

Research Article

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

R. P. Meena^{1,2}, K. Anver Basha^{2*}

¹Department of Chemistry, L.N. Government College, Ponneri, Tamil Nadu, India, ²Department of Chemistry, C. Abdul Hakeem College, Melvisharam, Tamil Nadu, India

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, ¹H 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.

Address for

correspondence: K. Anver Basha, Department of Chemistry, C. Abdul Hakeem College, Melvisharam, Tamil Nadu, India.
E-mail: kanverbasha@gmail.com

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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



$60 \pm 5^\circ\text{C}$. 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 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 $-\text{CH}_3$ stretch vibration. CH_2 stretch vibration appears at 2931 cm^{-1} . A very strong band at 1725 cm^{-1} belongs to the carbonyl group and $-\text{C}-\text{O}-\text{C}-$ 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 $1870-1770\text{ cm}^{-1}$.^[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 ($^1\text{H-NMR}$) spectrum

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

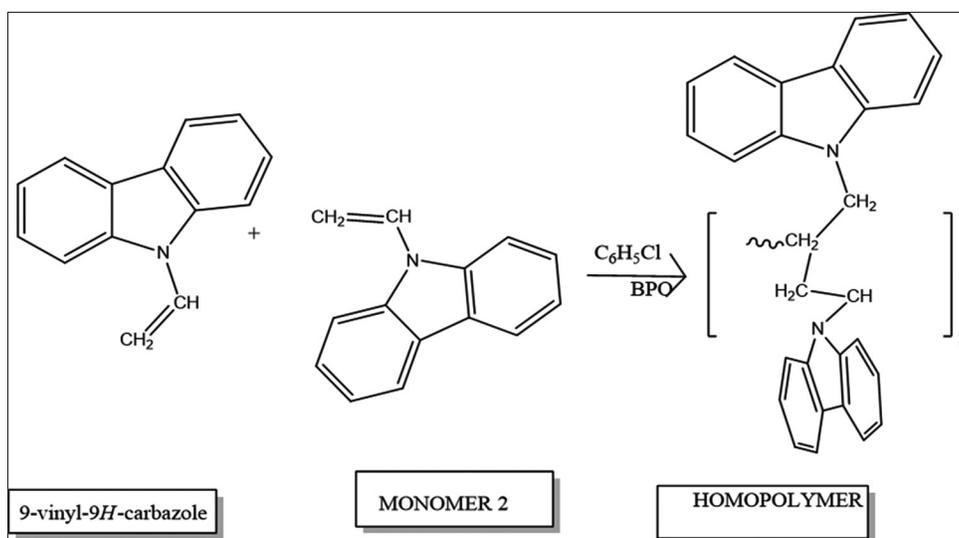


Figure 1: Synthesis of the homopolymer

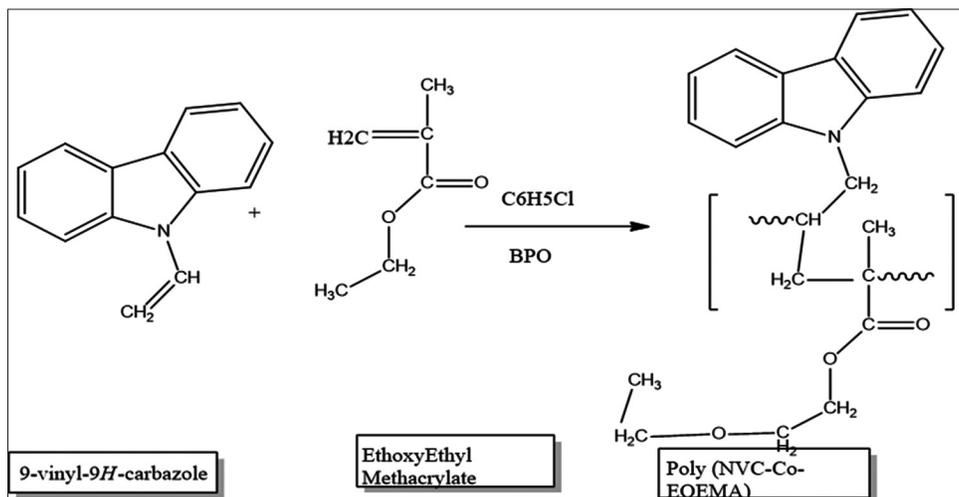


Figure 2: Synthesis of poly (N-vinylcarbazole - co-ethoxyethyl methacrylate)

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

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

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

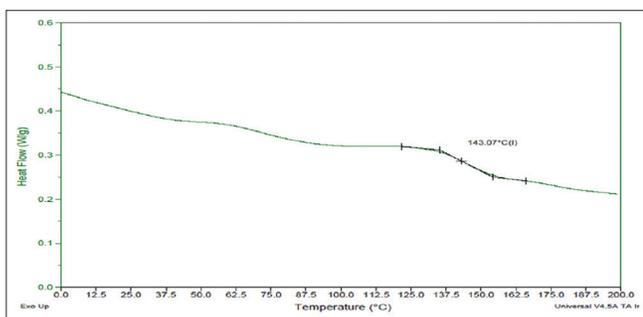


Figure 6: Differential scanning calorimetry of poly (N-vinylcarbazole - co-ethoxyethyl methacrylate)

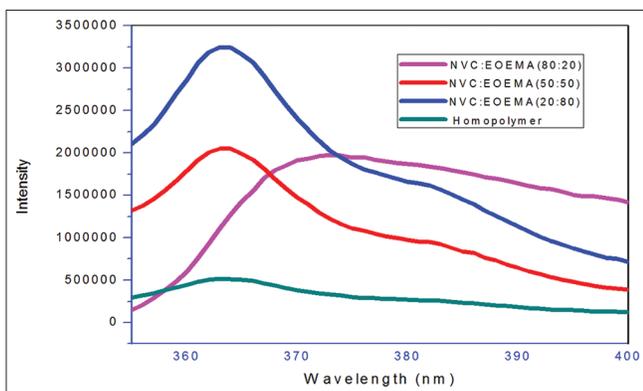


Figure 7: Fluorescence emission spectra of homopolymer and poly (N-vinylcarbazole - co-ethoxyethyl methacrylate) copolymers

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 low-energy 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 high-energy 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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