Synthesis and Emission Properties of Poly(*N*-ethyl-4-vinylcarbazole)

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ABSTRACT: N-Ethyl-4-vinylcarbazole has been synthesized and subsequently polymerized by free radial, anionic, and cationic methods to give poly(N-ethyl-4-vinylcarbazole). ¹H NMR spectroscopy indicates that increased steric interference between neighboring pendant chromophores results when bonding to the polymer backbone occurs at the 4 position as opposed to the 2 or 3 ring carbon atom or at the 9 nitrogen atom. A comparison of the emission properties of poly(N-ethyl-2-vinylcarbazole), poly(N-ethyl-3-vinylcarbazole), poly(N-ethyl-4-vinylcarbazole), and poly(N-vinylcarbazole) is made, using steady state fluorescence spectroscopy and fluorescence decay measurements, and in this manner the effect of a variation in position of chain emplacement on the formation of the intrachain excimer state is determined. The three isomeric vinylcarbazole polymers exhibit both carbazole monomer-like and intrachain excimer fluorescence whereas poly(N-vinylcarbazole) differs fundamentally by exhibiting only excimer fluorescence from two distinct intrachain excimer states. The emission spectra of poly(N-ethyl-2-vinylcarbazole) and poly(N-ethyl-4-vinylcarbazole) are nearly indistinguishable; however, fluorescence decay measurements indicate significant differences in their kinetics of intrachain excimer formation and dissociation. Bonding of the pendant chromophore to the chain at the 4 position imposes a ground state conformation which requires only relatively small changes to achieve the overlapping sandwich geometry required for excimer formation. Attachment of the chromophore at the 2 position requires rather large conformational changes. The large excimer to monomer-like fluorescence ratio observed in poly(N-ethyl-3-vinylcarbazole) compared to the 2 and 4 isomers is attributed to the higher isotactic content of the 3 isomer resulting from its cationic polymerization.

Interest in the complex photophysical processes which occur in organic polymers has increased rapidly in recent years.^{1,2} One such process, namely the formation of a metastable excimer state, results from the association of two like pendant chromophores, one of which has been electronically excited. Since the excited molecular complex (excimer) has a dissociative ground state, no change in the absorption spectrum due to direct excitation to the excimer state can be observed, and the excimer emission band is characteristically unstructured. Thus, vinyl aromatic polymers in which excimer formation is possible typically exhibit, in addition to the normal molecular fluorescence characteristic of the pendant group, a new, structureless emission band which appears at lower energies.³ The situation is thus analogous to the concentration-dependent, diffusion-limited formation of excimers observed for many aromatic and heteroaromatics in solution, except that the association step (at least for dilute polymer solutions) is unimolecular.

Previously we,⁴⁻⁶ and others,⁷ have reported the emission properties of a number of polymers containing carbazole groups, and it is clear that the relative intensities of fluorescence emission from excimers and isolated carbazole units depend upon both the sequence length of carbazole-containing polymer segments and on the way in which the carbazole substituent is linked to the polymer backbone.

Of particular interest is the fact that poly(N-vinylcarbazole) (PVK) appears to exhibit only excimer fluorescence (from two distinct intrachain excimers), whereas the closely related poly(*N*-ethyl-2-vinylcarbazole) [P(N-Et-2VK)] and poly(N-ethyl-3-vinylcarbazole) [P(N-Et-3VK)] exhibit strong monomeric carbazole emission together with weaker excimer emission.⁴

The carbazole group affords a highly convenient probe for determining the ways in which substituent configurational and polymer chain conformational effects control intrachain excimer emission in polymers. Accordingly, we have synthesized the difficultly accessible N-ethyl-4vinylcarbazole monomer and now report a comparison of the emission properties of poly(*N*-ethyl-4-vinylcarbazole) [P(N-ET-4VK)], its two positional isomers P(N-ET-2VK)and P(N-Et-3VK), and PVK.

Experimental Section

1. Synthetic Procedures. 3-Carboxy-6-chlorophenyldiazonium Chloride (1). To a suspension of 100 g (0.583 mol) of p-chloro-m-aminobenzoic acid (FLUKA), 750 mL of concentrated hydrochloric acid, and 500 g of ice, a solution of 44.0 g (0.6 mol) of sodium nitrite in 250 mL of water was added dropwise with stirring. The rate of addition was controlled so that the reaction temperature was maintained at 3 °C. A clear brownish solution resulted which, after being stirred at this temperature for a further 30 min, gave a positive test with starch-iodide paper. The clear solution of the diazonium salt was diluted with 350 mL of ice water and directly used in the next step.

3-Hydrazino-4-chlorobenzoic Acid Hydrochloride (2). About 4 L of water was saturated with sulfur dioxide at 0.5 °C and the solution of the diazonium chloride (1) was added in portions at a rate which maintained the reaction temperature at 5-10 °C. During the addition, a brisk stream of sulfur dioxide was passed through the reaction mixture; the addition was completed after ca. 30 min. The cooling bath was removed at this time, but sulfur dioxide was passed through the mixture for an additional 30 min. The resulting colored suspension was allowed to stand at room temperature for 12 h and cooled to about 5 °C and an equal volume of concentrated hydrochloric acid was slowly added. The white crystalline product was filtered, dried (yield 107 g, 82.5%), and used in the next step of synthesis.

1-Chloro-4-carboxy-5,6,7,8-tetrahydrocarbazole (4). To a suspension of 107 g of hydrazino hydrochloride (2) and 400 mL of water was added 50 mL of concentrated sulfuric acid. The resulting mixture was heated on a steam bath and 90 mL of cyclohexanone added in portions while the mixture was stirred vigorously. It was noticed that after the addition of ca. 30 mL of the reagent, the suspension transformed to a clear solution and then an orange solid separated. After the addition was completed, the resulting mixture was stirred vigorously at 80-90 °C for 3 h. The highly crystalline product was filtered and recrystallized from glacial acetic acid, yielding 90 g (75%) of a light tan product: mp 220–222 °C dec; ν_{max} 3340 (NH), 1660 (C=O), 1600 (C=C), 765 and 735 cm⁻¹; τ (D₂O; K₂CO₃) 1.9, 2.3, 2.42, 2.58 (2 H, two d, ArH), 6.7 (4 H, m, H for the saturated ring), 7.7 (4 H, broad, two d, protons for the saturated ring); m/e 221/223 [(M CO)⁺, 100],

249/251 (M⁺, 50), 204/206 (18.7). Anal. Calcd for $C_{13}H_{12}ClNO_2$: C, 62.53; H, 4.86. Found: C, 62.40; H, 4.89.

9-Ethyl-1-chloro-4-carboxy-5,6,7,8-tetrahydrocarbazole (5). To a solution of 115 g of 4 in 450 mL of dry dimethyl sulfoxide was added 4 equiv of potassium hydroxide powder, while maintaining a temperature of 15 °C by means of an ice bath. The dark mixture was then stirred at room temperature for 1 h, and 150 g of ethyl iodide was added dropwise with stirring and cooling. The resulting mixture was stirred overnight and poured into ice water and extracted three times with dichloromethane. After the extracts were washed with water and dried (MgSO₄), removal of solvent yielded 82.0 g (91%) of the product: mp 142–143 °C; ν_{max} 1675 (C=O), 1598 (C=C), 1270, 1225, 1190, 1125, 1090, 1015, 970, 835, 780, 750 cm⁻¹.

Methyl [9-Ethyl-1-chloro-5,6,7,8-tetrahydrocarbazole]-4carboxylate (6). A mixture of 85.0 g of 5, 1 L of methanol, and 20 mL of concentrated sulfuric acid was refluxed for 5 h. The mixture was concentrated to about 100 mL, diluted with water, and neutralized to pH 7. The product was filtered, recrystallized from alcohol-water, and dried to give 72 g (80%): mp 90-91 °C; ν_{max} 1715 (C=O), 1600 (C=C), 1560, 1270, 1250, 1180, 1125, 1090, 1010, 820, 783, 770, 740, 665, 640 cm⁻¹; τ (CDCl₃, ext Me₄Si) 2.08, 2.2-2.46, 2.6 (2 H, q, ArH), 4.95, 5.1, 5.2, 5.3 (2 H, q, ethyl group), 5.65 (3 H, s, CH₃), 6.85 (4 H, m, protons of the saturated ring), 7.75 (4 H, m, protons of the saturated ring), 8.15, 8.3, 8.4 (3 H, t, ethyl group); m/e 291/293 (M⁺, 100), 276/278 (82.5), 260/262 (20.2), 231/233 (65), 167 (21.5).

Methyl (9-Ethyl-1-chlorocarbazole)-4-carboxylate (7). A mixture of 72.0 g (0.247 mol) of 6, 200 mL of dry xylene, and 122.9 g (0.5 mol) of pure chloranil was refluxed for 65 h. The hot solution was filtered through a Celite pad and the filtrate evaporated to dryness in vacuo. The residue was extracted with chloroform and washed with dilute NaOH solution several times followed by water. After being dried (MgSO₄) it was evaporated to dryness in vacuo, leaving 42.0 g of a thick syrup (60%): m/e 272/274 [(M - CH₃)⁺, 100], 287/289 (M⁺, 63), 256/258 (37), 244/246 (39), 228/230 (26), 209/211 (52); τ (CDCl₃, ext Me₄Si) 1.3, 1.42 (1 H, ArH), 2.06, 211, 2.2, 2.35, 2.5 (5 H, complex m, ArH), 4.5, 4.63, 4.76, 4.89 (2 H, q, ethyl group), 5.62 (3 H, s, CH₃), 7.82, 7.95, 8.19 (3 H, t, ethyl group).

9-Ethyl-1-chloro-4-hydroxymethylcarbazole (8). To a solution of 42.0 g (0.17 mol) of 7 in 250 mL of dry tetrahydrofuran was added 13.0 g (0.34 mol) of lithium aluminum hydride in portions during 1 h, with continued stirring under nitrogen at 2 °C. After the addition was completed, the resulting mixture was stirred at room temperature for an additional 15 min. The mixture was stirred and cooled to 1-2 °C, and a few milliliters of water were added dropwise to decompose the excess lithium aluminum hydride. The small amount of precipitate was filtered and the filtrate evaporated to dryness in vacuo, leaving a colorless syrup which crystallized upon cooling. The crystalline product was collected on filter paper and recrystallized from benzene, yielding 22.0 g of pure compound: mp 133-134 °C; $\nu_{\rm max}$ 3300-3200 (OH), 1610 (C=C), 1590, 1370, 1350, 1320, 1260, 1230, 1130, 1080, 1050, 970, 930, 800, 770, 750, 725, 680 cm⁻¹; τ (CDCl₃, ext Me₄Si) 1.3, 1.42, (1 H, ArH), 2.06-2.5 (5 H, m, ArH), 4.31 (2 H, s, CH₂), 4.51–4.89 (2 H, q, ethyl group), 7.4 (1 H, s, OH), 7.82–8.09 (3 H, t, ethyl group); m/e 224/246 [(M – CH₃)⁺, 100], 259/261 (M⁺, 83), 229/231 (41), 214/216 (79), 200/202 (8.4). Anal. Calcd for C₁₅H₁₄ClNO: C, 69.37; H, 5.39; N, 5.39. Found: C, 69.39; H, 5.40; N, 5.14.

4-(Hydroxymethyl)-9-ethylcarbazole (9). A mixture of 17.0 g (0.066 mol) of 8, 650 mL of 0.2 M methanolic potassium hydroxide, and ca. 5.0 g of fresh Raney nickel (wet with H₂O) was shaken at 40 °C under a hydrogen pressure of 4.5 atm for ca. 20 h. The autoclave was carefully opened and the catalyst was filtered off through a Celite pad. The filtrate was evaporated to dryness in vacuo, leaving a tan colored crystalline solid. The product was suspended in water, neutralized to pH 7, filtered, recrystallized from ethanol, and dried to give 10.6 g (75%) of white needles: mp 142–143 °C; TLC (silica gel/CHCl₃/I₂ R_f 0.4); ν_{max} 3300, 3200 (OH), 1620 (C=C of the aromatic), 1600, 1330, 1240, 1075, 1050, 780, 760, 750, 720; τ (CDCl₃, ext Me₄Si) 1.22–1.35 (1 H, ArH), 1.9–2.4 (6 H, complex m, ArH), 4.25 (2 H, s, CH₂), 5.35–4.9 (2 H, q, ethyl group), 7.58 (1 H, s, OH), 8.23–8 (3 H, t, ethyl group); m/e 180 [(M – CH₂OH – CH₂)⁺, 100], 194 (96), 210 (86), 225 (M⁺,

53.5). Anal. Calcd for $\rm C_{15}H_{15}NO:\,$ C, 79.77; H, 6.66; N, 6.22. Found: C, 79.75; H, 6.61; N, 6.42.

Pyridinium Chlorochromate (10). To 18.4 mL of 6 M hydrochloric acid (0.11 mol) was added 10.0 g (0.1 mol) of chromic anhydride. The resulting mixture was cooled to 0 °C and 7.91 g (0.1 mol) of pyridine were added dropwise with stirring. The orange colored mixture was cooled to 0 °C, filtered, and dried in vacuo to yield 13.0 g of orange colored crystalline product.

9-Ethyl-4-formylcarbazole (11). A solution of 2.25 g (10 mm) of 9 in 30 mL of dichloromethane was added to a suspension of 3.23 g (15 mm) of 10 in 50 mL of dry dichloromethane. The mixture turned dark immediately and was stirred at room temperature for 2 h during which time a dark tarry material separated. This product was treated with 350 mL of dry diethyl ether, stirred for 0.5 h, and filtered through a celite pad. The filtrate was evaporated to dryness in vacuo, leaving a yellow crystalline product. After recrystallization of the crude product from cyclohexane-isopropyl alcohol (90:10), the pure compound was filtered and dried in vacuo to yield 1.83 g (81%) of the formyl carbazole: mp 60–61 °C; $\nu_{\rm max}$ 1680 (C==O), 1610, 1590, 1560, 1400, 1320, 1290, 1215, 1150, 1070, 1020, 990, 790, 750, 720 695 cm⁻¹; δ (CDCl₃, Me₄Si) 10.87 (1 H, s, CHO), 9.55 and 9.4 (1 H, two m, ArH), 8.2-7.6 (6 H, complex m, ArH), 4.9-4.5 (2 H, q, ethyl group), 1.85–1.6 (3 H, t, ethyl group); m/e 208 [(M – CH₃)⁺, 100], 223 $(M^+, 70)$, 194 (9), 180 (13.5), 166 (7.4). Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87. Found: C, 80.67; H, 5.70.

9-Ethyl-4-vinylcarbazole (12). To a suspension of 8.57 g (0.024 mol) of triphenylmethylphosphonium bromide in 100 mL of dry, inhibitor free tetrahydrofuran was added dropwise 15.3 mL (0.024 mol) of a 1.6 M solution of n-butyllithium in hexane. After the resulting orange colored mixture was stirred for 2 h at room temperature, 5.4 g of 11 in 50 mL of tetrahydrofuran was added and the solution refluxed for 1 h. The reddish colored mixture was concentrated to half its volume and poured into 1.5 L of hexane. The precipitate was filtered and the filtrate evaporated to dryness in vacuo leaving a liquid. The crude product was dissolved in a minimum volume of benzene and eluted through a silica gel column, using a 90:10 hexane:benzene mixture. After the solvent was evaporated, a coloress oil was obtained which was dried in vacuo to give 6.8 g (63.5%) of the product: TLC (R_f 0.25; silica gel, 90:10 hexane-benzene UV detected); ν_{max} (neat film) 3050-2980-2940 (CH stretch), 1620 (C=C), 1590, 1570, 1490, 1470, 1430, 1410, 13.80, 1325, 1290, 1250, 1215, 1150, 1100, 990, 980, 910, 800, 760, 740, 725 cm⁻¹; τ (CDCl₃ ext Me₄Si) 1.28 and 1.39 (1 H, two d, ArH), 1.62-2.7 (7 H, complex m, ArH and one olefinic proton), 3.6, 3.9, 4.0, 4.2 (2 H, four d, olefinic protons), 5.15-5.5 (2 H, q, ethyl group), 8.15-8.4 (3 H, t, ethyl group); m/e 206 [(M - CH_3)⁺, 100], 221 (M⁺, 80), 191 (18), 178 (8), 165 (4). Anal. Calcd for C_{16}H_{15}N^{-1}/_{6}H_2O: C, 85.71; H, 6.83; N, 6.25. Found: C, 85.84; H, 6.83; N, 6.19.

Poly(9-ethyl-4-vinylcarbazole). I. Free-Radical Polymerization. A solution of 2.5 g of 12, 1.0 mL of dry tetrahydrofuran, and 20 mg of AIBN was degassed, sealed, and heated at 60 °C for 15 h. The reaction mixture was poured into 100 mL of methanol and the precipitate filtered, purified, and dried as usual to give 515 mg (20.6%) of polymer: M_n 20 000; ν_{max} (Nujol mull) 1610 (C=C aromatic), 1595, 1575, 1328, 1245, 1150, 800, 760, 740, 725 cm⁻¹; τ (CDCl₃, int Me₄Si) 3.35 (ArH, broad, ca. 6 H), 4.1 (ca. 1 H, shoulder, ArH), 5.4–7.4 (aliphatic H, broad ca. 3 H), 8–9.5 (aliphatic H, broad, ca. 4 H).

II. Cationic Polymerization. (a) Tropylium hexachloroantimonate initiator: A solution of 0.442 g (2 mmol) of 12 in 1 mL of purified dichloromethane was mixed at 0 °C with a solution of 10 mg (2.36×10^{-6} mol; 6×10^{-3} M) of tropylium hexachloroantimonate in 4 mL of dichloromethane. The resulting dark solution was allowed to stand for 15 min at 0 °C; the reaction mixture was then added to methanol, filtered, purified, and dried as usual to obtain 120 mg (28.5%) of white solid material: $\bar{M}_{\rm n}$ = 2000; IR spectrum was identical with that of the polymer obtained from free-radical polymerization. (b) Boron trifluoride initiator: A stock initiator solution was made by diluting 0.5 mL of a 45% solution of boron trifluoride in diethyl ether with 9.5 mL of purified dichloromethane. One-half milliliter of this solution was injected at -70 °C into a solution of 0.442 g (2 mmol) of 12 in 5 mL of dichloromethane, and the mixture was allowed to stand, at -70 °C, for 20 h. The reaction mixture was then



poured into methanol, filtered, purified, and dried to give 23 mg of a solid material (5.2%), $\bar{M}_n = 2000$ (oligomer).

III. Anionic Polymerization. A solution of 0.5 g of 12 in 10 mL of purified tetrahydrofuran was degassed before injecting 1.4 mL of a solution of *n*-butyllithium (1.6 M) in hexane. A deep red color formed immediately, the reaction mixture was stirred at room temperature for 15 min and poured into methanol, and the polymer was filtered. After further purification and drying, 310 mg (62%) of pure polymer was obtained (M 17000).

2. General Techniques. Infrared spectra were recorded as Nujol mulls with a Perkin-Elmer Model 257 infrared spectrophotometer, unless otherwise specified. ¹H NMR spectra were recorded on a 60 MHz, Perkin-Elmer RB12, using deuterated solvents with tetramethylsilane as external standard, unless otherwise specified. Mass spectra were measured by a V.G. Micromass 12. Ultraviolet spectra were recorded by a Unicam SP1800 ultraviolet spectrophotometer.

Molecular weights (\overline{M}_n) were determined by means of a Hewlett Packard Membrane Osmometer or, for very low molecular weights, a Mechrolab Vapour Pressure Osmometer.

Emission spectra were recorded on a Perkin-Elmer Model MPF-44A fluorescence spectrophotometer and are fully corrected for instrumental response. Fluorescence decays were measured by the method of time-correlated single-photon counting. The nanosecond fluorometer was assembled using electronic components from Ortec, Inc. Details of this apparatus can be found in an earlier publication.⁸

Results and Discussion

Monomer Synthesis and Reactivity. The monomer N-ethyl-4-vinylcarbazole (12) was successfully synthesized by the method described in Scheme I. Details are described in the Experimental Section.

The synthetic route described in Scheme I is essentially the same as that employed by Manske and Kulka⁹ for the synthesis of 4-acetylcarbazole except that 4-hydroxymethyl-9-ethylcarbazole (9) was prepared starting with 3-amino-4-chlorobenzoic acid. Commercial starting material was diazotized and the diazonium salt 1 reduced to the hydrazino compound 2 by the action of sulfurous acid. This compound, after reaction with cyclohexanone in the presence of a strong acid to produce the hydrazone 3 in situ, underwent ring closure to give an overall yield of 75% of the tetrahydrocarbazole 4. Alkylation of 4 with potassium hydroxide and ethyl iodide gave 5 which was esterified to prevent decarboxylation in the dehydrogenation of 6.

Chloranil was found to be superior to palladium on charcoal in large scale dehydrogenation of 6 in boiling xylene, and from such reactions approximately 50-60% of the carbazole 7 was obtained. Reduction of the ester group in 7 with lithium aluminum hydride gave 8 in 50% yield, which could be purified by recrystallization. Removal of the chlorine substitutent in 8 proved difficult and was eventually accomplished by the recently described¹⁰ action of Raney nickel in alkaline medium with a hydrogen pressure of ca. 5 atm at 40-50 °C. Ultimately 9 was oxidized to the aldehyde 11 by means of pyridinium chlorochromate, from which the desired monomer 12 was obtained by a Wittig reaction. The monomer 12 is an oily liquid at room temperature and must, therefore, be purified before polymerization by column chromatography. The resulting material appeared pure by all the usual spectroscopic techniques and gave only a single spot on TLC plates.

Polymerization was readily accomplished by free-radical and anionic methods with molecular weights (\overline{M}_n) in the region of 20000. In contrast, attempts to polymerize *N*-ethyl-4-vinylcarbazole with cationic initiators yielded only low molecular weight (\bar{M}_n 2000) oligomers. Thus in reactivity, N-ethyl-4-vinylcarbazole (NE4VC) is similar to the closely related N-ethyl-2-vinylcarbazole (NE2VC)^{11,12} but very different from the other isomer, N-ethyl-3vinylcarbazole (NE3VC), for which cationic polymerization is most effective.¹³ These observations may be readily understood since in NE4VC and NE2VC the nitrogen atom is not conjugated with the olefinic group and hence these monomers behave essentially as substituted styrenes forming relatively stable propagating radical and anionic intermediates. For NE3VC and NVC, the nitrogen atom lone pairs help to stabilize cationic intermediates and effectively destablize corresponding carbanions.¹² NE4VC and NE2VC have very similar electronic structures and this is reflected in the absorption maximum for the two corresponding propagating carbanions. In the present work it was found that the anion (-NE4VC)⁻Li⁺ had λ_{max} 486 nm (THF) and previously it has been shown¹² that (mNE2VC)⁻Li⁺ has λ_{max} 485 nm in the same solvent. However, qualitative observations indicate that NE4VC reacts more slowly than NE₂VC in all types of polymerization and this can, no doubt, be ascribed to the increased steric hindrance (due to the neighboring benzene ring) when bonding to the polymer backbone occurs at the 4 position of the carbazole ring system. Steric hindrance will be maximized at the 1 position of carbazole but, so far, it has not proved possible to synthesize the corresponding vinyl derivative.

Polymer Structure. Examination of the molecular structures for the isomeric vinylcarbazole polymers indicates considerable differences in steric interference between neighboring monomer segments due to the different modes of attachment to the polymer backbone.

Through space interactions of neighboring carbazole groups are thought to influence the shielding parameters of certain of the carbazole-ring hydrogens as evidenced by ¹H NMR spectroscopy. Previously it was shown conclusively¹⁴ that the poorly resolved ¹H NMR solution spectra of PVK and P(N-Et-2VK) include at least two resonances from the aromatic ring protons, one of which appeared significantly upfield from the resonance of low molecular



P(N-Et-3VK) P(N-Et-4VK)

weight carbazole models. In contrast, P(N-Et-3VK) did not exhibit such a shielding effect on the ring protons.¹⁴ Data for all four vinylcarbazole polymers are given in Table I from which it can be seen that P(N-Et-4VK) gives resonances for all the aromatic protons which are rather more shielded than the other polymers. This result presumably reflects increased steric hindrance when bonding to the polymer backbone occurs at the 4 position.

Luminescence Properties. A. Emission Spectra. As noted in the introduction, a major driving force in carrying out the very difficult synthesis of P(N-Et-4VK)was our interest in gaining further understanding of how a variation in chain emplacement affects the emission properties of vinylcarbazole polymers. The fluorescence spectra of the four vinylcarbazole polymers are shown in Figures 1–4. In all cases, the spectra were recorded for dilute solutions ($\sim 5 \times 10^{-5}$ M in monomer units) in tetrahydrofuran (THF) solvent. Spectra for each material were recorded under two conditions, first for an air equilibrated solution and then following purging with high purity nitrogen gas to remove dissolved oxygen. The two spectra recorded for each polymer were then normalized to the (0,0) band of the monomer-like fluorescence of P(N-Et-2VK), P(N-Et-3VK), and P(N-Et-4VK) and to the peak of the structureless band at \sim 380 nm in the case of PVK. The difference between the nitrogen purged and air equilibrated spectra yields in all cases a component at longer wavelengths whose structureless appearance and spectral location is like that observed for 1,3-bis(N-carbazolyl)propane, a compound utilized as a model for PVK. On the basis of investigations concerning the emission properties of the model compound, the structureless emission peaking at about 430 nm has been assigned as that resulting from the formation of an intramolecular excimer in which the two carbazole groups, one of which is electronically excited, have achieved an overlapping, sandwich-like conformation.^{15,16} The four vinylcarbazole polymers exhibit the same structureless fluorescence band, and this can be assigned with confidence as resulting from the formation of an intrachain excimer whose structure is like that achieved in the model compound. This forms a degree of commonality between all four of the vinyl carbazole polymers; however, differences do exist, some of which are apparent from the emission spectra of Figures 1-4 while others are more subtle and can only be ascertained from the results of fluorescence decay measurements.

On the basis of steady state fluorescence spectroscopy alone, one can conclude that these four different polymers can be broadly classified into two groups. PVK is distinct

Table IChemical Shifts (τ) and Approximate Number ofHydrogens for Vinylcarbazole Polymers

	chemical shifts (τ)		
polymer	aromatic	shielded aromatic	aliphatic
PVK	$2.4, 3.2, 3.8 (\sim 6)$	5.0 (~1)	6.8, 8.6 (3)
P(N-Et-2VK)	2.7, 3.1 (~6)	4.1 (~1)	6.7, 8.3, 9.4 (8)
P(N-Et-3VK)	$2.3, 2.7, 3.4 (\sim 7)$		6.3, 8.0, 9.0 (8)
P(N-Et-4VK)	2.8, 3.4 (~6)	4.2 (~1)	6.5, 9.0 (8)



Figure 1. Emission spectra of nitrogen purged (-) and air equilibrated (--) solutions of poly(*N*-ethyl-2-vinylcarbazole) in THF at room temperature. The lower curve is the difference of the two normalized spectra.



Figure 2. Emission spectra of nitrogen purged (-) and air equilibrated (--) solutions of poly(*N*-ethyl-3-vinylcarbazole) in THF at room temperature. The lower curve is the difference of the two normalized spectra.

in its emission properties with no evidence for fluorescence characteristic of an isolated carbazole monomer unit. Instead, one observes a second structureless emission peaking at about 380 nm which has been assigned as that from a second higher energy excimer state.⁴ Furthermore, contrary to the low-energy excimer, the polymer conformation appropriate for formation of this state has been shown to exist prior to the initial excitation step.^{4,17} All three polymers in which bonding of the pendant group to the



Figure 3. Emission spectra of nitrogen purged (-) and air equilibrated (--) solutions of poly(*N*-ethyl-4-vinylcarbazole) in THF at room temperature. The lower curve is the difference of the two normalized spectra.



Figure 4. Emission spectra of nitrogen purged (--) and air equilibrated (---) solutions of poly(N-vinylcarbazole) in THF at room temperature. The lower curve is the difference of the two normalized spectra.

polymer backbone occurs at one of the ring carbon atoms are characterized by alkyl carbazole monomer-like fluorescence and fluorescence from the lower energy excimer state. In this regard, the fluorescence spectra of P(N-Et-2VK) and P(N-ET-4-VK) appear very similar with relatively large amounts of the structured monomer-like fluorescence and very little low-energy excimer fluorescence. P(N-ET-3VK), on the other hand, displays a relatively large amount of low-energy excimer fluorescence with respect to the monomer-like fluorescence. These differences, however, are basically one of degree and are unlike the case of PVK in which more fundamental changes in the emission properties are observed.

B. Fluorescence Decay Measurements. Fluorescence decay curves for dilute solutions of all four polymers in THF at room temperature are shown in Figures 5–8. In all cases, the emission response was measured at two wavelengths, namely at 370 nm, a wavelength corresponding to the monomer-like fluorescence of P(N-ET-2VK, P(N-ET-3VK), and P(N-ET-4VK) or the high energy excimer band of PVK, and at 440 nm, a wavelength where the fluorescence is due totally to the low-energy excimer fluorescence common to all four polymers. The fluorescence is due total four polymers.



Figure 5. Emission decay curves of poly(N-ethyl-2-vinyl-carbazole) in THF at room temperature: upper curve measured at 370 nm; lower curve measured at 440 nm.



Figure 6. Emission decay curves of poly(*N*-ethyl-3-vinyl-carbazole) in THF at room temperature: upper curve measured at 370 nm; lower curve measured at 440 nm.



Figure 7. Emission decay curves of poly(N-ethyl-4-vinyl-carbazole) in THF at room temperature: upper curve measured at 370 nm; lower curve measured at 440 nm.

cence response curves of P(N-ET-2VK), P(N-ET-3VK), and PVK are quite similar and qualitatively, at least, the fluorescence response at 370 nm can be considered to behave as the sum of two exponentials while that at 440 nm behaves more like the difference of two exponential



Figure 8. Emission decay curves of poly(N-vinylcarbazole) in THF at room temperature: upper curve measured at 370 nm; lower curve measured at 440 nm.

terms. The fluorescence response curves of P(N-ET-4VK)are more complex and in particular it should be noted that the intrachain excimer response curve at 440 nm exhibits significant departure from what might be considered, even qualitatively, to be the difference of two exponential terms. This behavior apparently results from the fact that there is a distribution of intrachain excimer decay constants, a conclusion arrived at through calculations simulating the experimental 440 nm response curve.

For the purpose of subsequent discussion, the simplest possible kinetic scheme appropriate for the polymer systems (with the exception of PVK) is presented in eq 1,

$$(-M-M^{*}-) \xrightarrow{k_{DM} + k_{E} t_{D}} D^{*}$$

$$(1)$$

$$/k_{FM} \xrightarrow{2} k_{IM} / k_{FD} \xrightarrow{2} k_{ID}$$

$$(-M-M-) + h v_{FD} (-M-M-)$$

where -M*- represents an electronically excited carbazole pendant group along the polymer chain and D* the intrachain excimer. The notation for the various rate constants follows that of Birks.¹⁸ The scheme is identical with that utilized to describe the kinetics for the formation and deactivation of intramolecular excimers in model compounds such as 1,3-bis(N-carbazolyl)propane¹⁶ with the exception of the $k_{\rm E} f_{\rm D}$ term which corresponds to the product of the rate constant for energy migration along the polymer chain and the concentration, $f_{\rm D}$, of preformed excimer sites which can serve as traps for the migrating excitation.¹⁹ It is this latter term which makes an analysis of the photophysical properties of the various isomeric polymers in terms of substituent configurational and chain conformational mobility effects a difficult task indeed. Solution of the rate equations for the kinetic scheme of eq 1 subsequent to a δ function excitation light pulse yields the following expressions for the time dependence of the monomer fluorescence (or high-energy excimer fluorescence in PVK), $I_{\rm M}(t)$, and the intrachain excimer fluorescence, $I_{\rm D}(t)$.²⁰

$$I_{\rm M}(t) = k_{\rm FM} \left(\frac{X - \beta_1}{\beta_2 - \beta_1} \right) \left\{ e^{-\beta_2 t} + \left(\frac{\beta_2 - X}{X - \beta_1} \right) e^{-\beta_1 t} \right\}$$
$$I_{\rm D}(t) = \frac{k_{\rm FD} k_{\rm DM}}{\beta_2 - \beta_1} (e^{-\beta_1 t} - e^{-\beta_2 t})$$
(2)

where $\beta_{1,2} = \frac{1}{2} \{ (X + Y) + [(X - Y)^2 + 4k_{\text{DM}}k_{\text{MD}}]^{1/2} \}$ with $X = k_{\text{FM}} + k_{\text{IM}} + k_{\text{DM}} + k_{\text{E}}f_{\text{D}}$ and $Y = k_{\text{FD}} + k_{\text{ID}} + k_{\text{MD}}$. Both emission response curves are complex functions in-

Table II

Results of Fluorescence Decay Measurements on Vinylcarbazole Polymers, Carbazole Double Molecules, and Carbazole Monomers in THF at Room Temperature

	X^{-1} , ns	Y^{-1} , ns	$k_{\rm DM}, {\rm s}^{-1}$
P(N-ET-2VK)	8 ± 0.8	22 ± 3	6.4×10^{7}
P(N-ET-3VK)	3.2 ± 0.5	17 ± 2	$2.4 imes10^{8}$
P(N-ET-4VK)	4 ± 0.8	11 ± 2	$1.7 imes 10^{8}$
PVK	5.7 ± 0.5	13 ± 2	1.1×10^{8}
1,3-bis(N- carbazolyl)propane	6.4 ± 0.5	15.9 ± 2	9.6×10^7
1,3-bis(N-ethyl-2- carbazolyl)propane	10.8 ± 0.8	14.7 ± 2	$3.2 imes 10^7$
<u>, , , , , , , , , , , , , , , , , , , </u>		flu	orescence

	lifetime, ns
N-ethyl-2-ethylcarbazole	16.4 ± 0.5
N-ethyl-3-ethylcarbazole	14.2 ± 0.5
N-ethyl-4-(hydroxymethyl)carbazole ^a	13.3 ± 0.5
N-isopropylcarbazole	16.6 ± 0.5

 a N-Ethyl-4-ethylcarbazole was not available for study. The fluorescence lifetime of N-ethyl-4-ethylcarbazole and N-ethyl-4-(hydroxymethyl)carbazole should, however, be virtually the same.

volving the sum or difference of two exponentials, where each decay constant, β_1 and β_2 , includes all the rate constants. The behavior of the emission response curves of the dilute polymer solutions (with the exception of P(N-ET-4VK)) is thus, qualitatively at least, in accord with the solutions of the rate equations for the sample kinetic scheme of eq 1. In principle, one should be able to extract the decay constants β_1 and β_2 by proper analysis of the decay curves in the manner described elsewhere.⁸ Knowing the values for β_1 and β_2 and the fraction of the slowly decaying component in the monomer decay curve β_2 - $X/X - \overline{\beta}_1$, one can determine X and Y since $\beta_1 + \beta_2 = X$ + Y. X is the sum of the rate constants for all modes of deactivation of the initially excited pendant chromophore and Y is the sum of the rate constants for all modes of deactivation of the intrachain excimer state.

As seen in Figures 5, 6, and 8 a unique value for β_1 can be determined for P(N-ET-2VK), P(N-ET-3VK), and PVK from the negative gradient of either the monomer or excimer emission response curves at long times where the contribution from the $e^{-\beta_2 t}$ term becomes negligibly small. However, contrary to the case of a model component like 1,3-BCP, a unique value for β_2 cannot be obtained for the polymers since extrapolation of the slowly decaying component back to t = 0 and subtracting from the total 370 nm response curve leads to a nonexponential fast decay component. Thus for the polymers the decay constant β_2 appears to be time dependent and apparently reflects predominantly on the variation in rate constant for production of the intrachain excimer state from the very large number of energetically different ground state chain segment conformers which exist along the flexible polymer chain.

In these cases, a value for β_2^{-1} was obtained by simply determining the time required for the rapidly decaying component to reach e^{-1} of its initial value, a procedure which perhaps is not too unreasonable since the fast component over the first decade of intensity does not exhibit large deviations from first order behavior. From these values of β_1 , β_2 , and $\beta_2 - X/X - \beta_1$, values for X and Y are obtained and their inverses which correspond to the lifetimes of the monomer (PVK high-energy excimer) and intrachain excimer are tabulated in Table II.

As noted above, the response curves for P(N-ET-4VK) are even more complex and their analysis made exceed-

ingly difficult as a result of the fact that it is not possible to determine a unique value for β_1 . In this case, the procedure was to take an average value of the various β_1 's determined over the first approximately 70 ns of the 440-nm decay and to utilize this to determine $\beta_2 - X/X$ $-\beta_1$, and hence to proceed as with the other polymers in determining X and Y. These results along with the fluorescence decay times for various model monomer compounds are also tabulated in Table II. The values for the various monomer fluorescence lifetimes are utilized to determine the values for $k_{\rm FM} + k_{\rm IM}$ for the pendant carbazole groups in the various isomeric polymers assuming that the sum of the radiative and nonradiative rate constants $(k_{\rm FM} + k_{\rm IM})$ for an isolated monomer unit is equal to that for the group bonded to the polymer chain. From this the values for $k_{\rm DM}$ (or $k_{\rm DM} + k_{\rm E}f_{\rm D}$) for the various polymers are calculated. Also to be found in the table are results for two carbazole double molecules which are included for comparison with the two polymers for which they serve as model compounds.

In what follows, we attempt to relate the results of the steady state fluorescence and fluorescence decay time measurements on the three isomeric vinylcarbazole polymers and PVK to variations in polymer structure resulting from the different mode of attachment to the polymer chain backbone. This, it should be realized, can only be qualitative because of the exceedingly complex situation that exists for dilute solutions of high molecular weight polymers. However, in spite of the qualitative nature of the conclusions, it is quite clear that fluorescence decay measurements are a particularly powerful method of probing the complex photophysics of polymers and lead to considerably greater insight than that available from the fluorescence spectra alone. For example, the fluorescence spectra of P(N-ET-2VK) and P(N-ET-4VK)shown in Figures 1 and 3 respectively are very similar, and one would conclude from this alone that both polymers exhibit virtually identical kinetics with very little formation of the low-energy, intrachain excimer which yields the structureless emission band in the 430-nm spectral region. The fluorescence decay measurements on the other hand indicate very significant differences in the kinetics of these two polymers. The rate constant for formation of the intrachain excimer, $k_{\rm DM}$, is nearly three times greater for P(N-ET-4VK) than for P(N-ET-2-VK). The fact that one observes very similar emission spectra for both polymers must then be a result of a larger rate constant for thermal dissociation of the intrachain excimer in P(N-ET-4VK)than in P(NET-2VK) to give back their respective excited state monomer units. (This last assertion is based on the assumption that the intrachain excimer for both polymers, once formed, has the same rate constants for radiative and nonradiative deactivation. Thus $k_{\rm FD} + k_{\rm ID}$ is assumed equal for both polymers and variations in Y^{-1} reflect primarily variations in k_{MD} .) The experimental results are in accord with this since the fluorescence lifetime of the low-energy excimer fluorescence of P(N-ET-4VK) is half that of P(N-ET-2VK). If one assumes that the fluorescence lifetime of the low-energy excimer in P(N-ET-2VK)and P(N-ET-4VK) in the absence of thermal dissociation is equal to 42 ns as previously determined for this state in 1,3-BCP and PVK, then one can determine the rate constant $k_{\rm MD}$ for production of excited state monomer due to thermal dissociation of the metastable excimer state for the respective polymers. The values of $k_{\rm MD}$ are 2.05×10^7 s⁻¹ and 6.6×10^7 s⁻¹ for P(*N*-ET-2VK) and P(*N*-ET-4VK), respectively. Utilizing these values for $k_{\rm MD}$ along with those for $k_{\rm DM}$ the equilibrium constant for the reversible

formation and dissociation of the intrachain excimer, $K = k_{\rm DM}/k_{\rm MD}$, yields 3.1 and 2.6 for P(N-ET-2VK) and P-(N-ET-4VK), respectively, values which account for the similarity of their fluorescence spectra.

The emission spectrum of P(N-ET-3VK) clearly shows a considerably greater amount of low-energy intrachain excimer fluorescence relative to the monomer fluorescence than either the 2- or 4-vinyl isomers. The reason for this is also evident from the results of fluorescence decay measurements. The rate constant for formation of the intrachain excimer, k_{DM} , is greater than that for all the other vinylcarbazole polymers, and secondly the lifetime of the excimer state is relatively long lived. Following the same arguments as before yields 7.1 for the equilibrium constant, a value which is in accord with the significantly greater amount of excimer fluorescence relative to the monomer fluorescence.

Thus we find that the results obtained by fluorescence decay measurements are certainly consistent with the steady state fluorescence spectra of these three vinylcarbazole polymers; however, this consistency is the result of rather unexpected variations in the individual rate constants for formation and dissociation of the low-energy excimer state. Interpretation of this variation in rate constants in terms of alteration in the position of bonding to the polymer backbone in a manner other than in a very qualitative fashion seems to be a virtually impossible task. One observation, however, seems to be particularly significant with regard to the significantly greater ratio of excimer to monomer fluorescence in P(N-ET-3VK) compared to P(N-ET-2VK) and P(N-ET-4VK). Solution ¹H NMR spectra of all four polymers were distinguished by the lack of a shielded aromatic ring proton resonance in P(N-ET-3VK). As noted earlier, this presumably reflects a decrease in steric hindrance between neighboring carbazole groups when bonding to the polymer backbone occurs at the 3 position, and this perhaps allows for greater freedom for the polymer chain conformational transitions or rotational motion about the carbon-carbon bond linking the pendant group to the backbone required to bring two neighboring chromophores into the eclipsed sandwich-like structure characteristic of the low-energy excimer. However, a simple description based on an examination of the molecular structure of the various polymers would seem to be more agreeable if P(N-ET-2VK) and P(N-ET-3VK)were similar in behavior rather than significantly different as they are. In this regard, it should be noted that P(N-ET-3VK) was cationically polymerized whereas P(N-Et-2VK) was prepared via conventional free-radical techniques. It has been shown that cationically polymerized PVK is characterized by greater isotactic content than free-radically polymerized PVK.7 If the cationically polymerized sample of P(N-ET-3VK) utilized here contains a higher degree of isotacticity than the free-radically polymerized P(N-ET-2VK), then a significantly greater rate constant for production of the low-energy excimer state would be expected on this basis alone. A recent elegant study by Nishijima and Yamamoto²¹ in which the rate constants for formation of the intramolecular excimer $(k_{\rm DM})$ for a variety of dinaphthylalkanes were experimentally determined clearly showed that the variations in $k_{\rm DM}$ were related to the conformation of the ground state molecule and the facility of conformational relaxation to the excimer state. In particular the value of $k_{\rm DM}$ for 2,4dinaphthylpentane (meso) was much greater than that for 2,4-dinaphthylpentane (racemic), a result consistent with the greater amount of low-energy excimer fluorescence in cationically polymerized PVK than in free-radically polymerized PVK, if indeed the formation of this state depends on the ease of conformational relaxation within the various chain segments which comprise the polymer.

In conclusion, and by way of summary, we simply note that a new vinylcarbazole polymer, P(N-ET-4VK), has been prepared and its emission properties compared to those of P(N-ET-2VK), P(N-ET-3VK), and PVK. The isomeric vinylcarbazole polymers in which bonding to the backbone occurs at one of the ring carbon atoms all display emission spectra characteristic of that from their respective alkylcarbazole monomers and from a low-energy intrachain excimer state. The emission spectra of P(N-ET-2VK) and P(N-ET-4VK) are virtually indistinguishable; however, fluorescence decay measurements indicate considerable differences in the kinetics of formation and deactivation of the intrachain excimer state. These differences apparently reflect the variations in the preferred ground state geometry between neighboring pendant groups as determined by the position of bonding to the polymer backbone. In the case of P(N-ET-4VK) this geometry is such as to require only relatively minor conformational changes to achieve the overlapping sandwich-like geometry appropriate to the intrachain excimer state. The formation of the intrachain excimer state in P(N-ET-2VK) requires larger scale conformational changes to achieve the same intrachain excimer geometry. The basic cause leading to the differences in the kinetics of the photophysical processes in P(N-ET-2VK) and P(N-ET-4VK) appears to be that the geometrical constraints imposed by chain emplacement at the 4 position yield a higher density of ground state chain segment conformations in which achievement of the intrachain excimer geometry requires only small conformational variations. ¹H NMR spectroscopic results are in qualitative accord with this assertion. The relatively large amount of intrachain excimer fluorescence observed for P(N-ET-3VK), a polymer where interactions between neighboring pendant groups is minimal, is thought to result from an increase in isotactic content in the cationically polymerized sample. PVK, where chain emplacement occurs at the nitrogen atom, exhibits fundamentally different emission properties.

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Macroions and Macroion Pairs in the Anionic Polymerization of β -Propiolactone (β -PL)

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ABSTRACT: The dissociation constants $K_{\rm D}$ of the poly(β -propiolactone) ion pairs (carboxylate anion paired with crowned K⁺) were found to be almost independent of temperature and had the following values at 25 °C: $K_D = 5.6 \times 10^{-6}$ M at [β -PL] = 1.0 M and $K_D = 5.0 \times 10^{-5}$ M at [β -PL] = 3 M (CH₂Cl₂ solvent), the ⁶C: $K_{\rm D} = 5.6 \times 10^{-9}$ M at $[\beta - PL] = 1.0$ M and $K_{\rm D} = 5.0 \times 10^{-1}$ M at $[\beta - PL] = 5$ M $(C \Pi_2 C I_2 \text{ solven})$, the corresponding thermodynamic parameters being equal to $(\Delta H_{\rm D} \text{ in kcal mol}^{-1} \text{ and } \Delta S_{\rm D} \text{ in cal mol}^{-1} \text{ deg}^{-1}) \Delta H_{\rm D} = 0.6 \pm 0.5$, $\Delta S_{\rm D} = -22 \pm 2$, $\Delta H_{\rm D} = 0 \pm 2$, and $\Delta S_{\rm D} = -18 \pm 3$, respectively. Rate constants of propagation on macroions $(k_{\rm p}^{-})$ and macroion pairs $(k_{\rm p}^{-*})$ were determined, and it was found that the ratio $k_{\rm p}^{-}/k_{\rm p}^{\pm}$ changed with temperature. At -20 °C, $k_{\rm p}^{-}/k_{\rm p}^{\pm} = 5.6$ whereas this ratio increases up to 150 at 35 °C $([\beta - PL]_0 = 3.0$ M). Formally this dependence stems from differences in activation parameters $(\Delta H_{\rm p}^{\pm(+)} < \Delta H_{\rm p}^{\pm(-)})$; the larger value of the activation enthalpy for macroanions is interpreted in terms of their stronger solvation by highly polar monomer (D_{25} of β -PL equals 45.8). The macroion pair is less solvated because of the shielding effect of the cation.

Anionic polymerization of β lactones has been studied by several authors;¹⁻¹⁰ however until now no rate constants are available for propagation reactions on various kinds of active centers, which are macroion pairs and free ions, that are involved in this process. In the past¹¹ and more recently^{8,12,13} only several rate coefficients, without making distinction between different possible ionic states, were given.

In our previous paper, 9 we described application of crown ethers for complexing counterions in the polymer-