



Poly 4-Vinylpyridine and Polystyrene Based Interpenetrating Polymer Networks (IPNs): Synthesis and Characterization

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Received: 8 April 2021;

Accepted: 7 May 2021;

Published online: 26 July 2021;

AJC-20426

A study on synthesis of thin film of interpenetrating polymer network (IPN), of poly(4-vinylpyridine) (PVP) and polystyrene was carried out. A series of IPN was synthesized, using divinyl benzene (as cross linker) and benzoyl peroxide (as an initiator) and characterized using FT-IR spectroscopy, scanning electron microscopy (SEM), thermal (DSC, TGA) and fluorescent techniques. FTIR spectra revealed the presence of PVP at 1584 cm^{-1} and polystyrene at 1609 cm^{-1} . Shifting in band positions depicts formation of IPN. SEM images show a clear dual phase morphology. DSC thermogram reveals glass transition temperature (T_g) value of the polymer network at $350\text{ }^\circ\text{C}$. TGA graph depicts thermal stability of IPN upto $400\text{ }^\circ\text{C}$. The XRD pattern of IPN indicates semi crystalline nature. The properties such as average molecular weight between crosslinks (M_c), percentage swelling is found to be the direct function of initiator (BPO) and inverse function of concentration of cross linker (DVB) and styrene. Fluorescence spectra of IPN observed in visual range of 506 nm .

Keywords: Poly(4-vinylpyridine), Polystyrene, Glass transition temperature, Interpenetrating polymer network.

INTRODUCTION

Presently, polymer interpenetrating polymer network (IPN) may be regarded boon for many innovations [1]. Polymer hybrids consist in two or more chemically different polymers which have emerged useful material for a variety of applications [1]. The IPNs have enhanced physical and mechanical properties, differentiated from polymers blend in such a way that it swells but does not dissolve in the solvents and also prevent action of creep and flow as a result of mutual incompatibility. Various methods have been used to create polymeric hybrids materials including surface grafting [1-3], preparation of polymer blends [4] and interpenetrating polymer network [5,6]. The preparation of interpenetrating polymer network is very interesting and useful for the conventional polymers without compromising their intrinsic properties. Studies on synthesis of styrene and 4-vinyl pyridine with poly(ethylene terephthalate) using benzoyl peroxide as an initiator was carried by Paoprasert *et al.* [7]. There is a broad literature of ionically conducting polymer electrolyte [8-11]. Self organized interpenetrating polymer network based on poly(styrene)-block-poly(4-vinyl

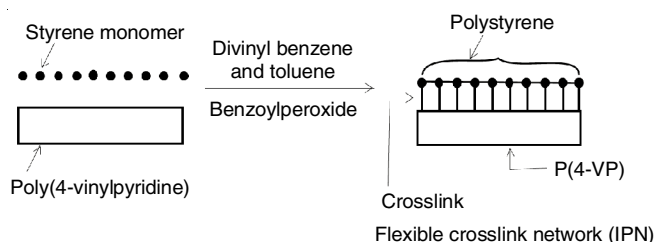
pyridine) with ethylene oxide oligomers and sulphonic acid bonded to the poly 4-vinyl pyridine was reported by Kosonen *et al.* [12]. Polymerization of 4-vinyl pyridine possess a problem for atom transfer radical polymerization since both poly(4-vinyl pyridine) and 4-vinyl pyridine are strong coordinating ligands that can play important role for the bonding metal catalysts in these systems [13]. Atom transfer radical polymerization technique is also used for polystyrene-*b*-poly-4-vinyl pyridine in two step process in the presence of ligand [14]. Inverse gas chromatography technique is also used to characterize the polymers of polystyrene-*b*-poly(4-vinyl pyridine) synthesized by ATRP [15]. Hyekyung *et al.* [16] also synthesized of microspheres of poly(styrene-*co*-4-vinyl pyridine) *via* dispersion polymerization process.

From the literature surveyed, it has been found that IPN polymers are much more stable and used in various industrial applications [17]. In present work, a synthetic methodology has been adopted to prepare IPNs from poly 4-vinyl pyridine and polystyrene. This research is aimed to develop a novel network system possessing enhanced inherent morphological, thermal and fluorescent characteristics.

EXPERIMENTAL

All the solvents (Merck), styrene (CDH 98%), divinyl benzene, poly(4-vinyl pyridine) (Sigma-Aldrich) were purchased from Aldrich Chemical Company, USA and were of analytical grade. Benzoyl peroxide was recrystallized from methanol.

Synthesis of IPN: Interpenetrating polymer networks of poly(4-vinyl pyridine) and polystyrene were synthesized by systematic variation of concentration of 4-vinylpyridine and styrene using benzoyl peroxide as an initiator and divinyl benzene as a crosslinker, toluene as a solvent. The system kept on water bath for 60-90 min at 60 ± 1 °C under nitrogen atmosphere. The obtained IPN was precipitated in methanol and vacuum dried (**Scheme-I**).



Scheme-I: Synthesis of IPN of poly(4-vinyl pyridine) and polystyrene

Characterization: The FT-IR spectra of synthesized IPNs were obtained on a Perkin-Elmer spectrum version 10-03-06 instrument using KBr pallet. The IR spectrum was carried out at wavelength $4000-500$ cm^{-1} . The fluorescence emission spectrum of pre-swollen polymer network was recorded on spectrofluorimeter (Fluorolog 3, Model FL 3.22). The phase identification of the samples was performed using X-ray diffraction (XRD, Bruker D8 Focus). The samples were gold-sputter coated. Scanning electron microscopy (SEM) analysis was carried out using JEOL JSM 840Å model. The thermal properties were analyzed by simultaneous DSC/TGA technique on an instrument model SDTQ600V20.9 Build 20, with temperature range between 0 to 900 °C with 100 mL/min flow of nitrogen.

Calculation of percentage extractable materials: The uncrosslinked component was removed with the help of soxhlet extractor using DMSO as a solvent. The percentage extractable material was calculated using eqn. 1:

$$\text{Extractable material (\%)} = \frac{W_b - W_a}{W_a} \times 100 \quad (1)$$

where W_a and W_b are the weights of the IPN after extraction and before extraction, respectively.

Swelling measurements: Swelling data were calculated by soaking the sample in 10 mL of different solvents such as DMF, benzene, DMSO, toluene until an swollen equilibrium was achieved (~ 24 h) weight measurements were made using filter paper. The sample was dried and immediately weighed. The weight of the swollen IPNs in each solvent were recorded [18]. The swollen percentage was calculated using eqn. 2:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_s and W_d weight of swollen IPN and dry IPN, respectively.

Crosslink density ($1/M_c$): The IPN sample was taken and its crosslink density of the network was calculated by using the swelling data of IPN in DMF with the help of Flory-Rehner equation [19]:

$$\frac{1}{M_c} = - \frac{[\ln(1 - V_p) + V_p + X_{12} V_p^2]}{\rho V_1 [V_p^{1/3} - V_p/2]} \quad (3)$$

where M_c = average molecular weight of network between crosslink density, ρ = density of the network, V_1 = molar volume of solvent, V_p = volume fraction of polymer in swollen gel, X_{12} = polymer solvent interaction parameter, calculated by using eqn. 4 [20]:

$$X_{12} = \frac{B + V_1(\delta_p - \delta_s)^2}{RT} \quad (4)$$

where δ_p and δ_s = solubility parameter of polymer and swelling solvent respectively and B = lattice constant, the value of which is taken as 0.34 .

RESULTS AND DISCUSSION

FT-IR studies: IR spectra of pure polystyrene is observed for the methylene group at 1465 cm^{-1} , for benzylic carbon-hydrogen at 3025 cm^{-1} and for carbon double bond of aromatic ring at 1728 cm^{-1} , for poly(4-vinyl pyridine), it is analyzed for carbon double bond of aromatic ring at 1550 cm^{-1} . While IR spectra of polymer network indicates absorption band at 3021 and 2925 cm^{-1} associated to the C-H bonds. The absorption band at 1609 and 1584 cm^{-1} is associated with the vibration of double bond in the aromatic ring of poly(4-vinyl pyridine-styrene). Band shifting and disappearance of peak at 1682 cm^{-1} correspond to C=C double bond stretching vibration of vinyl group in polymer network, which confirms the successful polymerization (Fig. 1). This more or less corresponds to the well defined bonding and interaction between the polymeric chains.

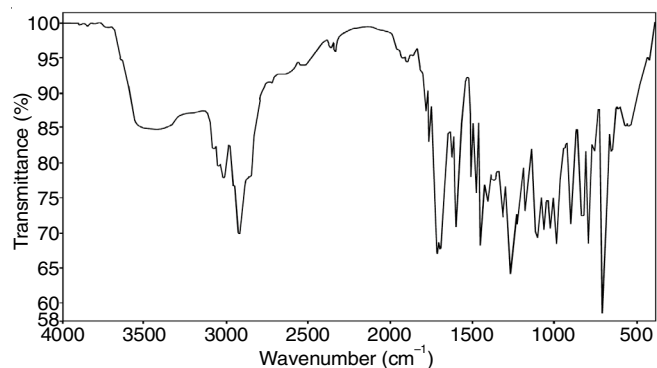


Fig. 1. IR spectroscopy of IPN

Florescent studies: Fluorescence emission spectra of the synthesized polymeric network (Fig. 2) reveals the fluorescent emission and excitation spectra and IPN nanosheets depict that the polymeric network exhibits analogous excitation and emission. The emission spectra reveal broad peak centered at about 506 nm, owing to $n \rightarrow \pi^*$ electronic transition found in

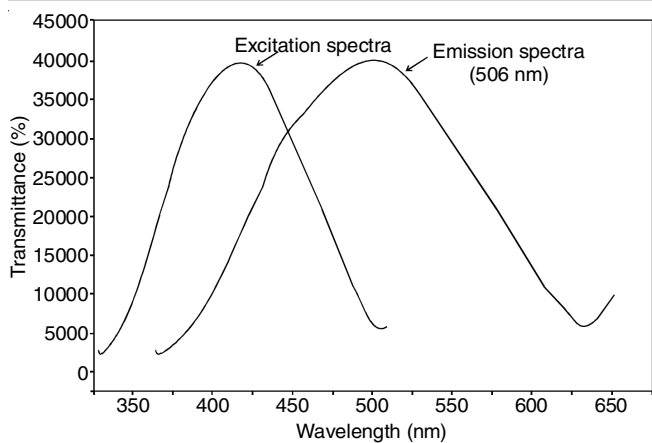


Fig. 2. Fluorescent curve of IPN

the polymeric network. Emission spectra generated by the radioactive decay of excitations exhibit a maximal peak at 506 nm, suggested that the synthesized IPN nanosheets are typically high intensity blue light emitting materials.

XRD studies: The XRD pattern of polystyrene reveals a sharp and intense peak of $2\theta = 28.5^\circ$ and interplanar distance is 4.45 Å. On the other hand, the XRD pattern of the synthesized polymeric network of poly(4-vinyl pyridine) and polystyrene indicates broader peak, which suggests for a relatively small sized crystals of the IPN system. Fig.3 reveals the XRD patterns of IPN is in between the corresponding monomeric units which is an indication of semi-crystalline nature.

Morphology: SEM images of the synthesized samples were recorded, which indicate that IPN exhibit a characteristic dual phase morphology at magnification of 30,000x and 50,000x resolution (Fig. 4). The surface of sample composed of poly(4-vinyl pyridine) and polystyrene which is not smooth, some protrusions of different size are observed. Thus, clear dual phase morphology of different regions is observed in IPN films, which might be due to the presence of both components. Thus, network structure is diversified, which indicates the sample heterogeneity of solution used for film preparation. This indicates that there must has been phase separation taken place.

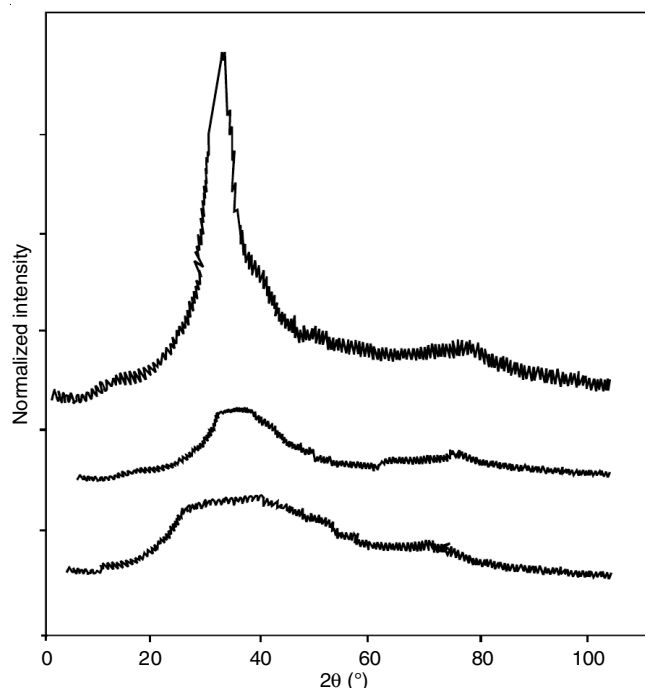


Fig. 3. XRD graph of IPN

This phase separation is clearly being distinguished in the microscopic images.

Thermal analysis: The TGA graph of IPN (Fig. 5) sample containing poly(4-vinyl pyridine-styrene) is stable upto 400 °C and started losing weight above this temperature. Almost complete volatilization of IPN occurred at ~ 550 °C. The DSC thermogram (Fig. 5) of IPN reveals the glass transition temperature (T_g) at 350 °C, which is higher than the T_g of polystyrene (100 °C) and T_g of poly(4-vinyl pyridine) (150 °C). This might be the outcome of high crosslink density in these IPNs. Thus, the result indicates the incorporation of styrene units in between the polymer network and enhanced crosslinking between the component polymeric chain. This crosslinked structure reduces the chain mobility thus causing a dense and strong immovable polymeric network for use formed.

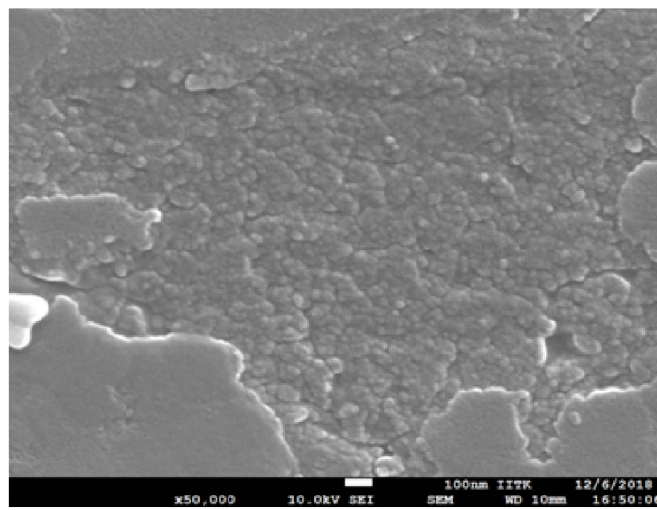
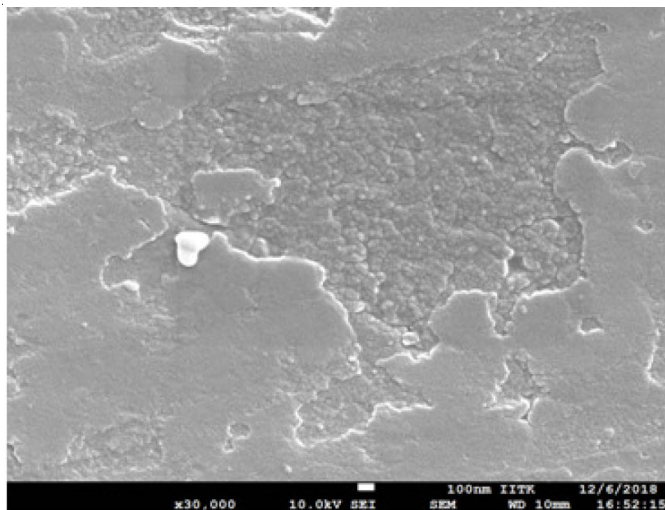


Fig. 4. SEM image of IPN

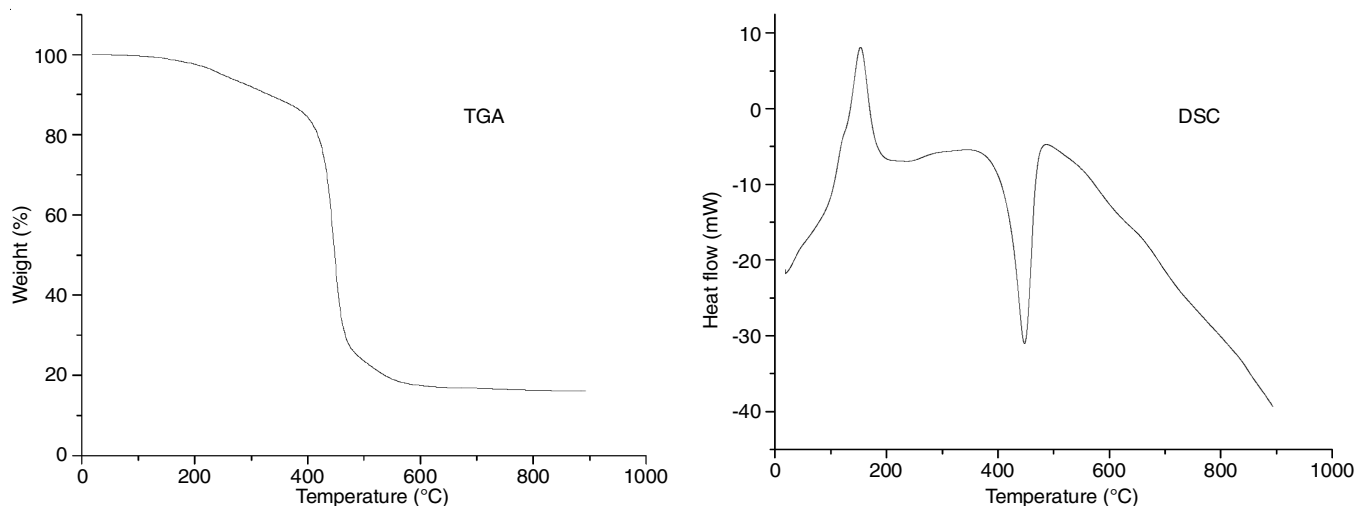


Fig. 5. TGA and DSC curve of IPN

Effect of composition: The swelling behaviour could be envisaged from (Table-1), which represents the swelling percentage of IPN in different solvents and extractable material. The effect of variation poly(4-vinylpyridine) (Table-2) reveals the increased swelling and molecular weight (M_c) values with the increase concentration of poly(4-vinylpyridine). This indicates that the presence of polystyrene restricts crosslinking of poly(4-vinylpyridine). This restriction is due to the overall decrease in the concentration of crosslinking of styrene. Furthermore, it is believed that poly(4-vinylpyridine) must be crosslinked to polystyrene. (As the concentration of the polymer increases the probability of grafting by styrene, which must have also enhanced crosslinking between the two polymers). A similar explanation is given for the percentage swelling and M_c which is the inverse function of concentration of styrene (Table-3).

Effect of initiator (BPO): The data depict that increasing molar concentration of initiator increases the M_c and swelling. Table-4 shows that the effect of variation of benzoylperoxide on M_c and swelling of IPN. It is clear that both swelling M_c increases with increasing under concentration of BPO. A detailed study is performed over the effect of composition of different chemicals of the different physical and chemical properties of IPN.

Sample used	DMF (%)	Benzene (%)	DMSO (%)	Toluene (%)	Extractable Material (%)
IPN 1	54	27	47	34	16.2
IPN 2	70	38	56	43	13.6
IPN 3	78	40	63	65	14.5
IPN 4	82	44	70	60	27.4
IPN 5	50	20	30	30	13.3
IPN 6	48	18	36	24	10.4
IPN 7	45	30	45	38	15.3
IPN 8	60	36	46	45	36.3
IPN 9	65	22	42	34	24.0
IPN 10	70	23	33	28	14.6
IPN 11	48	30	44	40	12.3
IPN 12	40	20	35	32	10.1
IPN 13	30	10	26	22	11.5

Sample	P4VP (mol L ⁻¹)	Yield	Swelling (%) in DMF	M_c in DMF
IPN 1	0.939	1.350	54	165
IPN 2	1.400	1.480	70	180
IPN 3	1.870	1.750	78	190
IPN 4	2.340	1.900	82	196

Sample	Styrene (mol L ⁻¹)	Yield	Swelling (%) in DMF	M_c in DMF
IPN 1	0.87	1.350	54	165
IPN 5	1.30	1.150	50	158
IPN 6	1.74	0.700	48	155
IPN 7	2.18	0.350	45	150

Sample	BPO $\times 10^{-2}$ (mol L ⁻¹)	Yield	Swelling (%) in DMF	M_c in DMF
IPN 1	0.412	1.350	54	165
IPN 8	0.619	1.850	60	180
IPN 9	0.825	1.560	65	192
IPN 10	1.030	2.150	70	198

Effect of crosslinker (DVB): Table-5 indicates that as the concentration of crosslinker increases, the value of percentage swelling and M_c decreases. This is due to an increase of concentration of crosslinker, which increases the crosslinking between the two polymeric chain resulting decreased M_c and swelling. It is interesting to note that increase in concentration of cross-

Sample	DVB (mol L ⁻¹)	Yield	Swelling (%) in DMF	M_c in DMF
IPN 1	0.70	1.350	54	165
IPN 11	1.05	1.550	48	160
IPN 12	1.40	1.680	40	152
IPN 13	1.70	2.130	30	140

linker enhances the crosslinking in the polymeric network and hence reduce the chain mobility. This ultimately increases the glass transition temperature. It is an evidence for crosslinking between two components.

Conclusion

Spectral analysis of IPN containing poly(4-vinyl pyridine) and polystyrene indicates ideal polymer network formation between poly(4-vinylpyridine) and styrene monomeric unit. IR spectra depicted a remarkable band shift of the characteristic functional group which clearly indicate the IPN formation. Disappearance of peak at 1682 cm^{-1} of corresponding C=C double bond of vinyl group inferred that interpenetration must have been the reason for this change. The DSC thermogram revealed the higher T_g for IPN, which was attributed due to the higher crosslink density and restricted chain mobility of the units. The crosslinked network slower down the chain mobility and resulted into the immovable polymeric network formation. The IPN shows characteristics dual phase morphology indicating crosslinking between the two components. Hence molecular weight is the direct function of initiator (copolymer), where as inverse function of crosslinker and styrene. It results into more dense and compact polymer network structure. The fluorescent excitation and emission spectra at 506 nm shown that such IPN system indicates the fluorescent behaviour of the materials.

ACKNOWLEDGEMENTS

The authors are thankful to the Principal, Christ Church P.G. College, Kanpur, India for providing the necessary facilities and also IIT, Kanpur, India for providing the characterization facilities to carry out the research work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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