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# Excimer Formation by Poly(*N*-vinylcarbazole) in Solution

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ABSTRACT: Excimer formation by poly(*N*-vinylcarbazole) and its copolymers with fumaronitrile, diethyl fumarate, and diethyl maleate in solution has been investigated. The 1:1 alternating copolymers with fumaronitrile and diethyl fumarate exhibit no excimer fluorescence, while the *N*-vinylcarbazole (VCz) homopolymer and VCz-rich copolymer with diethyl maleate, both having the VCz sequence, show excimer fluorescence. These observations lead to the conclusion that in the polymers having carbazole rings as pendant groups excimer formation is possible only between two adjacent chromophores which are separated by a main chain segment of three carbon atoms.

Some aromatic vinyl polymers such as polystyrene,[2,3] poly(1-vinylnaphthalene),[3,4] poly(1-vinylpyrene),[5,6] poly(*N*-vinylcarbazole),[7-9] poly(acenaphthylene),[6,10,11] and poly(naphthyl methacrylate)[12] show excimer fluorescence in solution as well as in solid film.[13] It is characteristic of such polymers to form excimers even in dilute solution, in contrast to the behavior of small molecules. Although the excimer formation of small molecules in solution has been attributed to a diffusion mechanism,[14] the mechanism in polymers has not yet been established. That the above mentioned polymers show excimer fluorescence even in dilute solution may simply be due to the polymers having a higher local concentration of chromophores along the main chain. Since the polymers have pendant chromophores in a one dimensional arrangement along the main chain in high density, the following three possibilities are conceivable as the structure of the excimer-forming site of the polymers in solution: (i) excimer formation between adjacent chromophores, which are separated by a main chain segment of three carbon atoms; (ii) excimer formation between two far-distant chromophores, which happen to be close to each other in the same chain as a result of folding of the polymer chain; (iii) excimer formation between two chromophores belonging to different chains. Cases i and ii correspond to the intramolecular excimer formation, and case iii to the intermolecular excimer formation. Although excimer formation in polystyrene and poly(1-vinylnaphthalene) has been considered to be mainly case i,[2] there is no explicit evidence so far. In poly(acenaphthylene),[10] however, only case ii or iii is possible, since two adjacent naphthalene rings cannot be arranged with the planes of the napthalene rings parallel to each other within the distance of excimer formation. The case iii can easily be distinguished from the other two cases by diluting the solution so that no intertwining of the polymer chains can occur. A clear distinction between i and ii is difficult to achieve. If we have an alternating copolymer in which each pendant chromophore is separated along the chain by a comonomer unit which does not participate in excimer formation, the spectroscopic behavior of such polymers will provide important information for distinguishing between cases i and ii.

Among the polymers which are known to show excimer fluorescence, poly(*N*-vinylcarbazole) (PVCz) is a thoroughly investigated and practically important polymer.[6-8] The present study deals with the problem of excimer formation in this polymer, especially with the use of alternating copolymers in which each pendant carbazole chromophore is separated regularly by a comonomer unit having no conjugated $\pi$ electrons. We recently found that *N*-vinylcarbazole (VCz) copolymerized with several electron accepting vinyl monomers such as fumaronitrile (FN),[15] diethyl fumarate (DEF),[16] and diethyl maleate (DEM) (Figure 1). In both FN and DEF, 1:1 alternating copolymers can be obtained regardless of the monomer feed ratios. Copolymerization with DEM yields a 1:1 alternating copolymer if the monomer feed ratio of VCz is less than 0.5, but if this ratio exceeds 0.5, the VCz contents in the copolymers increase continuously with an increase in VCz feed. In this polymer, the DEM–DEM sequence cannot exist, because DEM itself does not homopolymerize. Thus, we have succeeded in preparing several kinds of VCz copolymers. In the alternating copolymers, each VCz unit is separated regularly on both sides with comonomer units, and there are no adjacent carbazole chromophores which are separated by a main chain segment of three carbon atoms. But in random copolymers such as VCz–DEM, the sequence of VCz units is interrupted occasionally by a known amount of comonomers. The 1:1 alternating copolymers did not show excimer fluorescence, and only the VCz homopolymer and the VCz-rich copolymer with DEM, which have two adjacent carbazole chromophores, showed excimer fluorescence.

## Experimental Section

VCz homopolymers were obtained by radical polymerization with 2,2′-azobis(isobutyronitrile) in benzene solution at 80°. The polymers were reprecipitated more than three times from methanol and dried *in vacuo*. The resulting polymers had a molecular weight of $8 \times 10^3$ to $8 \times 10^4$. One-to-one alternating copolymers of the VCz–FN and VCz–DEF were obtained as described before.[15,16] The VCz–DEM copolymers having various VCz contents were prepared by radical copolymerization at different monomer feed ratios, and the copolymer compositions were determined by nitrogen analysis as well as by spectroscopically using the molar extinction coefficient of the VCz homopolymer. Copolymerization of the VCz–DEM system will be reported elsewhere.[17] The lowest $\pi$–$\pi^*$ absorption maxima in the VCz–FN and VCz–DEF copolymers shifted to the blue region by about 10 nm ($\lambda_{max}$ 333 nm) and about 5 nm (338.5 nm), respectively, compared with that of the VCz ho-

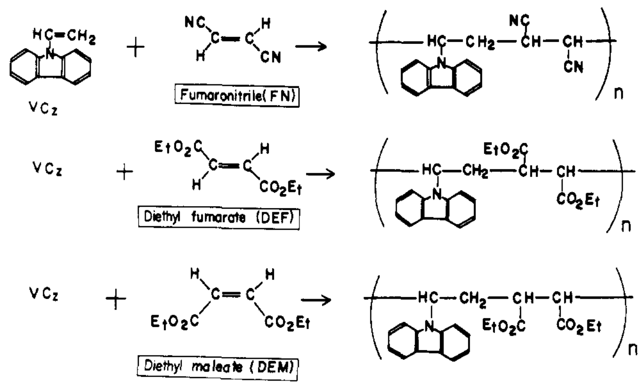

**Figure 1.** Three kinds of VCz copolymers with fumaronitrile (upper), diethyl fumarate (middle), and diethyl maleate (lower).

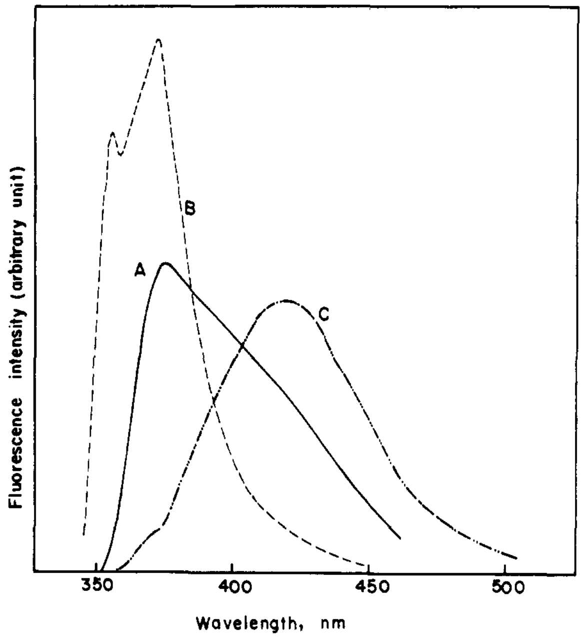

**Figure 2.** Fluorescence spectra of poly(*N*-vinylcarbazole) in a 8 × $10^{-4}$ mol/l. solution of 2-methyltetrahydrofuran at 300°K (A) and at 77°K (B), and in solid film at room temperature (C); excitation at 330 nm.

mopolymer (344 nm).[15,16] In the VCz-DEM copolymers, the absorption maximum showed a continuous blue shift with an increase in DEM contents from the VCz homopolymer to the 1:1 composition copolymer (339 nm). The molecular weight of the VCz-DEM copolymers as well as the VCz-FN and VCz-DEF 1:1 alternating copolymers was within the range of 6 × $10^3$ to 2 × $10^4$. These copolymer samples were purified sufficiently by reprecipitation two or three times before making spectroscopic measurements. *N*-Ethylcarbazole (EtCz) was synthesized starting from phenylhydrazine and cyclohexanone and was highly purified by several recrystallizations and zone meltings as described earlier.[18] 2-Methyltetrahydrofuran (MTHF) was distilled from sodium immediately before use.

Fluorescence spectra were recorded on a Hitachi MPF-3 fluorescence spectrophotometer, equipped with a 150 W-Xe excitation lamp and a R106F (S-19) photomultiplier tube. The copolymers were excited at their lowest $\pi$–$\pi^*$ absorption maxima. Spectra were uncorrected for either source output or detector response. Solution samples having an adequate concentration of Cz groups in MTHF were sealed in 3-mm Pyrex glass capillary tubes after several freeze-pump-thaw cycles. The lifetime measurements were made by the pulse method with a $N_2$ gas laser (excitation, 337 nm; half-width, 5 nsec; duty cycle, 20 per sec). Fluorescence was detected through a monochromator with a R446 (HTV) photomultiplier tube and its decay was determined by sampling oscilloscope traces.

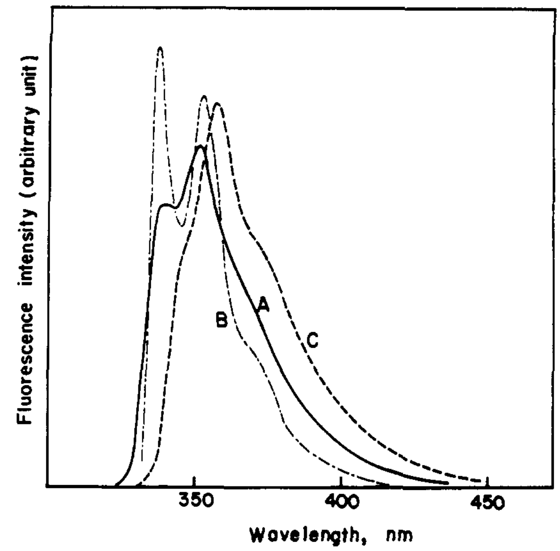

**Figure 3.** Fluorescence spectra of the VCz-FN copolymer in a $10^{-3}$ mol/l. solution at 300°K (A) and at 77°K (B), and fluorescence spectrum of the VCz-DEF copolymer in a $10^{-3}$ mol/l. solution at 300°K (C).

## Results

As shown in Figure 2, VCz homopolymer shows excimer fluorescence around 420 nm together with monomer fluorescence at 370 nm in solution at room temperature, and only excimer fluorescence in solid film. In rigid glass solution at 77°K, excimer emission has no appreciable intensity and only monomer fluorescence is observed. This may be due to a lack of excimer forming sites which are geometrically suitable for excimer formation in low temperature rigid glass.[19] The lifetimes of the monomer and excimer fluorescence were approximately 15 and 40 nsec, respectively, in solution at room temperature.

In Figure 3 are shown the fluorescence spectra of the VCz-FN and VCz-DEF copolymers in $10^{-3}$ mol/l. solution. The fluorescence spectra of these copolymers shift to the shorter wavelength side corresponding to the blue shift of their absorption maxima, as compared with the VCz homopolymer. Obviously, these 1:1 alternating copolymers exhibit no excimer fluorescence around 420 nm such as can be observed in VCz homopolymer, and the fluorescence spectra of the copolymers at room temperature bear a remarkable resemblance to those in rigid solution at 77°K, where excimer formation might be impossible. There is no conspicuous change in the spectrum when the solution concentration is increased tenfold ($10^{-2}$ mol/l.). The fluorescence of these copolymers shows an exponential decay with a lifetime of about 15 nsec at both 370 and 420 nm. The absence of an emission having a longer lifetime indicates again that there is no excimer fluorescence in the 1:1 alternating copolymers which have no adjacent carbazole groups separated by a main chain segment of three carbon atoms.

Figure 4 shows the fluorescence spectra of the VCz-DEM copolymers having various VCz contents. In the VCz-DEM copolymer with the 1:1 composition, that seems to have a sequence similar to the 1:1 alternating copolymer, no excimer fluorescence can be observed just as in the case of the other 1:1 alternating copolymers. This fact was also confirmed by decay measurements. However, in the VCz-DEM copolymer with VCz contents of more than 50 mol %, excimer fluorescence appears and the intensity of excimer fluorescence increases with an increase in VCz content. In the VCz-rich copolymers, the fluorescence decay at 420 nm shows the presence of a component with a long lifetime of

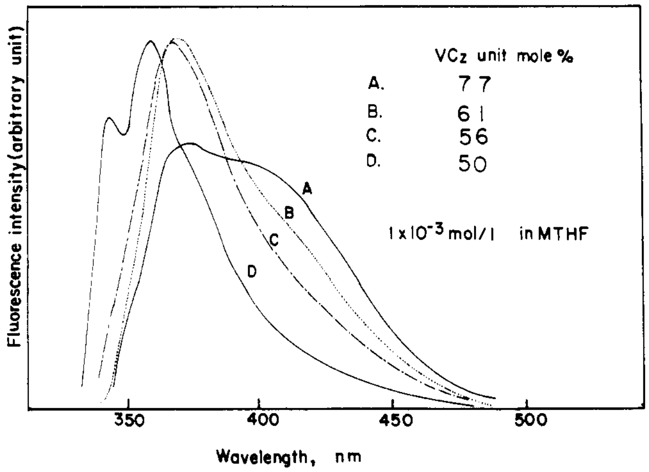

**Figure 4.** Fluorescence spectra of the VCz–DEM copolymers with various VCz contents in a solution of $10^{-3}$ mol/l. VCz units at 300°K.

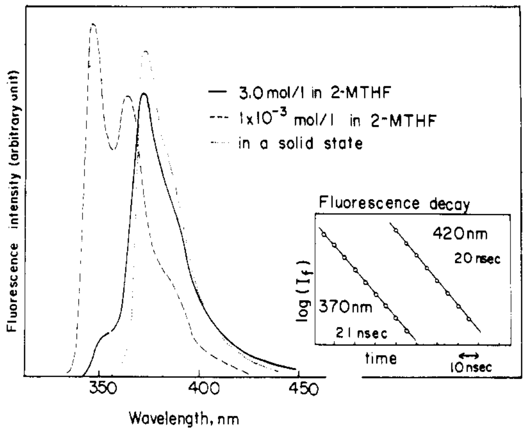

**Figure 5.** Fluorescence spectra of EtCz in solutions of $10^{-3}$ mol/l. (- - -) and 3 mol/l. (——), and in a solid state (· · ·) at room temperature. Fluorescence decay is given for the 3 mol/l. solution.

about 40 nsec in addition to a fast component with a lifetime of about 15 nsec.

In Figure 5 are shown the fluorescence spectra of EtCz in $10^{-3}$ and 3 mol/l. in solutions as well as in the solid state. The disappearance of the shorter wavelength part of the spectra in concentrated solution and in the solid state is due to the reabsorption of fluorescence. As can be seen in the figure, EtCz, contrary to other aromatic hydrocarbons,[14] exhibits no excimer fluorescence even in concentrated solution, and even in molten state no excimer emission was observed. The lifetime of fluorescence in 3 mol/l. solution remains constant (20 nsec) throughout the whole spectral region of 370–430 nm. This result supports the spectroscopic observation of the absence of excimer fluorescence in EtCz.

## Discussion

Both in dilute solution and in more concentrated solution, 1:1 alternating copolymers show exclusively monomer fluorescence from a carbazole chromophore, and excimer fluorescence, expected at around 420 nm, was not detected even in a trace amount. In VCz–DEM copolymers, excimer fluorescence begins to appear with an increase in VCz contents of more than 50%, *i.e.*, only when the VCz–VCz sequence is contained in the copolymers.

These results lead to the conclusion that in the carbazole system two carbazole chromophores can form an excimer state, a sandwich arrangement of chromophores, only when they are in the nearest neighbor positions separated by three carbon atoms of the polymer chain, *i.e.*, excimer is formed only with the structure of case i. This result extends the so-called "$n = 3$ rule" of intramolecular excimer formation to polymeric materials. This rule claims that intramolecular excimer formation occurs only when the chromophores are separated by three carbon atoms as proposed by Hirayama[20] from his investigation of diphenyl and triphenyl alkanes. The rule has been confirmed in low molecular compounds such as 1,3-bis(naphthyl)propane[21] and 1,3-bis(carbazolyl)propane.[22]

The absence of excimer fluorescence in the 1:1 alternating copolymers indicates also that no intramolecular excimer formation exists between two far-distant chromophores in the same chain, *i.e.*, that the excimer formation of case ii is not possible at least in solution. However, a question now arises about whether the case ii structure cannot form an excimer even when a chromophore belonging to this structure is excited, or whether case ii cannot form an excimer because such a structure has no chance of being excited because of the difficulty of singlet exciton migration along the polymer chain even though it should be possible to convert into an excimer. Generally, it is possible to conceive of two possible mechanisms for exciting the excimer-forming structure of aromatic vinyl polymers in solution, but the true mechanism has not yet been established. One mechanism involves a singlet exciton migration along the polymer chain and an excitation of an excimer site which is geometrically suitable for excimer formation. In the other case a singlet exciton migration is assumed to be impossible and excimer formation occurs on a particular excited chromophore with a nearby ground state chromophore which comes into a suitable geometrical position by the chain segmental motion due to solvent collision. Obviously, information on the possibility of energy migration is crucial in discriminating between these two cases in our 1:1 alternating copolymers.

**Table I**
**The Degree of Polarization of Fluorescence in Rigid Solution at 77°K**

| Sample[a] | Degree of polarization ($P$)[b] |
|---|---|
| *N*-Ethylcarbazole | 0.30 |
| 1,3-Bis(carbazolyl)propane | 0.08 |
| 1,4-Bis(carbazolyl)butane | 0.20 |
| VCz homopolymer | ~0.0 |
| VCz–FN alternating copolymer | ~0.0 |
| VCz–DEF alternating copolymer | ~0.0 |
| VCz–DEM copolymer<br>(VCz contents: 50 mol %) | ~0.0 |

[a] Concentration: $10^{-4}$ mol/l. in MTHF. [b] $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$; $I_{\parallel}$ and $I_{\perp}$ denote the polarized fluorescence intensities having the electric vector parallel and perpendicular, respectively, to the polarized excitation at 300 nm.

Table I shows the degree of polarization of fluorescence for the polymers and model compounds in rigid solution at 77°K. Not only the homopolymer but also the 1:1 alternating copolymers give almost perfect depolarization of fluorescence. This fact indicates that even in the 1:1 alternating copolymers singlet energy migration occurs efficiently along the polymer chain. Therefore, if excimer formation at a case ii structure were intrinsically possible, one could observe excimer fluorescence emitted from this kind of exciton trap site which happens to be formed by the folding of the polymer chain. Thus, the absence of excimer fluorescence in the copolymers indicates that case ii should be excluded in the present carbazole system.

Excimer formation case iii, *i.e.*, between two chromophores belonging to two different polymer chains, should also be excluded by the following findings. Although in such a dilute solution as $10^{-3}$ mol/l. any intertwining of the polymer chains seems to be unlikely, in a solution as concentrated as $10^{-2}$ mol/l. no excimer emission was observed. Moreover, a model compound, EtCz, showed no excimer fluorescence in concentrated solution, in the molten state, and even in the solid state.

Consequently, in vinyl polymers having carbazole units, an excimer state can be formed only when the polymers have at least two carbazole rings connected to the main chain by a separation of three carbon atoms, *viz.*, the structure of case i.

Thus, we have obtained new information for excimer formation in aromatic vinyl polymers having large pendant $\pi$-electron systems. The study with the 1:1 alternating copolymers is a useful method for distinguishing between excimer formation cases i and ii. As mentioned above, the absence of excimer fluorescence even in concentrated solutions of EtCz is characteristic of the carbazole molecule. This leads us successfully to the above conclusion. Actually, the rule does not apply to pyrene derivatives because concentrated solutions of 1-ethylpyrene exhibit excimer fluorescence. Recently, we obtained the 1:1 alternating copolymer of 1-vinylpyrene and maleic anhydride, and observed excimer fluorescence of pyrene rings despite their separation by maleic anhydride units in the rigid skeleton. The details of this result will be reported elsewhere.

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# Polyamides from Phenylenediamines and Aliphatic Diacids

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ABSTRACT: High molecular weight polyamides were made from *o*-, *m*-, and *p*-phenylenediamines and 4- to 12-carbon aliphatic diacid chlorides by interfacial and solution methods. Polymerization in cold tertiary amide solvents was preferred. The polymers were examined in terms of melting temperatures, solubility, and light stability. Melting temperatures increased in going from ortho to meta to para structures and as the chain length of the aliphatic diacid decreased. Solubility decreased in the above order. In solubility this group of polymers resembles both wholly aromatic polyamides and wholly aliphatic polyamides in that most members of the series dissolve in the basic amide solvents, at least in the presence of lithium chloride, and in acidic solvents such as *m*-cresol and trifluoroacetic acid. Polymers from aliphatic diamines and aromatic acids dissolve only in acids and phenols. Outstanding resistance to yellowing and degradation by ultraviolet light was demonstrated for several of the polymers in film and fiber form. Bright, strong fibers were prepared from poly(*m*-phenyleneadipamide). They could be obtained in an amorphous state and in a highly crystalline form. Matched pairs of para-linked aliphatic–aromatic and aromatic–aliphatic polyamides, such as poly(octamethyleneterephthalamide) and poly(*p*-phenylenesebacamide) had nearly coincident melting temperatures in several instances. Repeat spacings from X-ray diffraction patterns indicated that the polymer chain segments were fully extended in the crystalline state. However, the repeat spacing for the aliphatic–aromatic polymer was slightly less than that of the aromatic–aliphatic polymer in each pair.

There are numerous references to polyamides from aliphatic diamines with aromatic diacids and a far lesser number to polyamides from phenylene diamines with aliphatic diacids.[1,2] Two early references are those of Lum and Carlston[3] on poly(hexamethyleneisophthalamide) and Beaman and coworkers[4] on poly(*m*-phenylenesebacamide). Within the aliphatic–aromatic group of polyamides Shashoua and Eareckson[5] made one of the more extensive comparative studies of terephthalamides. This covered diamines with 2–7 chain-carbon atoms, as well as *N*-alkyl and some chain-alkyl substituents. Hopff and Krieger[6] prepared the polymers from 6-, 8-, and 10-carbon diamines and diacids with the complementary *o*-, *m*-, and *p*-phenylene intermediates. Recently Gorton[7] has explored a series of poly(methyleneisophthalamides). Bonner[8] has described the crystallization of poly(tetramethyleneisophthalamide) and poly(hexamethyleneisophthalamide), which were previously thought to be uncrystallizable.[2,3] Most of the unsubstituted aliphatic–aromatic polyamides which have been reported are listed in Table I. For brevity only selected references are noted.

Of this group poly(hexamethyleneterephthalamide) has received the most attention. Not only has it been prepared in a number of ways but it has been the subject of extensive spinning studies and characterization in fiber form.[5,12–14]

Probably the reason that aliphatic–aromatic polyamides