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Research Article

A Comparative Study of Fluorescent Emission Spectra of N-Vinylcarbazole – Co-Ethoxyethyl Methacrylate Copolymers with its Homopolymer

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ABSTRACT

The fluorescence excitation and emission spectroscopy have been used to make a comparative study of the photophysical natures of copolymers of *N*-vinylcarbazole (NVC) - co-ethoxyethyl methacrylate copolymer with its homopolymer. The copolymer was synthesized by mixing different feed ratios of the monomers, NVC and ethoxyethyl methacrylate by free-radical polymerization using BPO as initiator. Using similar procedure synthesized the homopolymer as well. The copolymers were characterized by Fourier-transform infrared,¹ H nuclear magnetic resonance. The thermal stability of the copolymers was tested by thermogravimetric analysis and differential scanning calorimetry. The fluorescence studies show that the copolymer is more active toward fluorescence than its homopolymer.

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INTRODUCTION

Modification of low-cost materials by chemical ways is an attractive methodology for obtaining new, high-value materials with specific properties.^[1-3] Copolymerization in which a small mole fraction of a second monomer is used to enhance the properties is one of the approaches toward it.^[4-9] Poly (N-vinylcarbazole) (PNVCz) is an electroluminescent polymer, although the efficiency of its devices is very low.^[10,11] To improve the efficiency, PNVCz must be copolymerized with small organic molecules or with other polymers.^[12-15]

The photophysics of PNVC has attracted the attention of both polymer scientists and photophysicists mainly for two points.^[16] PNVC has photoconducting properties.^[17] Besides monomer carbazole fluorescence band, the fluorescence spectrum of NVC consists of two other fluorescence bands maxima at 370 and 420 nm. To understand the effect of copolymerization of NVC on the photoconducting behavior, spectral characteristics and mechanism of excimer formation, copolymers of NVC were synthesized. This has further opened up new areas and new challenges.

The present work involves to highlight the effect of copolymerization of NVC with ethoxyethyl methacrylate (EOEMA) on the fluorescence spectra. Fluorescence excitation and emission

spectra studies have been carried out in dilute solutions of these copolymers in dimethyl sulfoxide. The proportion of excimers found was governed by the carbazole content, their location on the chain and stereochemistry of different comonomers.

Synthesis of homopolymer

Free-radical solution polymerization was used to synthesize the homopolymer (P NVC). It was carried out in Pyrex glass tube containing inlet and outlets for passing nitrogen gas. The monomer, BPO, and the solvents were taken in a polymer tube and flushed with nitrogen gas for 20 min, and the tube was sealed to ensure an inert atmosphere. The sealed tube was kept in a thermostat maintained at 60°C. When the polymerization was complete, the contents were poured into the non-solvent (methanol) to precipitate the polymer [Figure 1].

Synthesis of copolymers

The copolymers were synthesized from the appropriate amounts of different monomer using BPO as initiator. The reactants were dissolved in 25 mL of chlorobenzene to obtain a homogeneous solution in a standard polymer tube. Dry nitrogen gas was flushed into the reaction mixture. The reaction vessel was then immersed in a thermostatic water bath maintained at

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 $60 \pm 5^{\circ}$ C. After desired period, the tubes are removed from the water bath and cooling was done under running tap water. The solution was then poured into ice-cold methanol to precipitate the copolymer. The copolymers were purified by repeated precipitation of chloroform from solution in chloroform and dried in vacuum oven at 45°C for 24 h. The schematic representation of the synthesis of copolymers is shown in Table 1.

The schematic representation of the synthesis of poly (NVC - co-EOEMA) is shown in Figure 2.

CHARACTERIZATION OF COPOLYMER 1: POLY (NVC - CO-EOEMA)

Fourier-transform infrared (FT-IR) spectrum

The FT-IR spectrum of poly (NVC - co-EOEMA) is shown in Figure 3. The band at 2931 $\rm cm^{-1}can$ be assigned to the aromatic

C–H asymmetric stretching. The bands at 1450 and 1480 cm⁻¹ may be attributed to the ring vibration of NVC moiety. The C–H in-plane deformation of aromatic ring has been observed at 1216 cm⁻¹ and that of vinylidene group at 1329 cm⁻¹. The band at 3053 cm⁻¹ can be assigned to the -CH₃ stretch vibration. CH₂ stretch vibration appears at 2931 cm⁻¹. A very strong band at 1725 cm⁻¹ belongs to the carbonyl group and -C-O-C- bands at 1216 cm⁻¹. The -CH bending mode of vinyl group appears at 862 cm⁻¹, while the rocking mode at 749 cm⁻¹. The anhydride groups band can be assigned around 1870–1770 cm⁻¹.^[18] The aromatic ring and the oxygen bond appears around 1725 cm⁻¹, while aromatic C-C appears around 1620 cm⁻¹. The C-O frequency can be attributed to the band at 1329 cm⁻¹.

¹H Nuclear magnetic resonance (¹H-NMR) spectrum

¹H-NMR spectra of poly (NVC - CO-EOEMA) is shown in Figure 4. A hump at 0 ppm corresponds to transcranial magnetic



Figure 1: Synthesis of the homopolymer



Figure 2: Synthesis of poly (N-vinylcarbazole - co-ethoxyethyl methacrylate)

stimulation, an internal standard. The methyl protons occur at 2.60 ppm. The methylene protons appeared at 1.43 ppm. The signals at $\delta = 0.87$ ppm and the multiplet between $\delta = 1.0-2.60$ ppm are due to methyl and backbone protons of NVC. The alkoxy protons appeared at 4.04 ppm. Characteristics peak signals corresponding to $\delta = 0.9$ for methyl $\delta = 3.8$ for the O–CH₂ of ethoxyethyl methacrylate are obtained.^[18] Thus, the ¹H-NMR spectrum confirms the chemical structure of the copolymer.

THERMOGRAVIMETRIC ANALYSIS (TGA) OF POLY (NVC - CO-EOEMA)

The thermal decomposition of the copolymer was characterized by TG curves. The TGA curves in Figure 5 clearly indicate that all the copolymers undergo single-step decomposition process. The measured results were shown in Table 2. Different copolymer ratio exhibits excellent thermal stability with decomposition temperature ranges from 0 to 600°C. The copolymers exhibited no significant weight loss on being heated to 600°C. The thermal stability of the copolymer increases as the NVC moiety is increased.

Differential scanning calorimetry (DSC) of poly (NVC - co-EOEMA)

The glass transition temperature of the polymer was studied by DSC in the temperature range 0–200°C under nitrogen atmosphere. The glass transition temperature (*Tg*) of poly (NVC - co-EOEMA) was found to be 98.19°C [Figure 6]. Tg increased by the copolymerization. This is due to the presence of EOEMA and complex group which are polar in nature that increase the intermolecular force, inter chain attraction, and cohesion which lead to decrease in free volume and increase in Tg.

RESULTS AND DISCUSSION

The fluorescence emission spectra of PNVC and the copolymers of NVC with EOEMA containing different amount of NVC were recorded in U-2800 Spectrophotometer using excitation wavelengths as 340 nm. The fluorescence emission spectra of all the four species using are depicted in Figure 7. The fluorescence emission spectrum of PNVC is very different from that containing other comonomer units. The main features of the fluorescence emission spectrum of PNVC are that, it is less sharp, broad, and structureless. 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.^[19,20] The fluorescence emission spectrum of PNVC is also independent of λ exc, suggesting that all the physical processes occurring are taking place from the S1 state.

The florescence emission spectra of the copolymers of NVC depend on the NVC content in them. At low carbazole content (20%, 0.2577), the spectral features are quite similar to that of isolated carbazole moiety. As the carbazole content in the copolymers increases (50%, 0.3865, 80%, 0.3875), broadening of the fluorescence emission spectrum tending more toward

Table 1: Synthesis of poly (NVC - co-EOEMA)

Monomer 1:Monomer 2 ratio	NVC	EOEMA	Yield (%)
0.20:0.80	0.2577	0.8436	80
0.50:0.50	0.3865	0.3281	83
0.80:0.20	0.3875	0.0820	79

NVC: N-vinylcarbazole, EOEMA: Ethoxyethyl methacrylate



Figure 3: Fourier-transform infrared spectrum of poly (N-vinylcarbazole - co-ethoxyethyl methacrylate)



Figure 4: ¹H nuclear magnetic resonance spectrum of poly (N-vinylcarbazole - co-ethoxyethyl methacrylate)



Figure 5: Thermogravimetric analysis spectrum of poly (N-vinylcarbazole - co-ethoxyethyl methacrylate)

red occurs. As the concentration of the carbazole in the copolymer increases, structure in the emission spectrum gets diffused, spectrum broadens, respectively, intensity of the tail of emission spectrum toward red increases. A slight red shift in the λ max is also observed at the maximum carbazole content in the copolymers. These observations indicate the formation of

Poly (NVC – CO-EOEMA) composition	IDT	Decomposition temperature range (°C)	Temperature (°C) of weight loss (%) of the copolymers				
			10	30	50	70	90
20:80	242	0–600	289	317	357	426	473
50:50	245	0–600	293	323	364	431	482
80:20	240	0–600	284	303	350	412	456

Table 2: TGA analysis data of poly (NVC - CO-EOEMA)

NVC: N-vinylcarbazole, EOEMA: Ethoxyethyl methacrylate, TGA: Thermogravimetric analysis



Figure 6: Differential scanning calorimetry of poly (N-vinylcarbazole - co-ethoxyethyl methacrylate)



Figure 7: Fluorescence emission spectra of homopolymer and poly (N-vinylcarbazole - co-ethoxyethyl methacrylate) copolymers

intramolecular excimers in these copolymers with the increase in NVC content.

These observations suggest that efficient energy transfer from the host to the guest takes place and the intensity increases with increasing NVC content. This spectrum shows only the fluorescence of the high-energy excimer. The lowenergy sandwich excimer emission is virtually absent or very weak on this time scale. It is obvious that the high-energy excimer is formed almost immediately on excitation. This is consistent with the formation of the high-energy excimer from traps preformed in the polymer chains. The low-energy sandwich excimer, as previously discussed, is probably formed from either a reorientation of the high-energy excimer or a direct interaction of an excited carbazolyl and a ground state carbazolyl chromophore.

In this context, it is important to remember that a flexible polymer chain in fluid solution undergoes dynamic conformational fluctuations such that at any instant of time a fraction of chain segments may exist in unfavorable highenergy conformations, or any segment may in a finite time "hunt" through a number of conformations of different energy.

CONCLUSION

Comparing the fluorescence emission spectra of homopolymer and copolymers shows that the copolymers were more effective and efficient in exhibiting fluorescence emission spectra, which in turn reflects the photophysical nature of the copolymers. This fluorescence nature of the copolymers can be used for many photophysical applications.

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