# Photophysical Studies of Copolymers of *N*-Vinylcarbazole

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**ABSTRACT:** The absorption, fluorescence excitation and emission spectroscopy, and time-dependent spectrofluorimetry have been used to study the photophysics of copolymers of *N*-vinylcarbazole with different monomers like vinyl acetate, methyl acrylate, methyl methacrylate, butyl acrylate, and butyl methacrylate in dichloromethane. In all the copolymers and at different *N*-vinylcarbazole content, the absorption spectra reflect only the monomer carbazole units. The two kinds of excited monomer species of *N*-vinylcarbazole are present in $S_1$ state. Short-lived ($\sim$3 ns) excited monomer decays forming low energy excimer obtained by the complete overlap of the excited carbazole monomer. The long-lived excited monomer ($\sim$8 ns) decays to ground state without formation of any excimer. The high energy excimer is relatively short-lived and is formed by the partial overlap of the carbazole units. The presence of bulky group in the copolymer chain hinders the formation of excimers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 372–380, 2006

**Key words:** poly(*N*-vinylcarbazole); copolymerization; photophysics; fluorescence; excimer

## INTRODUCTION

The photophysics of poly(*N*-vinylcarbazole) (PVK) has attracted the attention of both polymer scientists and photophysicists mainly for two points, besides others.[1–3]

Firstly, PVK has photoconducting properties[2] and secondly PVK forms different kinds of excimers by the interactions of the intramolecular carbazole moieties. Besides monomer carbazole fluorescence band, the fluorescence spectrum of PVK consists of two other fluorescence band maxima at $\sim$370 and 420 nm. Depending upon the structural or spectral aspects, the former band is either called a partially eclipsed or high energy excimer, whereas the latter is known as completely sandwiched or low energy band. In this paper, we name them as high energy and low energy excimers, respectively. A lot of work has been carried out to understand the mechanism of their formation and the structural origin of these excimers.[4–24] Theoretical treatments, as well as, molecular dynamic simulations have also been carried out to strengthen the experimental findings.[25,26] Further, to understand the effect of copolymerization of *N*-vinylcarbazole on the photoconducting behavior, spectral characteristics and mechanism of excimer formation, copolymers of *N*-vinylcarbazole were synthesized. This has further opened up new areas and new challenges. For example, the proportion of excimers found is governed by the carbazole content, their location on the chain and stereochemistry of different comonomers.

We had reported the NMR studies of these copolymers in our earlier papers.[27–30] The reactivity ratios of these copolymers were determined by Kelen–Tudos method and nonlinear error in variable method, which are based on the terminal model of copolymerization. By comparing the experimental out-feed values and those calculated by these reactivity ratios, it is confirmed that these copolymers follow First Order Markov model. The sequencing and characterization of these copolymers are well-described using one- and two-dimensional NMR spectroscopy in our earlier publications on these copolymers.[27–30]

The present work involves the effect of copolymerization of *N*-vinylcarbazole (V) with different monomers like vinyl acetate (A), methyl acrylate (M), methyl methacrylate (**M**), butyl acrylate (B), and butyl methacrylate (**B**) on the photophysics of poly(*N*-vinylcarbazole). Absorption, fluorescence excitation and emission spectra, and time-dependent spectrofluorometric studies have been carried out in dilute solutions of these copolymers in dichloromethane. The carbazole content, the photon absorbing species, has been varied to study the intramolecular excimer formation.

## EXPERIMENTAL

### Materials

The copolymers of *N*-vinylcarbazole (Aldrich, UK) with vinyl acetate (Fluka, Switzerland), methyl acry-

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**TABLE I**
**Copolymer Composition Data and Molecular Weight Averages of *N*-vinylcarbazole Copolymers**

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| Sample no. | $f_v$ | $F_v$ | $F_{vv}$ | $\overline{M}_n \times 10^{-5}$ (g/mole) | $\overline{M}_w \times 10^{-5}$ (g/mole) |
|---|---|---|---|---|---|
| *N*-vinylcarbazole / vinyl acetate | | | | | |
| VA1 | 0.05 | 0.19 | 0.044 | 2.2 | 3.6 |
| VA2 | 0.15 | 0.45 | 0.314 | 2.7 | 4.9 |
| VA3 | 0.35 | 0.73 | 0.544 | 2.8 | 5.4 |
| *N*-vinylcarbazole / methyl acrylate | | | | | |
| VM1 | 0.15 | 0.14 | 0.002 | 2.4 | 4.5 |
| VM2 | 0.60 | 0.44 | 0.028 | 4.0 | 5.8 |
| VM3 | 0.95 | 0.70 | 0.427 | 4.2 | 5.7 |
| *N*-vinylcarbazole / methyl methacrylate | | | | | |
| VM1 | 0.30 | 0.16 | 0.017 | 1.8 | 3.2 |
| VM2 | 0.65 | 0.38 | 0.142 | 1.8 | 3.9 |
| VM3 | 0.85 | 0.68 | 0.401 | 2.0 | 3.8 |
| *N*-vinylcarbazole / butyl acrylate | | | | | |
| VBl | 0.30 | 0.31 | 0.011 | 1.1 | 2.1 |
| VB2 | 0.60 | 0.48 | 0.053 | 2.7 | 3.6 |
| VB3 | 0.90 | 0.65 | 0.281 | 3.3 | 4.9 |
| *N*-vinylcarbazole / butyl methacrylate | | | | | |
| VB1 | 0.30 | 0.17 | 0.008 | 1.1 | 1.9 |
| VB2 | 0.80 | 0.53 | 0.164 | 1.7 | 3.1 |
| VB3 | 0.95 | 0.83 | 0.521 | 3.4 | 4.9 |

$f_v$ and $F_v$ are the mole fraction of *V* in feed and in the copolymers, respectively; $F_{vv}$ is the mole fraction of VV dyad in the copolymers; $M_n$ and $M_w$ are number average and weight average molecular weight of copolymers.

late, methyl methacrylate, butyl acrylate (Central Drug House, Pvt. Ltd., India) and butyl methacrylate (Merck, Germany) of different compositions were prepared by solution polymerization using benzene as the solvent and azobisisobutyronitrile (Aldrich) (0.5% by weight) as an initiator at 60–70°C under nitrogen atmosphere. The copolymers were precipitated in methanol. The precipitate was dissolved in chloroform and reprecipitation was again done in methanol. The process was repeated five to six times to remove unreacted monomer and solvent from the copolymers. The copolymers were dried in vacuum.

Dichloromethane (DCM) used was of spectroscopic grade from E-Merck and was used as received. The spurious emission was checked by exciting the solvent at the same wavelength as that used for the samples.

## Methods

The compositions of copolymers were determined from quantitative $^{13}C\{^1H\}$ NMR spectroscopy.[27–30] The mole fraction of *N*-vinylcarbazole (V) in feed and in the copolymer and that of VV dyad and the molecular weight averages of these copolymers are shown in Table I.

The absorption spectra were recorded on Shimadzu UV–Visible spectrophotometer, equipped with 135 U-Chart recorder. Steady-state fluorescence and fluorescence excitation spectra were recoded on a Fluoralog-3 spectrofluorimeter (ISA Jobin Yoon Spex Instruments S.A. Inc.) and all the spectra reported were

corrected once. Band pass used for recording fluorescence and fluorescence excitation spectra were 2 nm. Lifetimes in different solutions were measured on a nanosecond single photon counting spectrofluorimeter (PS 70/80) supplied by Applied Photophysics, England. The electronic processing equipment and multi-channel analyzer were from Ortec and Norland, respectively. Nitrogen gas was used in the flash lamp. The flash lamp profile, defined by the full width at half the maximum height (FWHM) is 2 ns at the lamp frequency of 30 kHz. The fluorescence decay was analyzed by the reconvolution technique (software provided by IBH consultants, UK). The computer system was an IBM based AT386. Lifetimes so reported have the $\chi^2$ in the range $1 \pm 0.2$ and good autocorrelation functions. The error involved in the measurements of emission lifetime, taking into account the experimental fact is 10% and 0.2 ns is the shortest lifetime that can be measured under the best conditions of the experiments. The concentration of each *N*-vinylcarbazole copolymer was kept at concentration having absorbance less than 0.1 at the excitation wavelength of carbazole as photoabsorbing species.

## RESULTS

### Absorption spectra

The absorption spectra of all five copolymers of *N*-vinylcarbazole i.e., V/A, V/M, V/**M,** V/B, and V/**B** containing different content of carbazole were re-
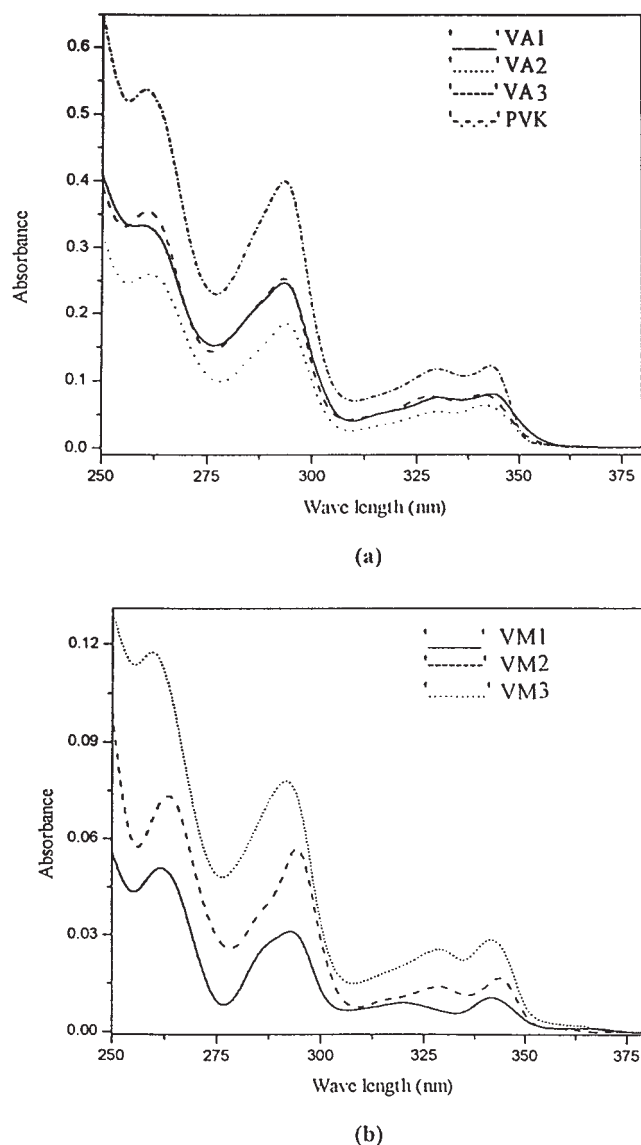
**Figure 1** The absorption spectra of (a) *N*-vinylcarbazole/vinyl acetate copolymers and PVK and (b) *N*-vinylcarbazole/methyl acrylate copolymers in dichloromethane.

corded in DCM. The absorption spectra of V/A and V/M copolymers are shown in Figures 1(a) and 1(b), respectively. The absorption spectrum in each case consists of four band systems above 250 nm. i.e., 260, 295, 330, and 343 nm. These band systems resemble in each respect the absorption band systems of pure isolated carbazole moiety. Irrespective of the nature of the copolymer and the amount of carbazole present in each sample, absorption band maxima ($\lambda^{ab}_{max}$), FWHM, and relative absorbance of each band remain invariant in each sample and can be described by vibrational frequency $1300 \pm 50$ cm$^{-1}$. From the above results, it may be concluded that carbazole moiety in each copolymer and at each concentration behaves like a carbazole molecule. The substituents attached to the *N*-atom or the comonomers present in the copol-

ymer chain do not influence the absorption spectrum of carbazole. In other words, it may also be pointed out that carbazole moiety present in different parts of the chain do not form any complex in the ground state ($S_0$).

## Fluorescence excitation spectra

The fluorescence excitation spectrum of each copolymer containing different amounts of carbazole was recorded in DCM at different emission wavelengths ($\lambda_{em}$), in the range of 350–460 nm. Fluorescence excitation spectra of V/**B** copolymers, as a representative at different emission wavelengths are depicted in Figure 2. In each case, the band maxima are centered on 342, 328, and 291 nm with error limit of $\pm 1$–2 nm. The band shape (FWHM) is invariant to $\lambda_{em.}$ Further the fluorescence excitation spectra recorded in each case resemble each other and the absorption spectra of its respective copolymer molecule. This clearly indicates that the precursor for each emitting species in the $S_0$ state is the same (i.e., monomer carbazole moiety) and whatever the changes in the fluorescence spectrum are occurring (see later), either with excitation wavelength ($\lambda_{exc}$) or the amount of carbazole in the copolymer, are due to the reaction of excited carbazole moiety (see later).

## Fluorescence emission spectra

The fluorescence emission spectra of all the five *N*-vinylcarbazole copolymers in dilute solutions were studied in DCM at $\lambda_{exc}$ 290, 330, and 343 nm. The fluorescence spectra at these $\lambda_{exc}$ are invariant. The
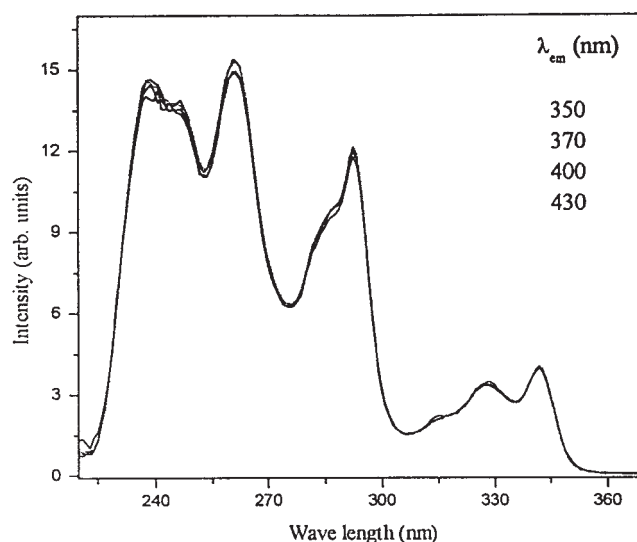


**Figure 2** The fluorescence excitation spectra of *N*-vinylcarbazole/butyl methacrylate copolymers at different $\lambda_{em}$ in dichloromethane.
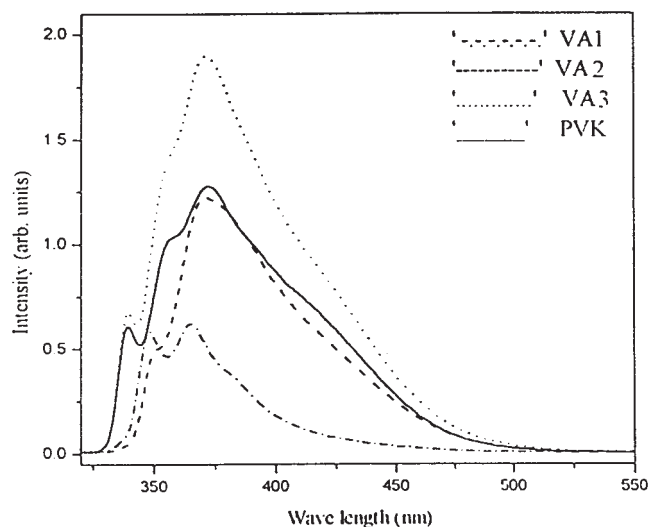
**Figure 3** The fluorescence emission spectra of *N*-vinylcarbazole/vinyl acetate copolymers and PVK at $\lambda_{exc}$ = 290 nm in dichloromethane.

first observation suggests that fluorescence is occurring from the most relaxed first excited singlet state ($S_1$), even though the carbazole moiety is excited to second singlet state, as well as, vibrationally hot first excited singlet state. This follows the Kasha's rule.[31] Whereas the second observation indicates that geometry of the fluorescence molecule, as expected, does not change on excitation.[31] Thus the overlap of the 0–0 band of the absorption and fluorescence spectra (Stoke's shift is only 450 cm$^{-1}$) is responsible for the distortion in the emission spectra. This is further substantiated by the increase in the carbazole content in the copolymer. Unlike the absorption spectrum, different structural features ($\lambda_{max}^{fl}$, FWHM, etc.) of the fluorescence spectrum of each copolymer depend upon the carbazole content as well as on the nature of copolymer substituent. Thus the emission characteristics of all the copolymers will be discussed separately.

## Poly(*N*-vinylcarbazole) and *N*-vinylcarbazole/vinyl acetate copolymers

The fluorescence emission spectra of PVK and the copolymers of *N*-vinylcarbazole with vinyl acetate containing different amount of *N*-vinylcarbazole i.e., VA1, VA2, VA3, and PVK ($F_V$ = 0.19, 0.53, 0.73, and 1.00, respectively) were recorded in DCM using excitation wavelengths as 290, 330, and 343 nm. The fluorescence emission spectra of all the four species using $\lambda_{exc}$ = 290 nm are depicted in Figure 3. The fluorescence emission spectrum of PVK is very different from that containing other comonomer units. The main features of the fluorescence emission spectrum of PVK are that, it is less sharp, broad, and structureless in high energy part of the spectrum except a sharp band

at ~338 nm. These features are very different from the structured emission observed from pure carbazole molecules in the dilute solution. The emission exhibits a monomer band and two intramolecular excimer bands, the high energy (370 nm) and low energy (420 nm). These results are in agreement with those reported by earlier workers.[6,24] The fluorescence emission spectrum of PVK is also independent of $\lambda_{exc}$, suggesting that all the physical processes occurring are taking place from the $S_1$ state.

The florescence emission spectra of the copolymers of *N*-vinylcarbazole depend upon the *N*-vinylcarbazole content in them. At low carbazole content (VA1, $F_V$ = 0.19), the spectral features are quite similar to that of isolated carbazole moiety. As the carbazole content in the V/A copolymers increases, broadening of the fluorescence emission spectrum tending more towards red occurs, (depicted by the FWHM as 3260, 3960, 4600, and 5045 cm$^{-1}$ for $F_V$ = 0.19, 0.53, 0.73, and 1.00, respectively). These features are similar to other copolymers of *N*-vinylcarbazole (see later).

## *N*-vinylcarbazole/methyl acrylate and *N*-vinylcarbazole/methyl methacrylate copolymers

The fluorescence emission spectra of the V/M and V/**M** copolymers are depicted in Figures 4(a) and 4(b), respectively when excited at 290 nm. At small carbazole content of both the series of copolymers (i.e., <20%), the fluorescence emission spectrum is very sharp and nearly resembles that of pure carbazole moiety. The vibrational frequency (1400 ± 50 cm$^{-1}$) observed in fluorescence emission spectrum is nearly equal to that observed in the absorption spectra. This indicates that the fluorescence emission spectra of the two series of copolymers at such a low carbazole concentration appear like a monomer predominantly. As the concentration of the carbazole in the copolymer increases, structure in the emission spectrum gets diffused, spectrum broadens [e.g., FWHM in VM1, VM2 and VM3 (i.e., $F_V$ = 0.14, 0.44, and 0.70) are 2290, 3840, and 5070 cm$^{-1}$, respectively, whereas in V**M**1, V**M**2 and V**M**3 (i.e., $F_V$ = 0.16, 0.38, and 0.68) FWHM are 2380, 2780, and 4020 cm$^{-1}$, respectively]. Intensity of the tail of emission spectrum towards red increases. A slight red shift in the $\lambda_{max}^{fl}$ is also observed at the maximum carbazole content in the copolymers. These observations indicate the formation of intramolecular excimers in these copolymers with the increase in *N*-vinylcarbazole content.

## *N*-vinylcarbazole/butyl acrylate and *N*-vinylcarbazole/butyl methacrylate copolymers

The fluorescence emission spectra of V/B and V/**B** copolymers are depicted in Figures 5(a) and 5(b), respectively at $\lambda_{exc}$ = 290 nm. The fluorescence

emission spectra of these copolymers are similar to those observed for V/M and V/**M** copolymers as far as $\lambda^{fl}_{max}$ and $\lambda_{exc}$ are concerned. Also the fluorescence emission spectra of the two series of copolymers at low carbazole concentration appear like a monomer and as the concentration of N-vinylcarbazole in the copolymer increases, broadening in the overall spectral profile occurs. These observations indicate the formation of intramolecular excimers in these copolymers with the increase in N-vinylcarbazole content.
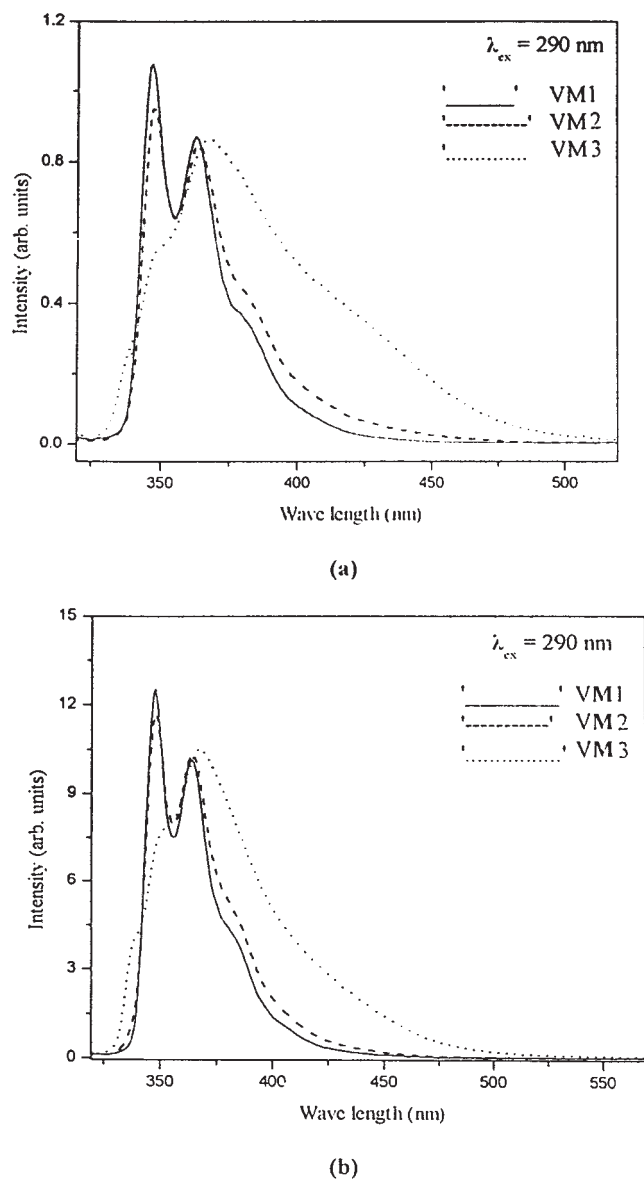


**Figure 4** The fluorescence emission spectra of (a) N-vinylcarbazole/methyl acrylate and (b) N-vinylcarbazole/methyl methacrylate copolymers at $\lambda_{exc} = 290$ nm in dichloromethane.
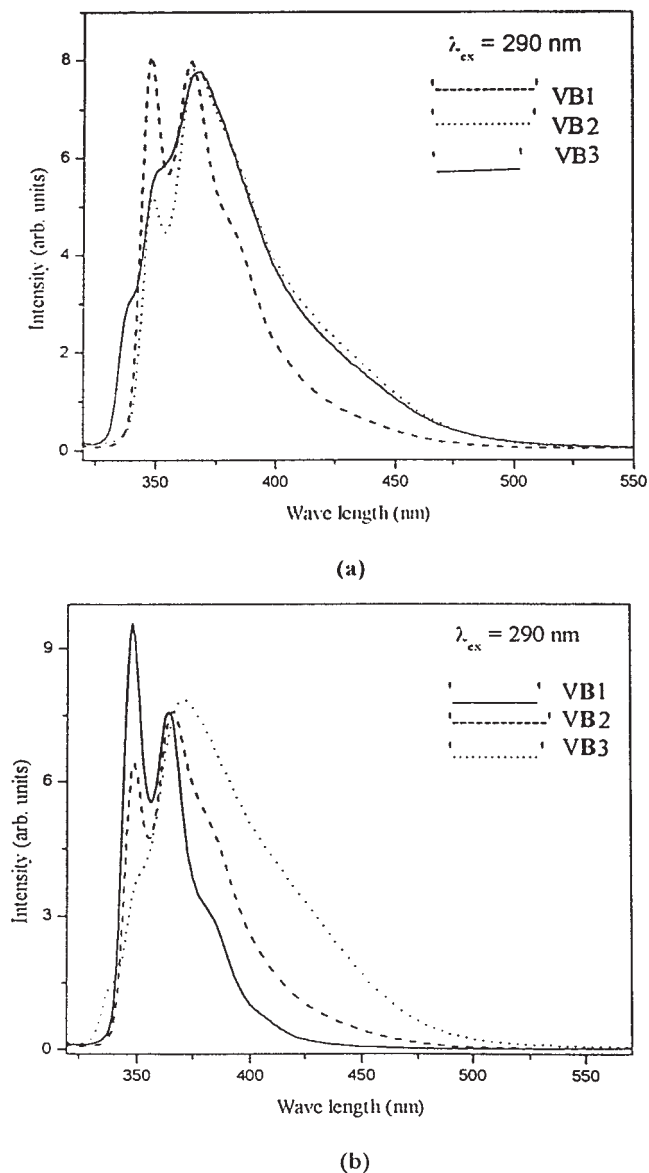


**Figure 5** The fluorescence emission spectra of (a) N-vinylcarbazole/butyl acrylate and (b) N-vinylcarbazole/butyl methacrylate copolymers at $\lambda_{exc} = 290$ nm in dichloromethane.

## Fluorescence decay profiles

The fluorescence intensity decay profiles of each copolymer in DCM containing different N-vinylcarbazole content, in dilute solutions were studied by using $\lambda_{exc} = 337$ nm and five emission wavelengths, depending upon each sample. The fluorescence decay profiles V/A copolymers were also observed at $\lambda_{exc} = 311$ nm. This shorter excitation wavelength was used when the fluorescence was recorded at $\lambda_{em} = 345$ nm, to reduce the possibility of distortion in decay data by the scattered radiation of $\lambda_{exc}$. The decay profile in each case was found to be independent of $\lambda_{exc}$. This suggests that the fluorescence is observed from the

**TABLE II**
**Lifetime Measurement Data for *N*-vinylcarbazole / Vinyl Acetate Copolymers and Poly(*N*-vinylcarbazole)**

| Sample no. | $\lambda_{exc}$ (nm) | $\lambda_{em}$ (nm) | $\tau_1$ (ns) (B$_1$) | $\tau_2$ (ns) (B$_2$) | $\chi^2$ |
|---|---|---|---|---|---|
| VA1 ($F_v = 0.19$) | 311 | 345 | 2.28 (0.38) | 7.04 (0.62) | 1.01 |
| | 337 | 360 | 7.09 | | 1.00 |
| | 337 | 380 | 7.56 | | 1.00 |
| | 337 | 400 | 4.61 (0.30) | 9.49 (0.70) | 1.08 |
| | 337 | 420 | 4.63 (021) | 11.08 (0.79) | 1.04 |
| VA2 ($F_v = 0.53$) | 311 | 345 | 2.85 (0.89) | 13.29 (0.11) | 1.06 |
| | 337 | 360 | 2.97 (0.83) | 9.47 (0.17) | 1.03 |
| | 337 | 380 | 3.37 (0.79) | 10.88 (0.21) | 1.07 |
| | 337 | 420 | 5.39 (0.25) | 14.03 (0.75) | 1.05 |
| | 337 | 460 | 1.37 (−0.19) | 13.58 (0.81) | 1.00 |
| VA3 ($F_v = 0.73$) | 311 | 345 | 3.15 (0.87) | 13.42 (0.13) | 1.07 |
| | 337 | 360 | 2.90 (0.76) | 8.15 (0.24) | 1.07 |
| | 337 | 380 | 2.97 (0.75) | 9.54 (0.25) | 1.05 |
| | 337 | 420 | 3.54 (0.57) | 12.72 (0.43) | 1.01 |
| | 337 | 460 | 3.53 (0.50) | 13.76 (0.50) | 1.09 |
| PVK | 311 | 345 | 4.44 (0.82) | 12.76 (0.18) | 1.07 |
| | 337 | 360 | 2.81 (0.78) | 8.99 (0.22) | 1.03 |
| | 337 | 380 | 2.92 (0.78) | 11.44 (0.22) | 1.01 |
| | 337 | 420 | 3.98 (0.14) | 14.33 (0.86) | 1.10 |
| | 337 | 460 | 3.20 (−0.15) | 14.26 (0.85) | 1.02 |

$\lambda_{exc}$ and $\lambda_{em}$ are the excitation and emission wavelengths, respectively; $\tau_1$ and $\tau_2$ are the lifetimes, B$_1$ and B$_2$ are the pre-exponential; factors and $\chi$ is the auto-correlation function.

**TABLE IV**
**Lifetime Measurement Data for *N*-vinylcarbazole / Methyl Methacrylate Copolymers**

| Sample no. | $\lambda_{exc}$ (nm) | $\lambda_{em}$ (nm) | $\tau_1$ (ns) (B$_1$) | $\tau_2$ (ns) (B$_2$) | $\chi^2$ |
|---|---|---|---|---|---|
| VM1 ($F_v = 0.16$) | 337 | 360 | 3.21 (0.02) | 7.32 (0.98) | 1.10 |
| | 337 | 380 | 4.62 (0.03) | 8.09 (0.97) | 1.01 |
| | 337 | 400 | 4.88 (0.06) | 8.73 (0.94) | 1.08 |
| | 337 | 420 | 3.19 (0.07) | 10.09 (0.93) | 1.11 |
| VM2 ($F_v = 0.38$) | 337 | 360 | 2.36 (0.08) | 6.92 (0.92) | 1.05 |
| | 337 | 380 | 3.14 (0.05) | 7.48 (0.95) | 0.99 |
| | 337 | 400 | 3.64 (0.28) | 9.46 (0.72) | 1.11 |
| | 337 | 420 | 8.66 (0.57) | 15.21 (0.43) | 0.94 |
| VM3 ($F_v = 0.68$) | 337 | 360 | 3.24 (0.37) | 7.46 (0.63) | 1.12 |
| | 337 | 380 | 3.54 (0.43) | 9.66 (0.57) | 1.03 |
| | 337 | 400 | 3.41 (0.22) | 16.13 (0.78) | 1.10 |
| | 337 | 420 | 3.18 (0.04) | 14.56 (0.96) | 0.97 |
| | 337 | 460 | 1.95 (−0.29) | 15.26 (0.71) | 1.01 |

$\lambda_{exc}$ and $\lambda_{em}$ are the excitation and emission wavelengths, respectively; $\tau_1$ and $\tau_2$ are the lifetimes, B$_1$ and B$_2$ are the pre-exponential; factors and $\chi$ is the auto-correlation function.

most relaxed state, as mentioned in the last section. The data so obtained are recorded in Tables II–VI. The relative amplitudes of each species are compiled in the parenthesis below the lifetime data.

The fluorescence decay profiles of PVK are similar to that mentioned in the literature,[11,12,22] i.e., the decay profiles of PVK on the average can be described by three lifetimes in the range 3, ~8, and ~15 ns. At high energy side (360–380 nm), double exponential decay observed in the fluorescence intensity corresponds to the higher energy excimer and the carbazole monomer. As the $\lambda_{em}$ increases, the amplitude of the high energy species with lifetime ~3 ns decreases and it is replaced by a low energy excimer with lifetime ~15 ns. The negative amplitude of high energy species suggests that low energy excimer is formed from this species, as suggested in the literature.[11,12,24]

**TABLE III**
**Lifetime Measurement Data for *N*-vinylcarbazole / Methyl Acrylate Copolymers**

| Sample no. | $\lambda_{exc}$ (nm) | $\lambda_{em}$ (nm) | $\tau_1$ (ns) (B$_1$) | $\tau_2$ (ns) (B$_2$) | $\chi^2$ |
|---|---|---|---|---|---|
| VM1 ($F_v = 0.14$) | 337 | 348 | 2.96 (0.12) | 8.36 (0.88) | 1.10 |
| | 337 | 363 | 3.33 (0.19) | 8.63 (0.81) | 1.07 |
| | 337 | 385 | 8.25 | | 1.05 |
| | 337 | 400 | 8.56 | | 0.99 |
| | 337 | 450 | 8.25 | | 1.12 |
| VM2 ($F_v = 0.44$) | 337 | 348 | 4.57 (0.37) | 8.42 (0.63) | 1.02 |
| | 337 | 363 | 7.62 | | 1.15 |
| | 337 | 385 | 7.05 (0.44) | 14.79 (0.56) | 1.09 |
| | 337 | 400 | 7.98 (0.87) | 18.21 (0.13) | 1.01 |
| | 337 | 450 | 2.62 (−0.28) | 15.56 (0.72) | 1.02 |
| VM3 ($F_v = 0.70$) | 337 | 348 | 3.67 (0.81) | 11.48 (0.19) | 1.09 |
| | 337 | 363 | 3.74 (0.85) | 12.74 (0.15) | 1.04 |
| | 337 | 385 | 3.45 (0.76) | 13.85 (0.24) | 1.07 |
| | 337 | 400 | 3.75 (0.55) | 15.52 (0.45) | 1.09 |
| | 337 | 450 | 1.62 (−0.30) | 17.20 (0.70) | 1.08 |

$\lambda_{exc}$ and $\lambda_{em}$ are the excitation and emission wavelengths, respectively; $\tau_1$ and $\tau_2$ are the lifetimes, B$_1$ and B$_2$ are the pre-exponential; factors and $\chi$ is the auto-correlation function.

**TABLE V**
**Lifetime Measurement Data for *N*-vinylcarbazole / Butyl Acrylate Copolymers**

| Sample no. | $\lambda_{exc}$ (nm) | $\lambda_{em}$ (nm) | $\tau_1$ (ns) (B$_1$) | $\tau_2$ (ns) (B$_2$) | $\chi^2$ |
|---|---|---|---|---|---|
| VB1 ($F_v = 0.31$) | 337 | 348 | 8.33 | | 1.05 |
| | 337 | 363 | 8.90 | | 1.08 |
| | 337 | 385 | 9.30 | | 1.09 |
| | 337 | 400 | 10.25 | | 1.03 |
| | 337 | 450 | 3.65 (−0.31) | 15.49 (0.69) | 1.03 |
| VB2 ($F_v = 0.48$) | 337 | 348 | 5.61 (0.78) | 10.46 (0.22) | 1.06 |
| | 337 | 363 | 5.87 (0.73) | 10.61 (0.27) | 1.08 |
| | 337 | 385 | 5.18 (0.60) | 11.41 (0.40) | 1.14 |
| | 337 | 400 | 8.04 (0.73) | 15.56 (0.27) | 1.08 |
| | 337 | 450 | 4.01 (−0.30) | 16.39 (0.70) | 1.02 |
| VB3 ($F_v = 0.65$) | 337 | 348 | 3.93 (0.85) | 11.10 (0.15) | 1.09 |
| | 337 | 363 | 3.90 (0.80) | 10.37 (0.20) | 1.08 |
| | 337 | 385 | 4.59 (0.76) | 14.80 (0.24) | 1.01 |
| | 337 | 400 | 4.07 (0.41) | 14.49 (0.59) | 1.04 |
| | 337 | 450 | 3.20 (−0.29) | 16.39 (0.71) | 1.03 |

$\lambda_{exc}$ and $\lambda_{em}$ are the excitation and emission wavelengths, respectively; $\tau_1$ and $\tau_2$ are the lifetimes, B$_1$ and B$_2$ are the pre-exponential; factors and $\chi$ is the auto-correlation function.

**TABLE VI**
**Lifetime Measurement Data for *N*-vinylcarbazole/**
**Butyl Methacrylate Copolymers**

| Sample no. | $\lambda_{exc}$ (nm) | $\lambda_{em}$ (nm) | $\tau_1$ (ns) (B$_1$) | $\tau_2$ (ns) (B$_2$) | $\chi^2$ |
|---|---|---|---|---|---|
| VB1 ($F_v = 0.17$) | 337 | 348 | 8.08 | | 1.03 |
| | 337 | 363 | 8.11 | | 1.05 |
| | 337 | 385 | 8.37 | | 1.04 |
| | 337 | 400 | 8.66 | | 1.05 |
| | 337 | 450 | 11.36 | | 1.04 |
| VB2 ($F_v = 0.53$) | 337 | 348 | 3.77 (0.56) | 8.38 (0.44) | 1.09 |
| | 337 | 363 | 4.54 (0.58) | 8.89 (0.42) | 1.03 |
| | 337 | 385 | 6.45 (0.45) | 14.53 (0.55) | 1.03 |
| | 337 | 400 | 6.73 (0.50) | 16.00 (0.50) | 1.06 |
| | 337 | 450 | 3.25 (−0.26) | 14.86 (0.74) | 1.04 |
| VB3 ($F_v = 0.83$) | 337 | 348 | 3.33 (0.74) | 10.93 (0.26) | 1.04 |
| | 337 | 363 | 3.65 (0.78) | 12.51 (0.22) | 1.04 |
| | 337 | 385 | 4.05 (0.72) | 14.27 (0.28) | 1.07 |
| | 337 | 400 | 4.24 (0.54) | 14.42 (0.46) | 1.08 |
| | 337 | 450 | 1.08 (−0.49) | 15.54 (0.51) | 1.01 |

$\lambda_{exc}$ and $\lambda_{em}$ are the excitation and emission wavelengths, respectively; $\tau_1$ and $\tau_2$ are the lifetimes, B$_1$ and B$_2$ are the pre-exponential; factors and $\chi$ is the auto-correlation function.

In general, fluorescence decay profile of V/A copolymers follow the same trend as observed in case of PVK, with the following differences. (i) At carbazole content less than 20%, the main contribution in the emission is from the carbazole monomer, (ii) As the carbazole content increases, the proportion of both the excimers increases, but the increase in the proportion of high energy excimer is greater than low energy excimer. This data supports the information obtained from the fluorescence emission spectra that at low *N*-vinylcarbazole concentration, the main contribution in the emission is from the carbazole monomer and as the carbazole content increases, the emission from the intramolecular excimers increases.

The Figures 6(a) and 6(b) depicts the fluorescence intensity decay profile of V/**B** copolymers ($F_V = 0.17$ and $F_V = 0.53$, respectively) at $\lambda_{exc} = 337$ nm and $\lambda_{em} = 400$ nm. Similar to V/A copolymers, the fluorescence decay profiles of the acrylate copolymers (i.e., V/M, V/**M**, V/B, V/**B**) also follow the similar trend. The observations are: (i) At carbazole content less than 20%, in all the four copolymers the fluorescence decay in general follow the single exponential with the lifetime similar to monomer carbazole moiety, with few exceptions. For example, in V/M and V/**M** copolymers, the fluorescence decay is biexponential but the proportion of the second component is less than 10%. (ii) Among methyl and methyl methacrylate or butyl and butyl methacrylate copolymers, the amount of both the excimers formed in the former copolymer of both the sets is greater than that formed in the latter.

## DISCUSSION

Similarity of the spectral characteristics (e.g., $\lambda^{ab}_{max}$, linear relation in the Beer Lambert's Law, FWHM, and vibrational structural) of the absorption spectra of all the *N*-vinylcarbazole copolymers containing different amount of carbazole with those observed for carbazole monomers at low concentrations clearly suggests that carbazole moiety present in all these molecules exists as an independent identity and does not interact with other moieties present in the copolymers. In other words, the carbazole moiety does not form either dimer or complex even at the highest carbazole content with the other species in the ground state. Similar behavior is also observed by others.[6,24] Further, fluorescence excitation spectra observed in each case and at different emission wavelengths resemble each other
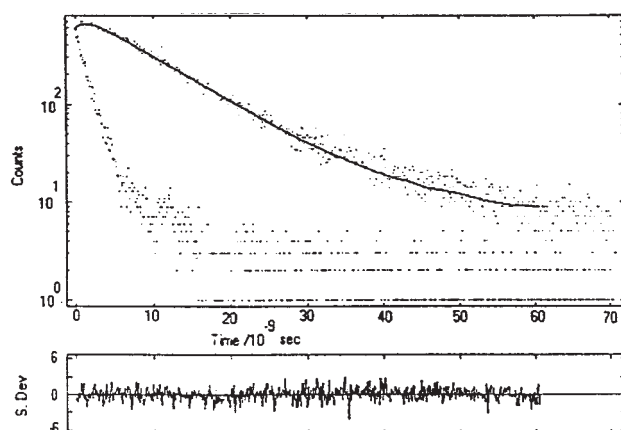


**(a)**
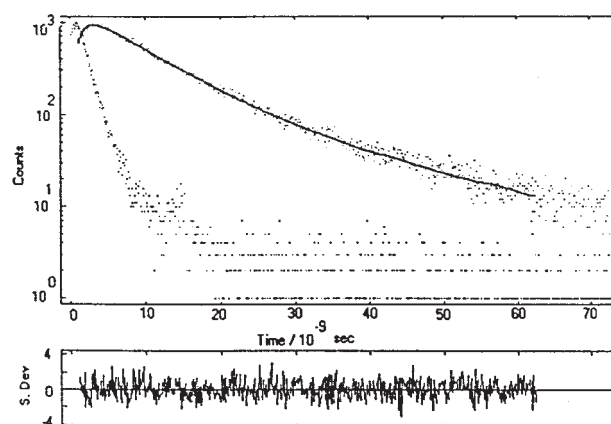


**(b)**

**Figure 6** The fluorescence decay profile of *N*-vinylcarbazole/butyl methacrylate copolymers (a) $F_V = 0.17$ and (b) $F_V = 0.53$ at $\lambda_{exc} = 337$ nm and $\lambda_{em} = 400$ nm.

and also with the respective absorption spectrum of the respective species. This confirms that the precursor for all the different spectral characteristics of the first singlet state is the same i.e., only one kind of species is present in the ground state and the absorbing and emitting species are the same.

The fluorescence spectral characteristics of PVK, which is used as a reference molecule, are similar to those observed by others.[6] The emission exhibits a monomer band and two well-resolved intramolecular excimer bands. The high energy (~370 nm) and the low energy (~420 nm) excimer bands arise from conformations with partial and total overlap of the carbazole moieties, respectively.[6,8] To provide additional support to the observation of two different kinds of excimers, PVK have been synthesized by different methods and modifications of PVK with pendant bulky *t*-butyl subsituents on the carbazole ring have been carried out by different workers.[19,20] Similarly, copolymers of *N*-vinylcarbazole with fumaronitrile, diethyl fumarate, diethyl maleate etc. have been prepared to confirm these two kinds of intramolecular overlap of the carbazoles.[21] In the light of the above discussion, we have interpreted our results as follows.

At low carbazole content (<20%), the fluorescence emission spectrum of any *N*-vinylcarbazole copolymer can be mainly assigned to the unassociated carbazole with two maxima centered at ~348 and 365 nm with a shoulder at ~385 nm. This has been further substantiated by either observing single exponential decay observed under these conditions, with lifetime similar to that of carbazole molecule or observing double exponential decay having the proportion of second component <10%. This clearly suggests that carbazole moieties at such a low content are present at large distance and thus intramolecular overlap is not possible. This also suggests that carbazole moieties at such a low amount are present on a chain separated by more than three carbon atoms and thus follows the *n* = 3 rule to observe the intramolecular excimer formation.[32] The presence of methyl group in methyl and butyl acrylate further hampers the overlap of the carbazole moieties because of the steric hindrance. The data of Tables II–VI and spectra shown in Figures 3–6 substantiate this.

Although we have not carried out the time resolved fluorescence spectroscopy, but based on the results available in the literature,[24] (i.e., for all the copolymers of *N*-vinylcarbazole with carbazole content <20%, the fluorescence intensity is dominated by that of excited carbazole monomer and there is no evidence of intramolecular excimer formation), we also conclude that the emission in these copolymers is from carbazole monomer. We also believe that the results, regarding the high energy and low energy excimers, can also be explained similarly and supplemented from the fluorescence decay profiles.

At higher carbazole content in each copolymer, the fluorescence decay profiles monitored above 420 nm are composed of negative pre-exponential term having lifetime of ~3 ns and positive pre-exponential term with lifetime of ~15 ns. This suggests that the species with lifetime of ~3 ns are responsible for the formation of species with lifetime ~15 ns. Similar results are observed in each case and are also similar to those observed by Davidson et al.[24] Thus it may be proposed that in our case also the carbazole monomer with lifetime of ~8 ns can not form the excimers whereas the excited carbazole unit with lifetime of ~3 ns reflects the presence of carbazole monomer in such a manner that these are in contact of each other and are quenched through the formation of excimer. Thus the mechanism of these excimers can be explained in the same lines as proposed by earlier workers.[11,12,24]

In conclusion, it may be pointed out from the above results that (i) at carbazole content less than 20%, the fluorescence spectra of all copolymers can be assigned largely to the carbazole monomer, (ii) there are two kinds of excited carbazole monomers, one with lifetime of ~3 ns leading to the formation of excimer and the other monomer with lifetime of ~8 ns, which cannot form excimers, (iii) the excimers are formed by the interaction of carbazole–carbazole overlap, present on the polymer chain and in contact with each other, and (iv) the size and number of the comonomers present in the *N*-vinylcarbazole copolymer chain hinder the formation of excimers by the steric hindrance.

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