

SUMMARY

The nitrogen heterocyclic polymer systems have enjoyed considerable research attention in the global context because of their many distinctive physico-chemical and optoelectronic properties. Two important and property-wise significant polymers of this series are represented by PPY - a wellknown conductive polymer and PNVC-a polymer known for its distinctive thermal stability and optoelectronic properties.

The research undertaken in the present study is concerned with the synthesis, structural characterization and property evaluation of some polymer systems derived from PY and NVC. In specific, the following systems have been investigated.

- (i) Homopolymerization of PY and NVC by inorganic and organic oxidants and charge transfer agents in nonaqueous and aqueous media.
- (ii) Copolymerization of PY and NVC by FeCl_3 and O-CA initiators in nonaqueous and aqueous systems.
- (iii) Chemical modification of PPY through copolycondensation of PPY with PA and PMDA.
- (iv) Novel synthesis of highly conductive PNVC in a biphasic (aqueous-nonaqueous) system.
- (v) Synthesis of a conductive composite from PNVC and conductive carbon black.

The above studies generated some useful and significant informations concerning the effect of different variables on the homopolymerization and copolymerization of PY and NVC using

different catalysts, and also on the properties and characteristics of the homo and copolymers obtained and some chemical modifications of these polymers. The informations are summarized as under.

All the polymers and copolymers of PY and PY+NVC were recovered as black powdery mass. These polymers were insoluble in all solvents including DMF and DMSO.

(i) IR spectra of PPY prepared in FeCl_3 - ether system showed some characteristic bands at $\sim 3309, 2316, 1530, 1040, 930, 785 \text{ cm}^{-1}$ which were probably due to 1,2,5 or 1,3,4 trisubstitution of PY ring whereas in case of FeCl_3 - H_2O system, N-H stretching band shifted to higher frequency with increasing amount of FeCl_3 in the feed due to lowering of intermolecular H-bonding. Kinetic studies on PPY-OCA bulk polymerization revealed that the polymerization was initially explosive with a characteristic high rate followed by the usual tendency to level off. The conversion decreased monotonously with increasing PY concentration (in case of solution polymerization) implying chain retardation.

For PPY, a single inflection at $\sim 165^\circ\text{C}$ in DSC curve might correspond to its T_g . Unfortunately, information in the literature corroborating this data was not available, despite a thorough search. A high dielectric constant in PPY at a low frequency was consistent with a conjugated structure which would facilitate the frequency induced dielectric polarization. The conductivity was also dependent on the dopant concentration and leveled off at a certain value.

(ii) PNVC prepared in different polymerization systems revealed the characteristic IR peaks. XRD patterns of PNVC suggested that percent crystallinity, could depend somewhat on the nature of the initiating moiety and the polymerization condition, including temperature. Suspension polymerization of NVC in toluene/water solvent initiated by FeCl_3 in varying mole ratios with the monomer, yielded a polymer with appreciably higher specific conductivity ($\sim 1 \times 10^{-4} \text{ S, cm}^{-1}$) than that of conventionally prepared PNVC.

(iii) Copolymerization of a mixture of NVC and PY by $\text{FeCl}_3/\text{O-CA}$ in toluene/water systems yielded insoluble black polymers P(PY-NVC) which exhibited properties distinct from those of PPY or PNVC. The inclusion of either monomer moieties in P(PY-NVC) was endorsed by IR spectroscopy. TGA revealed the stability order as : PNVC > P(PY-NVC) > PPY. DSC revealed a single glass-transition break at 180-200°C which was higher than the T_g for PPY ($\sim 165^\circ\text{C}$) but was lower than that of PNVC (227°C).

Dielectric constant values of the copolymer followed the trend : PPY > P(PY-NVC) > PNVC. DC conductivity reached a maximum value of $3.5 \times 10^{-3} \text{ S/cm}$ in $\text{FeCl}_3 - \text{H}_2\text{O}$ system. Notably, the specific conductivity of P(PY-NVC) was improved 10^3 fold relative to that observed for the FeCl_3 - ether initiated copolymer.

(iv) Characterization of anhydride modified copolycondensates.

The substitution reaction between PPY and the anhydrides presumably occurred by intra and interchain process resulting in the formation of intractable products. The characteristic

carbonyl absorption band expected for C=O and diketone groups in the proposed structure for the polycondensates could be observed in the IR spectra. The overall thermal stability was in the order PPY < PPY-PA < PPY-PMDA which could be rationalized in terms of intra and intermolecularly crosslinked structures of the polycondensates. IR spectral analyses of PPY-PA and PPY-PMDA subjected to heating at 300, 400, 500 and 550°C respectively were conducted to understand some of the structural changes in the polymer matrices. The conductivity values of PPY-PA and PPY-PMDA were in the range 10^{-3} to 10^{-4} S/cm which were conspicuously lower than that of unmodified PPY ($2.5 \frac{\text{S}}{\text{cm}}$) prepared in $\text{FeCl}_3/\text{H}_2\text{O}$ system. This might be due to the adverse effect of increasing temperature on the PPY chain stability whereby structural conjugation and eventually conductivity could be affected.

(v) Characterization of Conductive PNVC - CB Composite

Carbon black initiated PNVC yielded a composite which exhibited a conductivity as high as 1 S/cm. The value was the highest ever reported for PNVC based systems. The procedure might be regarded as a novel one for NVC since the monomer was polymerized rapidly by CB without any external cocatalyst or catalyst added and the polymers thus produced might be grafted onto the CB surface under selected polymerization conditions.

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