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Characterization of near infrared light emitting (benzene-co-pentacene) copolymer

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ABSTRACT

Copolymer of benzene and pentacene was synthesized with Kovcic method. Structure, morphology and thermal properties of the copolymer were studied by using Fourier transformation infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Themogravimetric Analysis (TGA) techniques. UV-Vis spectrum showed the peaks position at 345 and 424 nm. Photoluminescence emission (λ_{em}) *of thin film of the copolymer was observed at 791 nm in the near-infrared (NIR) region.*

Keywords: Copolymer, Near-infrared, Thin films and Photoluminescence.

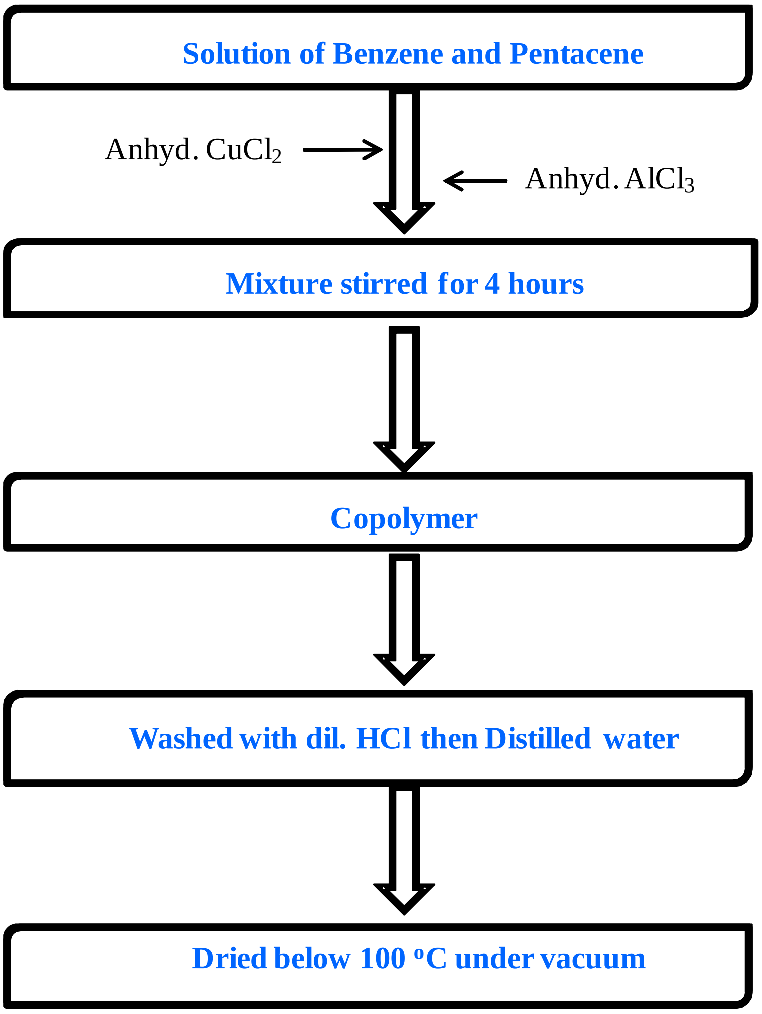
INTRODUCTION

Organic near-infrared (NIR) light emitting materials (700–2500 nm) have their potential applications in night-vision displays, sensors, optical communication, optical cosmetology and photodynamic diagnoses and therapies[1]. Usually the material research target is to design new organic semiconductors and conjugated polymers having the desired properties of their conducting behavior. Conducting polymers have their applications in electronic devices such as light-emitting diodes[2-3], photovoltaic cells[4-6], field-effect transistors[7] and photodetectors[8]. Polymers of p-phenylene's (PPP) are having rod-like polymeric structure and therefore become insoluble in organic or mineral solvents, hence difficult to process them for its further applications. To overcome the problem of processibility we can employ two methods i.e. either introduce some flexible non-conjugated segments in the polymer backbone[9-10] or as side-groups[11].

In present work, we have efficiently prepared the copolymer of benzene and pentacene by Kovacic method[12]. The prepared copolymer found to be having the ability of thermally evaporation so it can be successfully used for making electroluminescent devices. The synthesized copolymer was further characterized by using various spectroscopic techniques.

MATERIALS AND METHODS

The synthetic procedure of the copolymer involved the dehydro-coupling of benzene nuclei by catalyst-oxidant systems, leading to the formation of C-C bonds and provided copolymer in high yield. Benzene (2 moles or 156 g or 178 ml) and pentacene (0.002 mole or 0.50464 g) are mixed as monomers in 1:1000 ratio. Pentacene was completely dissolved in benzene then equi-molar mixture of anhydrous Cupric Chloride and Aluminum Chloride were added to the solution with constant stirring. With the addition of this mixture intense fumes of HCl came out and the color of the mixture turned dark green. Polymerization occurred under mild conditions (35-40°C) with continuous stirring of 4 hrs. The polymerized products were successively washed with 6N HCl and then with double distilled water. Finally the product dried below 100 °C under vacuum condition. The systematic synthetic procedure of copolymer is shown in the scheme-1.



Scheme-1: Chemical procedure for synthesis of copolymer

Instrumentation

The prepared copolymer was characterized using Fourier transformation infrared spectroscopy(FTIR), UV-Vis absorption spectroscopy, thermogravimetric Analysis(TGA), Scanning Electron Microscopy(SEM) and photoluminescence(PL) spectroscopic techniques. A UV-Vis spectrum was recorded with a Shimadzu UV-2401 spectrophotometer. The thermogravimetric analysis (TGA) was carried out with the Mettler Toledo Star system. Morphology of the copolymer was analyzed with LEO-440 Scanning Electron Microscope. The photoluminescence spectrum of the vacuum-deposited thin films on the glass was recorded using the Horiba Jobin Yvon luminescence spectrometer.

RESULTS AND DISCUSSION

The systematic chemical reaction for the preparation of the present copolymer is shown in the figure 1. The synthesized copolymer of benzene and pentacene was found to be completely insoluble in all the common organic solvents like chloroform, carbon tetrachloride, toluene, tetrahydrofuran, benzene, n-methyl pyrolidine, xylene etc.

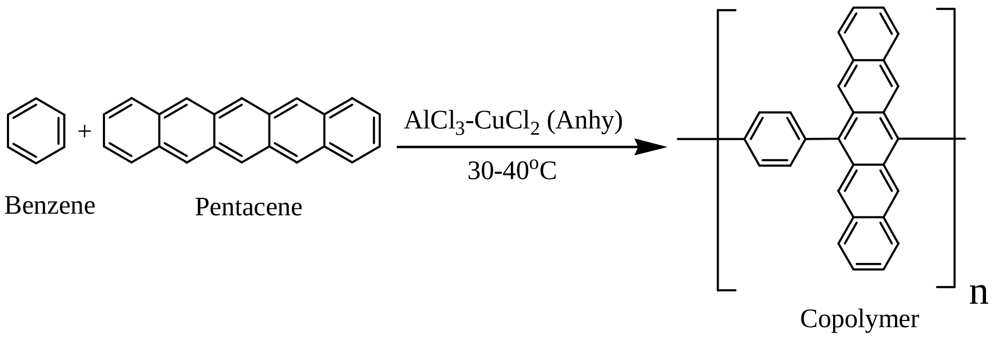


Figure 1. Synthetic chemical reaction of the copolymer

UV-VIS absorption spectrum of copolymer

The copolymer was deposited on the glass substrate for the optical analysis using vacuum deposition machine at below 150 °C and pressure of 10^{-4} to 10^{-5} bar. The thickness of the copolymer layer was used deposited ~300 nm. The absorption spectrum of the vacuum deposited polymer film showed peaks at 345 and 424 nm. The absorption bands at these wavelengths were associated with the different transitions of the conjugated aromatic system of the prepared copolymer.

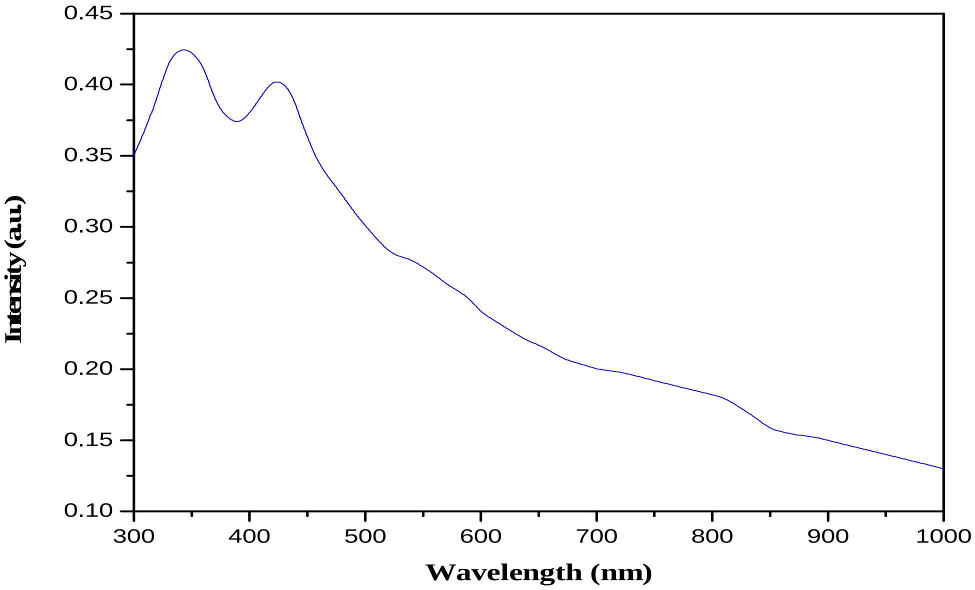


Figure 2. UV-VIS Absorption Spectra of copolymer

FTIR Spectrum of copolymer

FTIR analysis of the sample of the copolymer was taken in dry KBr pellet prepared by the hydraulic press. The FTIR spectrum of the copolymer is shown in figure 3. The peak at 3027 cm^{-1} was due to C-H stretching of benzene rings while the peaks at 2924 $cm^{-1}$and 2853 cm^{-1} were due to C—H stretching vibrations of pentacene ring which were available in the copolymer. The band occurred in the 2000 cm^{-1} to1700 cm^{-1} was due to the aromatic region of the copolymer. The peaks at 1628 cm^{-1} and 1480 cm^{-1} were due to quadrant and semi-circle stretching vibrations of rings. The C-C in plane stretching of aromatic ring was present at 1117 cm^{-1} and 1000 cm^{-1}. The peak at 806 cm^{-1} confirmed the para substitution of the copolymer. The C-H out of plane bending was also available in the spectrum at 764 cm^{-1} and 668 cm^{-1}.

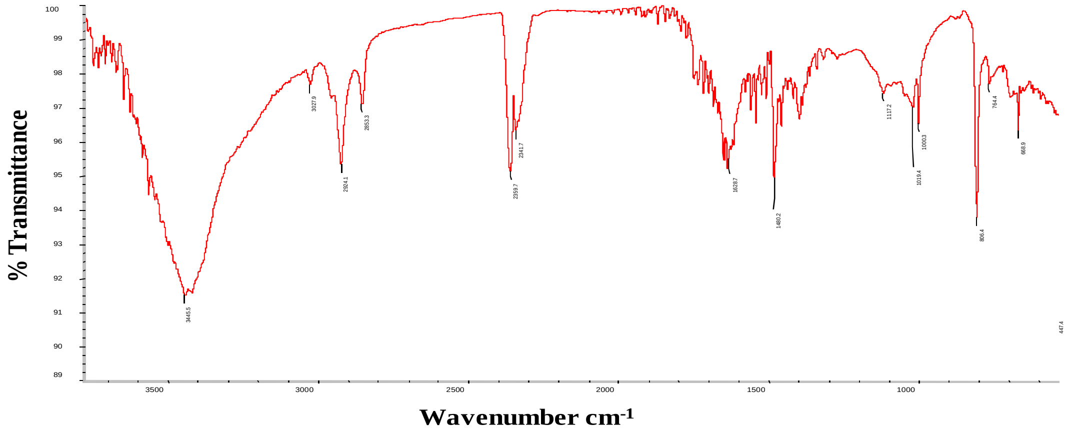


Figure 3. FTIR spectrum of copolymer

Themogravimetric analysis of the copolymer

The copolymer was heated in an inert atmosphere from 0 to 800 °C with a heating rate of 10 °C per minute. Weight loss at 200 °C might be attributed to the loss of some adsorbed water molecules into the copolymer. The TGA plot of the material showed the loss in mass of copolymer from the 200 °C due to the degradation of the polymeric chain and continues up to 620 °C and loss of mass was observed 7.8221 % of the total mass of copolymer. The degradation of the polymer continues up to 750 °C. The additional lose in the mass was also observed 12.3427 % upto 800 °C. Hence the present copolymer showed the good environmental and thermal stability.

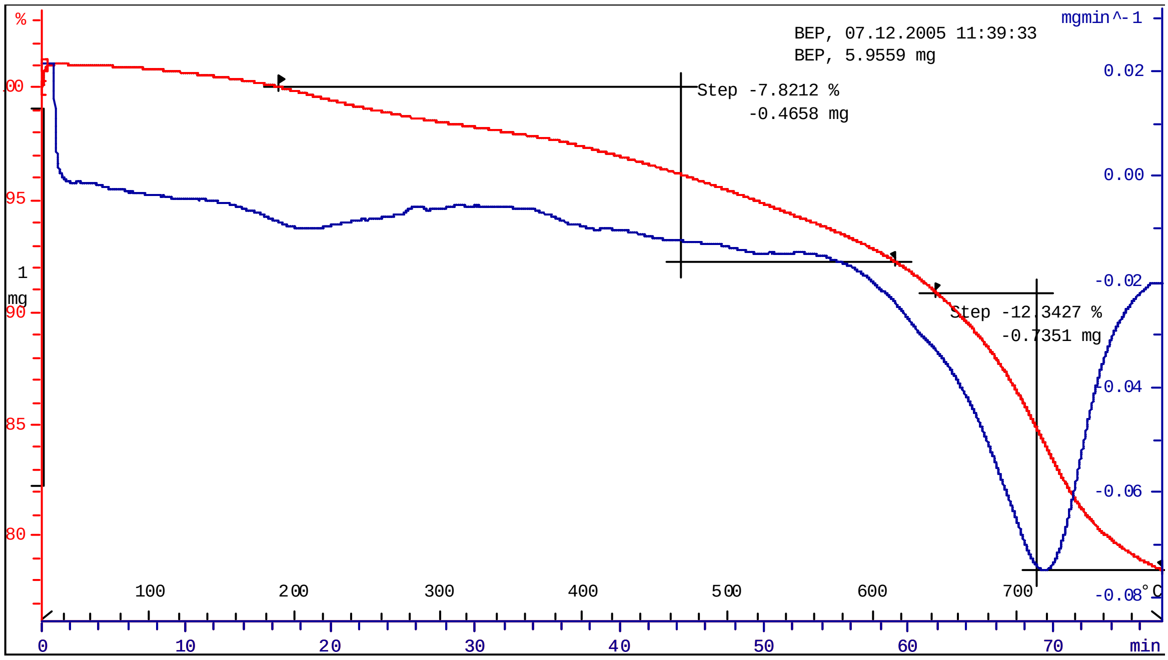


Figure 4. Themogravimetric analysis of the prepared copolymer

Photoluminescence (PL) spectra of copolymer

The photoluminescence spectrum of the material was studied after making the thin films with the vacuum deposition on the fused silica substrates. Under UV illumination (360 nm) generated from Xenon lamp, thin film of copolymer showed the photoluminescence (791 nm) in the infra red region as shown in the figure 5. The absorption spectrum was found to shift towards higher wavelength as compared to pure poly (p-phenylene), which was due to the Franck Condon Shift of electron-photon interaction.

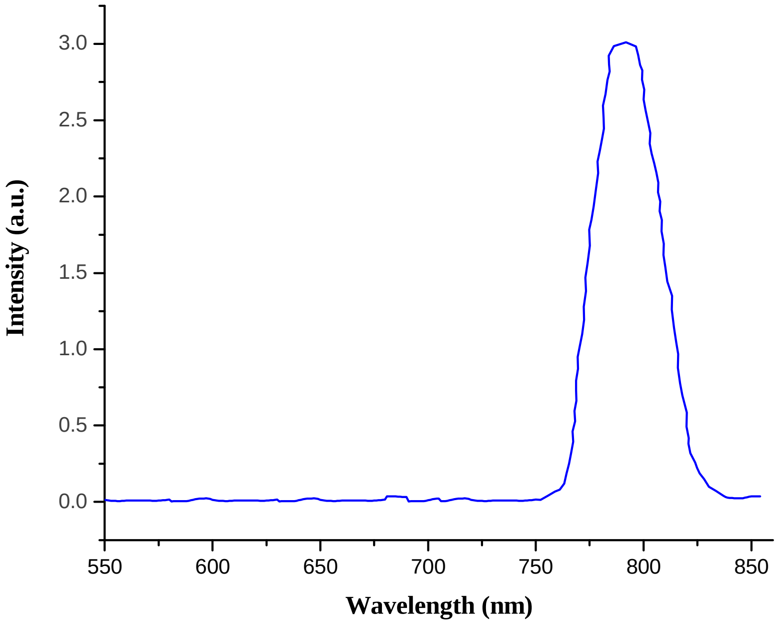


Figure 5. Photoluminescence (PL) spectrum of copolymer

Morphology of the copolymer

The scanning electron micrographs of the copolymer of benzene and pentacene were taken at different resolution from 1 to 10µm. It was observed that the copolymer was having spherical shape of the particle which was aggregated to form round sphere. These spheres were noticed to be dense. The overall surface morphology was observed to be heterogeneous and non uniform at low as well as at high resolutions. The particles was accumulated to confirm spherical in shape.

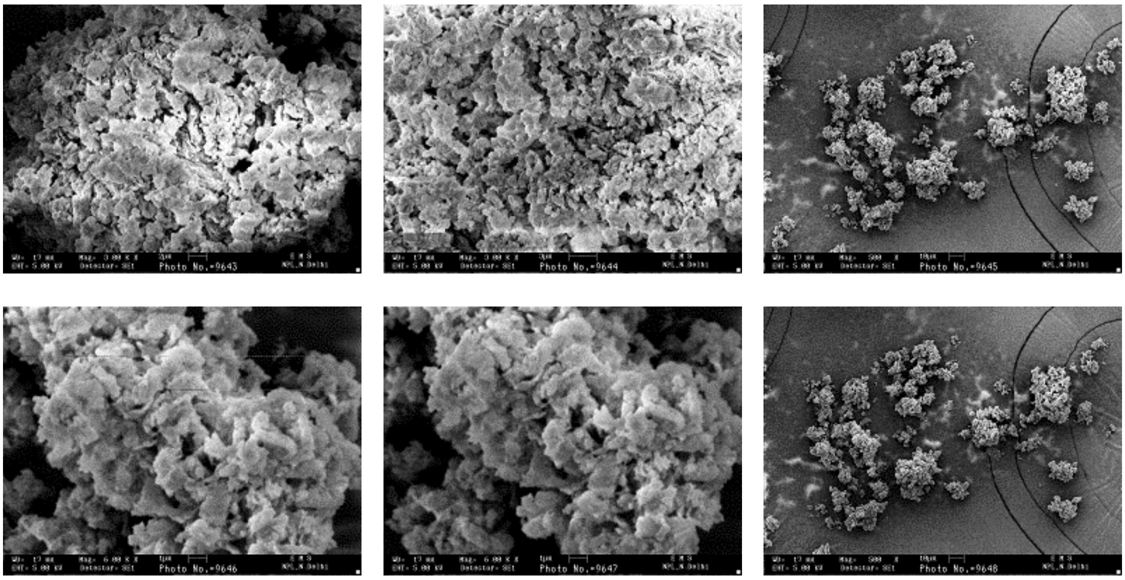


Figure 6. Scanning electron micrographs of the prepared copolymer

CONCLUSION

Successfully we have prepared the copolymer of the benzene and pentacene having the optical properties in near-infrared region. The synthesized copolymer was found to be having good thermal stability. Thin films of the copolymer shows the photoluminescence at 791 nm under the strong 360 nm UV source. The prepared copolymer having the near-infrared emissive properties could be suitably used in night-vision display and in sensors.

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