energy excimer emission (termed dimer emission for convenience), and a more usual excimer emission arising from conformationally eclipsed carbazole units. Correlations of fluorescence and fluorescence quenching by maleic anhydride, with chiroptical properties and copolymer compositions, suggest that excimer formation is a consequence of rotational freedom within or between isotactic carbazole sequences in the polymer backbones. The isotactic copolymers of (−)menthyl vinyl ether and 9-vinyl carbazole exhibit a relatively strong excimer fluorescence even though mean sequence lengths of carbazole units are comparatively short.

INTRODUCTION

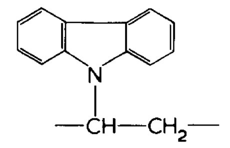
Although the photophysics of poly(9-vinyl carbazole) have been extensively studied in the last few years[1–8], the resolution of its fluorescence spectrum into the individual luminescing components is still controversial[2,3,6]. In a very recent publication, Williams and Froix[9] have reported detailed studies of the 260 MHz proton and 65.38 MHz C^{13} n.m.r. spectra of several types of poly(9-vinyl carbazole) (i.e. polyIV). The results confirm earlier conclusions by Okamoto *et al.*[10] that cationically polymerized samples have an increased isotactic content compared with free radically prepared polymer, but refute the notion that the cationic polymer consists either of long chains of isotactic and syndiotactic blocks, or is highly isotactic. Rather, because of the high mesoracemic triad contents of both types of polymer, it is concluded that the data are consistent with structures having a rather high frequency of disordered kinks at joints between blocks of (comparatively) higher stereo-ordered structures. Previously we have reported[11,12] details of the synthesis of several optically active polymers containing carbazole units including poly[(S)-3-sec-butyl-9-vinyl carbazole], (polyI); poly[(S)-9-(2-methylbutyl)-2-vinyl carbazole], (polyII); poly[(S)-9-(2-methylbutyl)-3-vinyl carbazole], (polyIII); poly(9-vinyl carbazole), (polyIV); poly[(9-vinyl carbazole-co-(−)-methyl vinyl ether (V)], (poly (IV-co-V)) and their low molecular weight model compounds: (S)-3-sec-butyl-9-isoproply carbazole, (Ia) and (S)-9-(2-methylbutyl)-2-ethyl carbazole, (IIa). (S)-9-(2-methylbutyl)-3-ethyl carbazole, (IIIa) and 9-isopropyl carbazole, (IVa) were also available from previous work and help in understanding photophysical properties of carbazole-containing polymers.


Poly (I)

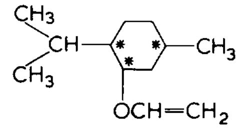

Poly (II)


Poly (III)

© 1978 IPC Business Press Ltd



Poly(IV)



V

The synthesis of optically active polymers essentially provides conformationally homogeneous macromolecular structures which can be characterized independently via their chiroptical properties.

The present paper reports the general properties of these new polymers with regard to their absorption and fluorescence spectra, relative fluorescence yields, and quenching of fluorescence by the electron acceptor, maleic anhydride.

The homopolymers derived from optically active carbazole monomers[11] and copolymers of 9-vinyl carbazole with optically active menthyl vinyl ether[12] exhibit, in solution, either strong circular dichroism or enchanced optical rotation resulting from their predominantly helical conformations. Helical conformations for stereoregular polymers of carbazole derivatives are indicated also by previous fluorescence studies in solution[6–8] and X-ray crystallographic studies in the solid state[13]. It follows therefore that excitation of the carbazole chromophores is located mainly in the ordered (i.e. helical) regions and defects are populated mainly by exciton migration.

EXPERIMENTAL

Methods

Absorption spectra were measured on Pye Unicam SP700 or Cary 14 spectrophotometers and fluorescence spectra on a Perkin–Elmer MPF3. All experiments were carried out in air equilibrated samples at room temperature in CH_2Cl_2 solution as there was little oxygen effect on the intensity and shape of the fluorescence spectra under the adopted experimental conditions.

The emission spectra were corrected for the wavelength response of the detection system and all spectra were recorded at sufficiently low concentrations of carbazole to avoid any correction due to non-linear effects (intensity–concentration). Typically the absorbance for a 1 cm path length was about 0.05 at the excitation wavelength, 330 nm.

Materials

Optically active poly(vinyl carbazoles). Poly[(S)-3-sec-butyl-9-vinyl carbazole] (polyI), poly[(S)-9-(2-methylbutyl)-2-vinyl carbazole] (polyII) and poly[(S)-9-(2-methylbutyl)-3-vinyl carbazole] (polyIII) were prepared as reported in a previous paper[11] (*Table 1*).

Poly(9-vinyl carbazole). Poly(9-vinyl carbazole)(polyIV), was prepared by using three different catalytic systems (*Table 2*).

Poly[9-vinyl carbazole-co-(–)-menthyl vinyl ether]. Various samples of poly[9-vinyl carbazole-co-(–)menthyl vinyl ether] (poly IV-co-V) having different contents of IV units were prepared as previously reported[12] by polymerization in CH_2Cl_2 at –78°C using $EtAlCl_2$ as initiator. Properties of polymeric samples are reported in *Table 3*.

Model compounds. (S)-3-sec-butyl-9-isopropyl carbazole (Ia) $\{[\alpha]_D^{25} = +12.3\ (CH_2Cl_2)\}$, (S)-2-ethyl-9-(2-methylbutyl) carbazole (IIa) {m.p. 29°–30°C, $[\alpha]_D^{25} = -13.0\ (CH_2Cl_2)\}$ and (S)-3-ethyl-9-(2-methylbutyl)carbazole (IIIa) $\{[\alpha]_D^{25} = -10.9\ (CH_2Cl_2)\}$ were prepared as previously reported[11]. 9-Isopropyl carbazole (IVa) was prepared according to the procedure reported by Lopatinskii[14] and recrystallized several times from hexane (m.p. 121°–122°C).

RESULTS

Absorption spectroscopy

The absorption spectra of IVa and polyIV are very similar and are essentially identical to those reported by Johnson[3];

Table 1 Polymerization of optically active vinyl carbazole derivatives

Polymerization conditions						Polymeric product		
Monomer								
Type	mmol	Catalyst	Molar ratio (monomer/ catalyst)	Solvent	Temperature (°C)	Conversion (%)	$\overline{DP}_n$ [a]	$[\alpha]_D^{25}$ [b]
I	2.8	$EtAlCl_2$	50	$C_6H_5CH_3$	–78	83	91	–6.2
II	3.9	nC_4H_9–Li	100	THF	25	82	64	–39.4
III	7.6	$C_7H_7SbCl_6$	1500	CH_2Cl_2	0	61	880	–19.6

[a] By osmometry in toluene at 37°C; [b] In dichloromethane solution

Table 2 Polymerization of 9-vinyl carbazole with different catalystic systems

Polymerization conditions				Polymeric product		
Catalyst	Molar ratio (monomer/catalyst)	Solvent	Temperature (°C)	Conversion (%)	$[\eta]$ [a] (dl/g)	$\overline{M}_v \times 10^{-4}$ [b]
AIBN	100	C_6H_6	60	91	0.26	8.5
$EtAlCl_2$	50	$C_6H_5CH_3$	–78	21	0.40	18.0
$TiCl_4/Al(i-C_4H_9)_3$ [c]	50[d]	$C_6H_5CH_3$	0	90	0.20	5.5

[a] In benzene at 25°C; [b] estimated from the equation $[\eta] = K\overline{M}_v^{\alpha}$ ($K = 3.55 \times 10^{-4}$, $\alpha = 0.58$); [c] molar ratio $Al(i\text{-}C_4H_9)_3/TiCl_4 = 3$; [d] referred to $TiCl_4$

the copolymers of 9-vinyl carbazole and optically active menthyl vinyl ether exhibited carbazole chromophore absorption spectra closely related to IVa and polyIV. The latter together with those copolymers having more than about 50 mol % carbazole monomeric units, had the $^1L_b \leftarrow {}^1A$ carbazole absorption band shifted towards the blue (3 nm) from that in IVa and copolymers with low carbazole contents. As noted in a previous paper[12], the carbazole content of copolymers may be estimated by absorption spectrophotometry assuming that the molar extinction coefficient does not vary with copolymer composition. Independent analyses by n.m.r. techniques support this assumption[12]. Absorption spectra for the other polymers and their model compounds are also closely related[11].

Fluorescence spectra

The fluorescence spectrum of IVa is concentration independent, if corrections for self-absorption are taken into account, and consists of three vibronic structures respectively at 352, 370 and ~390 nm (*Figure 1*). It is well established[3,6] that monomeric carbazole derivatives do not exhibit excimer formation.

The copolymers with low IV content yield spectra quite similar to IVa apart from some line broadening mainly on the low energy side. As the monomer segment ratio IV/V increases, the relative intensity of the 355 nm band decreases and the relative contribution of the 420–450 nm region becomes predominant. In *Figure 1*, the effect is illustrated for corrected fluorescence spectra after normalization at the same intensity at 370 nm. This wavelength was selected because it corresponds to the second vibronic band of IVa and consequently does not suffer distortion due to self-absorption; in homopolymers, as will be discussed later, this problem is rather difficult to resolve. *Table 4* gives data for the intensity

Table 3 Properties of various samples of poly[9-vinylcarbazole-co-(—)menthyl vinyl ether] [poly(IV-co-V)]

Sample	Co-units from IV[a] (mol %)	$[\alpha]^{25}_{D}$ [b]	$M_n \times 10^{-3}$ [c]
C6	93.8	−15.3	89.4
C7	88.0	−20.0	66.6
C8	78.1	−42.1	46.2
C9	52.0	−103.5	48.2
C10	16.7	−174.0	44.1
C11	9.6	−181.3	44.7
C12	4.8	−196.6	70.7
C13	1.0	−204.5	55.2
C14	0.1	−208.9	51.4

[a] Determined by u.v. and n.m.r. spectroscopy; [b] in $CHCl_3$ solution (c = 1–5 g/dl); [c] by osmometry in toluene at 37°C

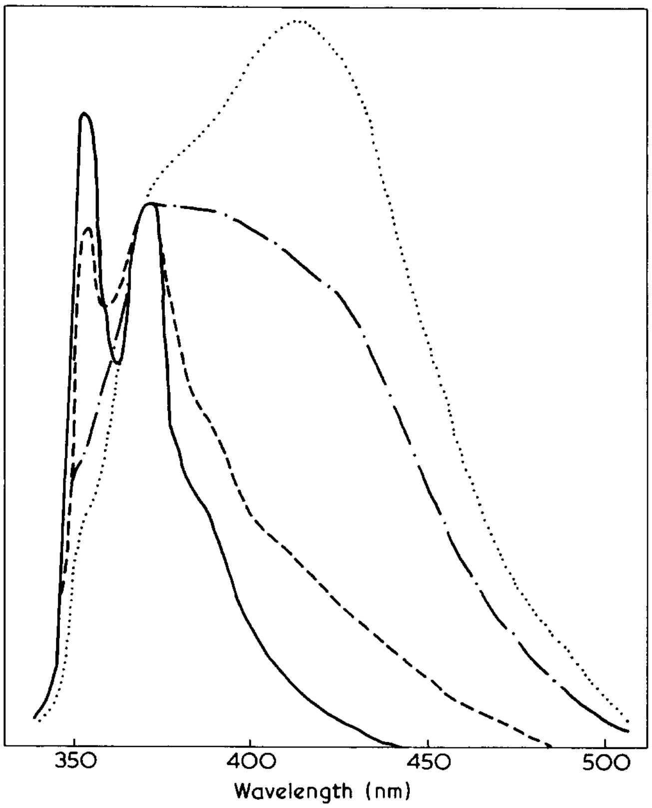


Figure 1 Corrected fluorescence spectra normalized at 370 nm: ———, 9-isopropyl carbazole and of poly[9-vinyl carbazole-co-(—)-menthyl vinyl ether] having different compositions. · · · ·, sample C7, · — · — ·, sample C9 and — — — —, sample C14

Table 4 Relative fluorescence intensities (I_λ) at various wavelengths (nm) determined in dichloromethane at room temperature for 9-isopropyl carbazole (IVa), poly(9-vinyl carbazole) (polyIV) and poly(9-vinyl carbazole -co-(—)-menthyl vinyl ether)[poly(IV-co-V)]

	Fluorescence intensity ratio												
	Sample												
		Poly IV			Poly (IV-co-V) (mol % of IV units)								
Ratio	IV_a	Radical	Ziegler–Natta	Cationic	93.8	88.0	78.1	52.0	16.7	9.6	4.8	1.0	0.1
$\frac{I_{355}}{I_{370}}$	1.2	0.45	0.45	0.49	0.45	0.41	0.41	0.50	0.58	0.66	0.83	0.82	0.92
$\frac{I_{355}}{I_{420}}$	20	0.58	0.41	0.39	0.36	0.32	0.34	0.63	1.28	1.87	2.38	3.60	4.10
$\frac{I_{370}}{I_{420}}$	17.2	1.29	0.91	0.80	0.80	0.78	0.83	1.26	2.03	2.83	2.87	4.40	4.46
Total intensity[a]	1.0	0.35	0.28	0.26	0.36	0.41	0.36	0.40	0.57	0.58	0.50	0.38	n.d.

[a] Evaluated as $\int I(\nu)d\nu$ assuming total fluorescence of IVa equal to 1

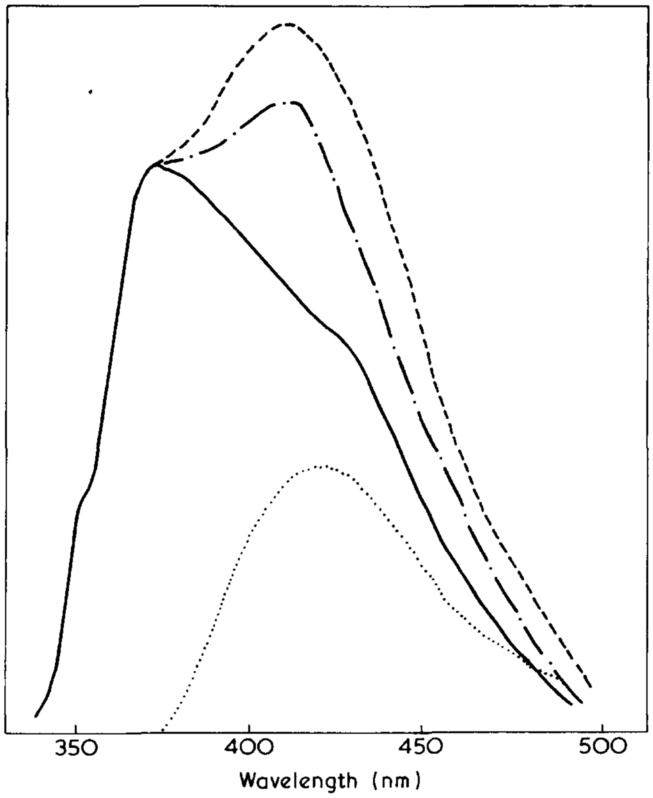


Figure 2 Corrected fluorescence spectra normalized at 370 nm of poly(9-vinyl carbazole) prepared by different catalytic systems: — · — · — ·, Ziegler–Natta [$TiCl_3/Al(i\text{-}C_4H_9)_3$]; — — — —, cationic ($EtAlCl_2$); ——, radical (AIBN); and · · · ·, difference spectrum between cationic and radical samples

ratios of the fluorescence emission bands at 355 and 370, 355 and 420, and 370 and 420 nm, respectively. It can be seen that these ratios remain fairly constant up to monomer segment ratio IV/V = 1 and then increase continuously. The relative intensity of the fluorescence emission (IVa fluorescence being taken as unity) is reported in the fourth row of *Table 4* after normalization at the same absorbance.

In *Figure 2,* the fluorescence spectra of the various samples of polyIV (radical, Ziegler–Natta and cationic) are reported. Rather important differences can be observed between the three samples in the long wavelength region as indicated by the difference spectrum between the two extreme cases, cationic and radical[6,7]. In particular, the sample of polyIV, prepared by low temperature cationic polymerization, which, in accord with n.m.r. data[9,10] is characterized by a more isotactic structure, exhibits the largest contribution by the 420 nm excimer band.

The other polymers exhibit two types of behaviour irrespective of the methods of polymerization. Thus polyII and to some extent polyIII have fluorescence spectra which are rather similar to those of their model compounds, IIa and IIIa, with only slight evidence for excimer formation, and some variations of the intensity ratios between the vibronic bands (*Figure 3*). In contrast the fluorescence spectrum of polyI is quite different from the fluorescence spectrum of its model compound Ia and consists of a broad poorly structured band with a maximum at 380 nm and a shoulder at ~356 nm (*Figure 3*). Significantly polyI and polyIV are the only homopolymers in which the carbazole ring is linked to the backbone through the nitrogen atom.

Fluorescence quenching by maleic anhydride

Fluorescence quenching by maleic anhydride may be complicated by the fact that it forms charge transfer complexes (*CTC*) with carbazole compounds due to the good electron donor properties of the latter. In such cases, fluorescence quenching may arise via two types of effects, static and dynamic, and the former can be assessed by rather careful measurements of appropriate absorption spectra[15].

Charge transfer interaction between IVa and maleic anhydride distorts the spectrum of IVa but the stability of the complex is too weak to allow precise measurements at the required low concentrations of carbazole and maleic anhydride. However, the long wavelength tail of the *CTC* band was used to estimate the equilibrium constant, K_e, and the molar extinction coefficient of the complexes, ϵ, by the Benesi–Hildebrand method[16] and for IVa $K_e = 1.3\ M^{-1}$ and $\epsilon = 200$ at 385 nm.

The precision of these measurements is not sufficient to allow a comparison between the various model compounds and polymers but, from the fact that the product $K_e\epsilon$ value does not vary from IVa to the polymers, it can be assumed

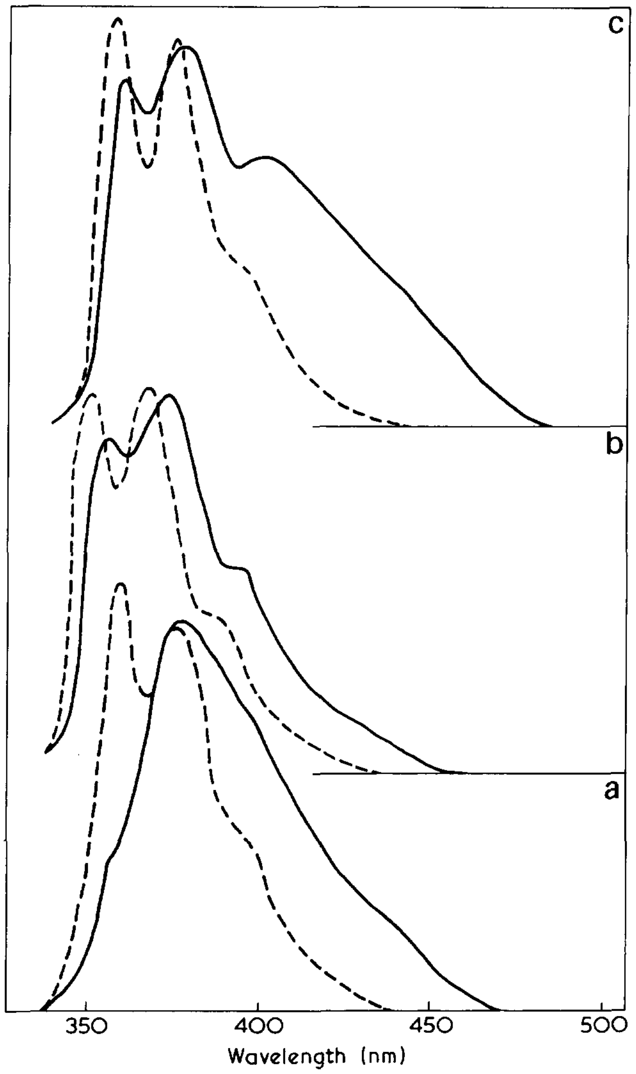


Figure 3 Corrected fluorescence spectra normalized at the second vibronic band (λ ~370 nm): (a) ——, poly[(S)-3-sec-butyl-9-vinyl carbazole]; — — — —, (S)-sec-butyl-9-isopropyl carbazole; (b) ——, poly[(S)-9-(2-methylbutyl)-2-vinyl carbazole]; — — — —, (S)-2-ethyl-9-(2-methylbutyl) carbazole; (c) ——, poly[(S)-9-(2-methylbutyl)-3-vinyl carbazole]; — — — —, (S)-3-ethyl-9-(2-methylbutyl) carbazole.

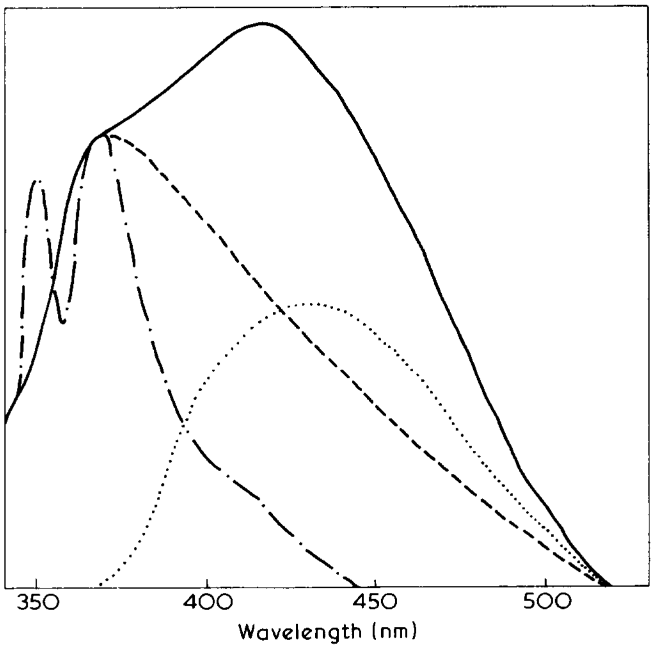


Figure 4 Corrected fluorescence spectra normalized at 370 nm of a 10^{-5} M dichloromethane solution of poly[9-vinyl carbazole-co-(−)-menthyl vinyl ether] containing 93.8% IV units, in the presence of maleic anhydride (MAn): ———, in absence of MAn; — — — —, MAn concentration 5 X 10^{-2} M; — · — · —, MAn concentration 1 X 10^{-1} M; . . . ., difference spectra between the first and second spectrum

that the polymer structures do not have a large effect on the stability of the complexes[17].

It is known from the Stern–Volmer relation $\{[(I_0/I) - 1] = K_{sv}Q\}$ that the fluorescence intensity should vary linearly with the quencher concentration. In our experiments, using a quencher concentration of 10^{-1}–10^{-4} M, we have found that this relation holds for IVa at all wavelengths and for polyIV and poly(IV-co-V) in the region between 420 and 500 nm. On the contrary a non-linear dependence is found between 350 and 400 nm, in accordance with the multi-exponential decay observed by Johnson[3].

The lack of precise lifetime measurements on all polymers precludes a detailed analysis of quenching data, but it seems useful to comment briefly on aspects as they give some insight into the type of curve resolution necessary to explain the fluorescence spectra. Certainly the lower energy emitting species will have a longer lifetime than the higher energy trap[3,4] and consistent with this is the observation that the longer wavelength region in the emission spectra of polyIV and poly(IV-co-V) is quenched much more efficiently than the region between 350 and 400 nm. The difference spectrum between normalized unquenched and quenched emission is a structureless broad band with maximum at about 420 nm. At the highest quencher concentration the emission spectrum after correction for solution absorbance is very similar to monomer emission (*Figure 4*).

These data can be easily interpreted in terms of three emitting species: a monomer like emission which is very difficult to quench, a species emitting in the 350–390 nm region, and a species emitting mainly above 420 nm.

DISCUSSION

The similarity between the first absorption band, $^1L_b \leftarrow {}^1A$ for polyIV and IVa on the one hand and the mirror symmetry of the absorption and fluorescence spectra of IVa on the other hand suggest that there should be little difference between the fluorescence of IVa and that of the monomer unit in the copolymers. Comparison of polyII and polyIII with IIa and IIIa confirms this hypothesis and suggest that self-absorption of the $O' \leftarrow O$ transition in the homopolymers does not reduce the intensity of the corresponding band by more than 17% at the emission maximum. For polymers, self-absorption of fluorescence can be expected to be higher than that predicted from pure absorbance data as the local concentration of chromophores around the emitting species is very high.

Discussion of the fluorescence spectra of the polymers requires detailed analysis and, compared with other aromatic systems, carbazole polymers present a few extra problems[1]. These can be summarized as follows: (a) poorly resolved spectra of IVa, copolymers, and polyIV; (b) strong overlap of the various components; (c) absence of excimer emission in solutions of IVa, (d) polarity of the carbazole ring system. It is, therefore, rather difficult to analyse all the data in a rigorous manner.

The fluorescence spectra given in *Figures 1–3* and the quenching effect of maleic anhydride (*Figure 4*) suggest that the emission spectra of polymers containing the carbazole chromophore may be analysed in terms of three contributing components. Thus the emission spectra of IVa, polyIV, and polyI, are significantly different from each other and, if that of IVa is taken to represent monomeric carbazole group emission, the differences between polyIV and polyI can only be explained by assuming contributions from two additional emitting species. Difference spectra for the emission of various samples of polyIV (*Figure 2*) and for quenching of the long wavelength luminescence of polyIV by maleic anhydride (*Figure 4*) are consistent in that they indicate an excimer species with a fluorescence maximum at approximately 420 nm. For purposes of the following discussion, the 420 nm emitting species will be referred to as the *excimer.* Johnson[3] and Powell[5] have independently suggested, on the basis of lifetime measurements, that the emission intensity in the 350–370 nm region for polyIV arises from more than one component. Close inspection of the emission spectra of polyIV and polyI suggests that the shoulder at ~356 nm represents residual monomeric carbazole-unit emission with a more intense excimer-like emission centred aroung 380 nm. For simplicity in the following discussion, the species responsible for 380 nm emission is referred to as the *dimer.* The nature of monomer, dimer, and excimer emission bands will now be considered in detail.

*Monomer fluorescence**

This component can be approximated to IVa emission after correction for self-absorption and line broadening. As discussed above, a value of 17% appears reasonable for self-absorption of the $O' \leftarrow O$ band in homopolymers. For copolymers the apparent absorbance was assumed to be proportional to the contents of IV unit. As line broadening is more difficult to account for, curve resolution was attempted without introducing any correction due to line broadening.

Dimer fluorescence

Use of the term dimer to describe the fluorescence of polyIV centred around 380 nm is not meant to imply true

---

* A referee has suggested that the observed monomer emission could arise from residual monomer or low molecular weight polymer impurities. However, the shoulder at 356 nm remains with the same relative intensity after ten precipitations into methanol.

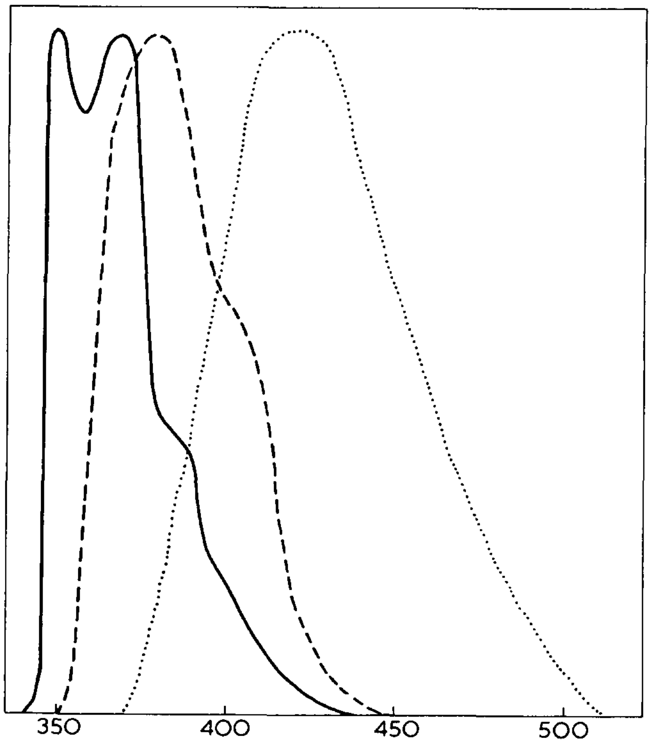


Figure 5 Normalized emission spectra: ———, monomer; — — — —, dimer; and · · · ·, excimer proposed for resolution of experimental fluorescence spectra of polymers containing 9-vinyl carbazole units

dimer formation in that there is no evidence for ground state association of carbazole units. However, as first clearly demonstrated by Johnson[3], this emission band arises from a species which is built into the polymer chain conformation and is not subject to the usual temperature effect associated with rotationally controlled excimer emission.

An approximated spectrum can be obtained from the difference between the fluorescence spectra of polyI and Ia after correction for self-absorption. Implicit in this analysis is the assumption that the emission spectrum of polyI arises mainly from monomer and dimer components. The lack or at least the weakness of excimer emission will be discussed later and it should be recognized that the emission spectra for polyI and Ia will probably be red-shifted by approximately 5–10 nm from those of polyIV and poly(IV-co-V) because of the alkyl substituents in the 3-position of the carbazole ring.

The spectrum obtained in this way exhibits a rather strong shoulder around 430 nm which may also be present in low temperature emission spectra[3]. However, the dimer spectrum reported by Itaya[6] does not show this feature. As a weak excimer emission could distort the long wavelength part of the dimer spectrum, the 400–450 nm region was adapted to obtain the best fit of all the emission spectra.

Excimer fluorescence

As already noted[1,3], the excimer emission of polyIV is influenced by many factors including conformational freedom of the polymer chain, temperature, solvent and molecular weight. In particular, dissolved oxygen has a quenching effect on the excimer luminescence in solvents like tetrahydrofuran[3]. In the present work the solvent chosen for experimental convenience was dichloromethane which in itself must be considered a weak luminescence quencher. As a result, dissolved air does not produce significant distortion of the emission spectra, but it must be acknowledged that apparent absence of excimer emission in dichloromethane solution does not preclude weak excimer emission in other solvents. Nevertheless the marked differences noted in *Figures 1–3* strongly suggest that excimer emission from polyI, polyII and polyIII is insignificant in comparison to that of polyIV and poly(IV-co-V).

The excimer emission spectrum of polyIV can be evaluated from the difference between the emission spectra of cationically and free radically polymerized samples (*Figure 2*) and from the quenching by maleic anhydride (*Figure 4*). Similar techniques have been used by other workers[2,6] and minor variations in the resolved excimer spectrum are readily understood because of the assumptions made in the band resolution procedures.

Emission spectra of monomer, dimer, and excimer, normalized to a common emission intensity, are indicated in *Figure 5* and in this way it is possible to simulate the experimentally observed total fluorescence spectra of samples of polyIV and poly(IV-co-V).

A typical simulation for the free radically prepared polyIV and for three samples of poly(IV-co-V) is indicated in *Figure 6*.

Origins of dimer and excimer sites

Explanations of the origins of the two excimer-like emitting sites in polyIV have been suggested independently by Johnson[3] and by Itaya, Okamoto, and Kusabayashi[6]. Both groups of workers agree that the long wavelength emission arises from the normal type of excimer in which two carbazole rings interact in an essentially eclipsed conformation. Johnson[3] suggested that the higher energy emission (termed dimer emission in the present work) arose from an interacting pair of carbazole units in which there was significant devia-

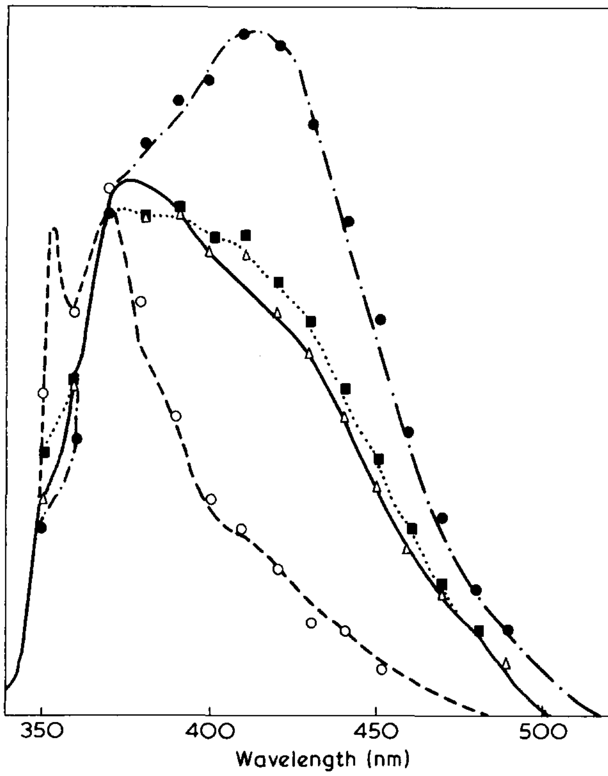


Figure 6 Experimental (lines) and computed (graphical points) fluorescence spectra: ———, △, radical polyIV; — · — · —, ●, poly(IV-co-V) (IV units, 88.0%); · · · · ·, ■, poly(IV-co-V) (IV units, 52.0%); — — —, ○, poly(IV-co-V) (IV units, 0.1%)

Table 5 Relative contributions of monomer, dimer and excimer to the fluorescence spectra of poly(9-vinyl carbazole) (poly IV) and poly(9-vinyl carbazole-co-(−)-menthyl vinyl ether)[poly (IV-co-V)][a]

	Relative contribution to fluorescence spectrum (%)											
	Sample											
	Poly IV			Poly (IV-co-V) (mol % of IV units)								
Components	Radical	Ziegler–Natta	Cationic	93.8	88.0	78.1	52.0	16.7	9.6	4.8	1.0	0.1
Monomer	19	15	15	15	13	10	23	33	52	49	61	57
Dimer	36	32	26	26	28	31	29	36	19	24	22	20
Excimer	45	53	59	59	59	59	48	31	29	27	17	23
Excimer/Dimer	1.3	1.7	2.3	2.3	2.1	1.9	1.7	0.9	1.5	1.1	0.8	1.1
Error[b] (%)	2.8	3.7	2.3	3.4	2.9	5.0	3.4	5.4	5.5	2.6	5.8	5.2

[a] Computed according to the best fitting of experimental data; [b] evaluated as $\int |\delta I(\upsilon)| d\upsilon / \int I(\upsilon) d\upsilon$ where $\delta I(\upsilon)$ is the difference between calculated and experimental intensities

tion from coplanarity. The Japanese workers[6] on the other hand envisage a situation in which two carbazole units interact with the overlapping of only one of the benzene rings.

Both explanations may be correct and it is conceivable that the dimer emission arises via a combination of both types of interaction. Experimentally, the data indicate the formation of an emitting species with a higher energy than the conformationally eclipsed excimer, and which is essentially built into the polymer chain conformation irrespective of polymerization mechanism or molecular weight. The present results do not in any way permit a more detailed understanding of the precise nature of the dimer but serve merely to support the widespread nature of its importance in carbazole-containing polymers.

A most important general observation from the present work is the comparative insignificance of excimer contributions to the fluorescence of polyI, polyII and polyIII. This is especially notable for the case of polyI, which like polyIV is a 9-vinyl carbazole and would be expected to show excimer emission. It has already been pointed out that the chiroptical properties of polyI provide very strong evidence for a largely isotactic and helical structure[11]. Therefore isotacticity by itself is not a sufficient condition for conformationally eclipsed excimer formation in carbazole polymers

Additional support for this conclusion is readily available from a consideration of the fluorescence of copolymers of 9-vinyl carbazole and optically active menthyl vinyl ether. In these cases the combination of polymerization mechanism and the optically active comonomer, should suffice to ensure a high degree of isotacticity in the resulting samples of poly(IV-co-V), and it is of special significance that copolymers with highest carbazole contents exhibit excimer fluorescence as intense as that of cationically prepared polyIV, when compared with the corresponding intensity of dimer fluorescence (*Table 5*). These observations are entirely consistent with those of Itaya *et al.*[6] in that the contributions of excimer *relative* to those of dimer are greatest for cationically (i.e. isotactic) prepared polymers, but this must not be taken as evidence for *preferred* formation of dimer sites in free radically prepared polymers.

An additional conclusion may be drawn from the emission spectra of the copolymer samples. Thus, as the carbazole content of poly(IV-co-V) decreases, the relative excimer to dimer contribution decreases (*Table 5*). Decreasing carbazole content may be assumed to imply decreasing length of carbazole-containing segment sequences with a consequent decrease in the possibility for exciton migration. For example, in copolymer C7 (*Figure 1*) the mean sequence length of carbazole units is approximately six[12]. It follows therefore that long sequences of carbazole units are not essential for excimer formation provided that stereochemical regularity is maintained and it may be that exciton migration between carbazole sequences is facilitated by main chain stereoregularity.

The recognition of two energy traps in carbazole polymers implies that the higher energy emitting species (dimer) may participate reversibly in exciton migration prior to ultimate population of the excimer traps and the copolymer emission data confirm, therefore, that facility for exciton migration is an important prerequisite for population of excimer sites. Of course, configurational regularity of the polymer backbone will have an influence on exciton migration but it is not necessary to conclude, as did Itaya *et al.*[6], that an increase (or decrease) of dimer emission implies a real increase (or decrease) of any particular type of dimer sites. In fact, in our opinion, it is not possible to compare the total fluorescence emission intensities of polymer samples prepared by different catalytic systems, as the resulting polymers will contain different terminal groups and impurities. It is apparent from *Table 4* that even samples of poly(IV-co-V) prepared by the same technique but having different compositions show scattered values of total emission intensity. Thus an increase in the absolute dimer emission intensity may not be related to a real increase of dimer sites.

In conclusion it may be stated that in polyIV and optically active poly(IV-co-V) cationically prepared, having predominantly isotactic structures, the assumed helical conformation permits efficient exciton migration with population of both conformationally eclipsed excimer sites and much less well defined dimer sites. Population of related excimer sites (but not dimer sites) is significantly reduced in samples of polyIV prepared radically and thought to be more syndiotactic. Optically active homopolymers, polyI, polyII, and polyIII have chiroptical properties indicating helical polymer chain conformations but exhibit insignificant excimer emission compared with polyIV. The contrast between polyI and polyIV, which are both polymers of 9-vinyl carbazoles, is clear evidence that the existence of isotactic sequences is not a sufficient condition for excimer emission. Presumably the alkyl substituent in the 3-position of polyI sterically inhibits formation of the eclipsed conformations required for excimer emission.

REFERENCES

1 Klöpffer, W. in 'Organic Molecular Photophysics' (Ed. J. B. Birks), Wiley, London, 1973, vol 1, p 357; Phillips, D. in 'Photochemistry–Specialist Periodical Report', Chem. Soc. London, 1974, vol 5, p 691

2 Johnson, P. C. and Offen, H. W. *J. Chem. Phys.* 1971, **55**, 2945

3 Johnson, G. E. *J. Chem. Phys.* 1975, **62**, 4697

4 Powell, R. C. and Kim, Q. *J. Lumin.* 1973, **6**, 351

5 Venikouas, G. E. and Powell, R. C. *Chem. Phys. Lett.* 1975, **34**, 601

6 Itaya, A., Okamoto, K. and Kusabayashi, S. *Bull. Chem. Soc. Jpn* 1976, **49**, 2082

7 Itaya, A., Okamoto, K. and Kusabayashi, S. *Bull. Chem. Soc. Jpn* 1977, **50**, 22

8 Okamoto, K., Itaya, A. and Kusabayashi, S. *Chem. Lett.* 1974, p 1167

9 Williams, D. J. and Froix, M. E. *Polym. Prepr.* 1977, **18**, 445

10 Okamoto, K., Yamadu, M., Itaya, A., Kimura, T. and Kusabayashi, S. *Macromolecules* 1976, **9**, 645

11 Chiellini, E., Solaro, R. and Ledwith, A. *Makromol. Chem.* in press

12 Chiellini, E., Solaro, R., Colella, O. and Ledwith, A. *Eur. Polym. J.* in press

13 Griffiths, C. H. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 1167

14 Lopatinskii, V. P., Sirotkina, E. E. Anosova, M. M., Tikhonova, L. G. and Pavlov, S. F. *Izv. Tomsk. Politekh. Inst.* 1964, **126**, 58; *Chem. Abstr.* 1965, **63**, 18007h

15 Birks, J. B. in 'Photophysics of Aromatic Molecules', Wiley, London, 1969

16 Benesi, H. A. and Hildebrand, J. H. *J. Am. Chem. Soc.* 1949, **71**, 2703

17 In the literature it has been shown that such a simple model does not apply. See for instance: Tazuke, S., Sato, K., Banba, F. and Matsuyama, Y. *J. Polym. Sci. (Polym. Lett. Edn)* 1976, **14**, 653