Synthesis and Characterization of Conducting
Poly-*N*-isopropylacrylamide-*N*-vinylcarbazole Polymers

Shashidhar[1,*], Ramprasad[1], C. Basavaraja[2] and T.K. Vishnuvardhan[3]

[1]Department of Chemistry, SDM College of Engineering and Technology, Dharwad-580 002, India
[2]Department of Chemistry and IFM, Inje University, Kimhae-621 749, South Korea
[3]Department of Chemistry, Acharya Institute of Technology, Bangalore-560 090, India

*Corresponding author: E-mail: nshashidharreddy@gmail.com

Polymers containing poly-*N*-isopropylacrylamide (PNI) and *N*-vinyl carbazole (nvc) were synthesized by dissolving different weight percentages of *N*-vinyl carbazole (10, 20, 30 and 40 %) during the polymerization of *N*-isopropylacrylamide. The structure and morphology of the poly-*N*-isopropylacrylamide-N-vinyl carbazole (PNI-nvc) polymer matrix were identified by UV-visible, fluorescence spectra and atomic force microscope (AFM). Further, the electrical conductivity in the temperature range of 300-525 K showed a semiconducting behaviour with a negative temperature coefficient of resistivity (TCR). In addition, the conductivity data were characterized by three different regions with increasing temperature.

Key Words: Conductivity, Poly-*N*-isopropylacrylamide, N-vinyl carbazole.

INTRODUCTION

Thermoreversible hydrogels exhibit an LCST-type (lower critical solution temperature) discontinuous first order volume transition phenomenon[1,2]. The current research interest in these hydrogels arises from potential biomedical applications[3-5]. The most widely studied thermoreversible gel, poly-*N*-isopropyl-acrylamide (PNI), is especially interesting as it exhibits the LCST at around 32 ℃ in water, which is close to the body temperature of homoeothermic animals[1,2]. The volume phase transition is reversible with temperature, which leads to some special applications like membranes for molecular separation[3], controlled drug releasing devices[4] and tissue culture substrates[5]. At the phase transition temperature there is a coil to globule transition present in this polymer, which has been extensively studied theoretically and experimentally[6]. The effect of additives such as salts and surfactants on the phase transition temperature of poly-*N*-isopropylacrylamide has been actively studied[7,8]. The presence of surfactants drastically change the behaviour of poly-*N*-isopropylacrylamide, especially the solubility in water and therefore phase transition. Generally, surfactants promote both inter and intra molecular solubility so that the phase transition temperature increases with the surfactant concentration. Wu *et al.*[8] have reported that the presence of sodium dodecyl sulfate (SDS) and dodecylpyridine bromide (DPB) shifts the phase transition temperature of poly-

N-isopropylacrylamide *ca.* 50 ℃ and *ca.* 35 ℃, respectively. Schild and Tirrell[9] have been carried out extensive studies of the effects of anionic surfactants on the phase transition temperature of poly-*N*-isopropylacrylamide and with surfac-tants having different chain lengths. They reported that the solubility of poly-*N*-isopropylacrylamide can be depressed or enhanced depending on the alkyl chain length and concentration.

In our earlier studies, we prepared new types of ternary polyaniline-poly-*N*-isopropylacrylamide-*co*-acrylic acid/ alumina (PANI-PNA/Al$_2$O$_3$) composites in the presence of DBSA by means of the oxidative polymerization of aniline with different wt % of Al$_2$O$_3$. The composite films formed a uniform distribution of Al$_2$O$_3$ over the polyaniline surface upon encapsulation. It was found that the substoichiometric or chemisorbed oxygen of aluminum verified the polycrystalline nature of these composites, which resulted in an increase in thermal stability and electrical conductivity[10,11].

N-Vinylcarbazole (nvc) is an organic compound used as a monomer in the production of poly(vinylcarbazole)[12,13], a photoconductive polymer used in the photoreceptors of photo-copiers[3]. Upon exposure to γ-irradiation, *N*-vinylcarbazole undergoes solid-state polymerization[14].

In recent years, much attention has been given to *N*-vinyl carbazole and its derivatives because of their unusual electrical and photoelectrical properties[15-17]. The common usage of *N*-vinyl carbazole material has been restricted due to the poor

processibility and the lack of stability[18]. Surface modifications by chemical and electrochemical means and plasma treatments enhance the wetting properties of the surface[19,20] and increase the possibility of forming attractive bonds (including polar interactions, hydrogen and covalent bonds) between the reinforcing fibers and the surrounding matrix polymer. The inclusion of acrylamide (AAm) into the polycarbazole (PCz) structure, even within just a few percent range by electro copolymerization, improved the thermal properties, flexibility and surface character of the resulting copolymer[21]. In this study, conducting poly-*N*-isopropylacrylamide-*N*-vinyl carbazole copolymers were synthesized by dissolving different weight percentages of *N*-vinyl carbazole. The morphology was studied by atomic force microscope (AFM). The temperature-dependent DC conductivity of poly-*N*-isopropylacrylamide-*N*-vinyl carbazole was studied to understand the transport properties of poly-*N*-isopropylacrylamide-*N*-vinyl carbazole.

EXPERIMENTAL

AR grade *N*-vinyl carbazole, *N*-isopropylacrylamide, potassium persulfate (KPS), ammonium persulfate (APS) and *N,N′*-methylenebisacrylamide (MBA) were purchased from Sigma-Aldrich. All the solutions were prepared in aqueous media using deionized water.

Synthesis procedure: Synthesis of poly-*N*-isopropyl-acrylamide was carried out using the equivalent grade *N*-isopropylacrylamide, MBA and KPS in 300 mL deionized water in a three-necked flask at 70 ºC under nitrogen atmosphere with vigorous stirring. In the case of copolymers, *N*-vinyl carbazole and/or powders were taken in a different molar % with respect to NiPaam concentration and the reaction mixtures were stirred thoroughly[10,11]. Fig. 1, indicates the schematic diagram showing the mixing of *N*-vinyl carbazole and NiPaam and the polymerization of *N*-isopropylacrylamide in an inert atmosphere to form poly-*N*-isopropylacrylamide-*N*-vinyl carbazole. In the following section, poly-*N*-isopropyl-acrylamide represents pure PNipaam, while the copolymers poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (20 %) and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (40 %) represent the molar concentration of *N*-vinyl carbazole in 20 and 40 %, respectively.
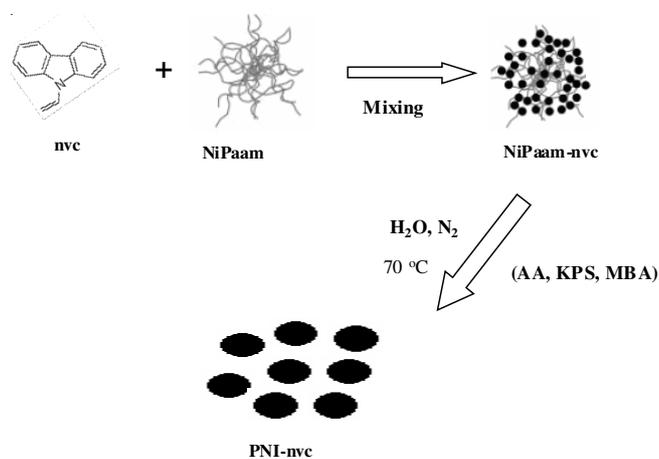
Fig. 1. Schematic diagram showing the mixing of *N*-vinyl carbazole and NiPaam and the polymerization of NiPaam in an inert atmosphere to form poly-*N*-isopropylacrylamide-*N*-vinyl carbazole

Characterization: Atomic force topographies were carried out using a Digital Instruments D3100 AFM with a Nanoscope IIIa controller operating in air at a constant relative humidity of about 60 %. UV-vis absorption spectrum was obtained using an Optizen 2120UV spectrometer. Fluorescence spectrum was taken with a Shimadzu RF-5310 PC spectro-meter. A solution containing 3 mg/mL in dichloromethane of poly-*N*-isopropylacrylamide and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole polymers were used to measure both UV-VIS and fluorescence spectral measurements. The measure-ments of complex impedance were performed at 300 K using impedance/gain-phase analyzer (Hewlett-Packard LF4194A) at 100 Hz. The 1.5-2.0 mm pellets were prepared by applying pressure of 9 M Pa. The parallel surfaces of pressed pellets were coated with gold by means of vacuum evaporation and silver electrodes were placed on both surfaces with the help of silver paste to obtain better contact which acts as electrodes. The conductivity/ resistivity values indicated here are the mean values during the measurements.

RESULTS AND DISCUSSION

Surface modification of poly-*N*-isopropylacrylamide-*N*-vinyl carbazole polymers: 2D AFM with 3 and 2 μm size of poly-*N*-isopropylacrylamide, poly-*N*-isopropylacrylamide-*N*-vinyl carbazole interfaces with an initial concentration of *N*-vinyl carbazole of 20 and 40 % are shown in Figs. 2(a)-(c); the surface of poly-*N*-isopropylacrylamide is smooth and homogeneous. The AFM image poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (20 %) shows some kind of irregular structures which are distributed all over the surface in an evenly manner. These irregular structures are may be due to the distribution of *N*-vinyl carbazole particles over the surface of the PNA particles. This makes a fine distribution of needle-like structures that appear as if the beads are floating over the water surface. There is an intermixing of poly-*N*-isopropyl-acrylamide and *N*-vinyl carbazole particles with the increasing amount of *N*-vinyl carbazole (2[c]). The irregular structures which were formed in poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (20%) were almost disappeared in poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (40 %), their appear some kind of both black and spots over the surface. It seems

(a)

(b)

(c)
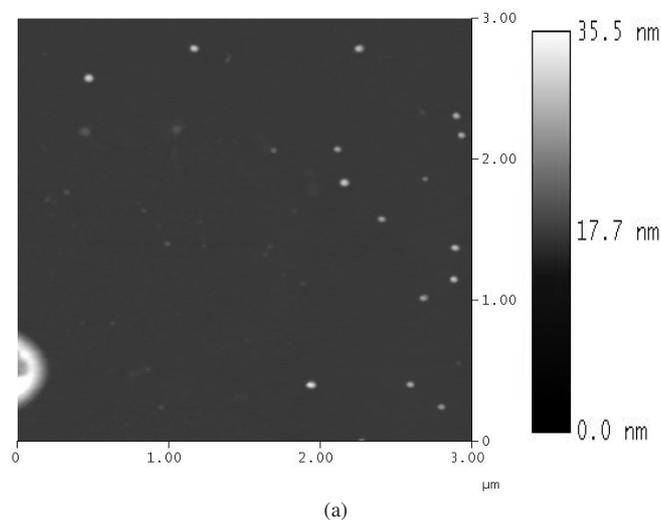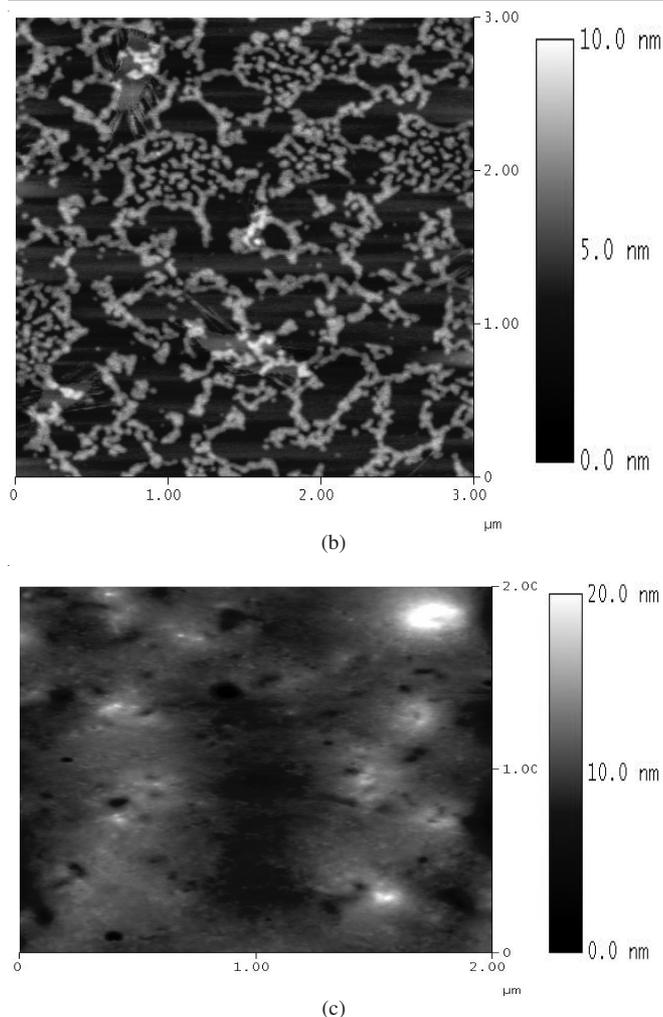
Fig. 2.   Surface topography of the polymers poly-*N*-isopropylacrylamide (a), poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (20%) (b) and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (40%) (c)

that the surface uniformity in terms of the distribution of features has significantly improved with the increase in the concentration of poly-*N*-isopropylacrylamide, as shown in Fig. 2(c). It can be concluded that the interfaces formed in poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (20 %) were almost disappear in poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (40 %).

Electronic spectra of poly-*N*-isopropylacrylamide-*N*-vinyl carbazole polymers: Fig. 3 shows the UV-visible while Fig. 4 shows the fluorescence spectra of poly-*N*-isopropylacrylamide, poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (20 %) and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (40 %) polymers. The UV-visible absorption reason is observed in the region between 200 and 300 nm. poly-*N*-isopropylacrylamide shows a broad band between 200 and 250 nm, which disappears in poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (20%) and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (40 %) and two new bands appear at around 240 to 250 nm and 290 nm[22,23]. These are the characteristic bands of *N*-vinyl carbazole, which show the formation of poly-*N*-isopropylacrylamide-*N*-vinyl carbazole copolymers. The shifts observed in the UV-visible region of the absorption spectra are related to the change in polymer structure, with the shift to
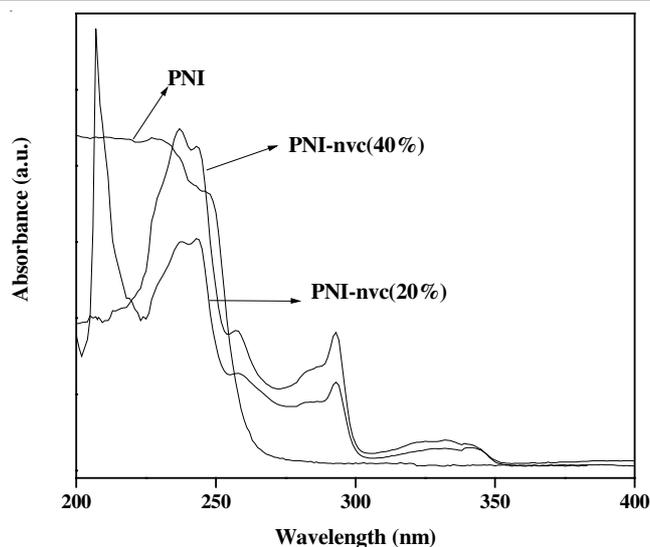
Fig. 3.   UV-visible spectra of poly-*N*-isopropylacrylamide (PNI), poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) (20 %) and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) (40 %) polymers
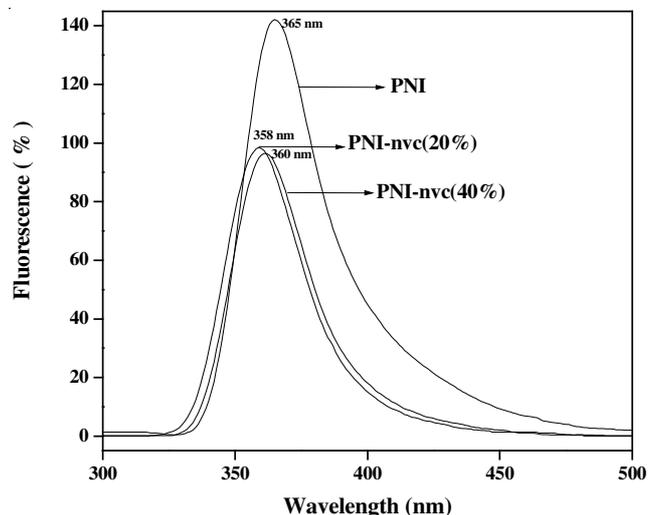
Fig. 4.   Fluorescence spectra of poly-*N*-isopropylacrylamide (PNI), poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) (20 %) and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) (40 %) polymers

a lower wave number indicating an increase in conjugation length. From these points, we can conclude that there is composite formation. The fluorescence spectra indicate only one band, which is around 365 nm for poly-*N*-isopropylacrylamide and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole polymers the same is shifted around 360 nm. The shift of the peaks position from 365 to 360 nm can be explained by the copolymer affecting the transfer of energy of the chromophore in the excited state. The bands become broader with the increase in concentration of *N*-vinyl carbazole, indicating the interaction of the poly-*N*-isopropylacrylamide and *N*-vinyl carbazole polymers. Thus, we can suppose that there is electronic interaction between poly-*N*-isopropylacrylamide and the *N*-vinyl carbazole electrons in the skeleton poly-*N*-isopropylacrylamide-*N*-vinyl carbazole.

DC electrical properties of poly-*N*-isopropylacrylamide-*N*-vinyl carbazole polymer: poly-*N*-isopropylacrylamide and its polymers with increasing *N*-vinyl carbazole concentration

have been characterized with respect to their DC electrical conductivity. The DC electrical conductivity of the polymer samples were measured in the range of 300-500 K. Fig. 5 shows the variation of electrical resistance with temperature for poly-*N*-isopropylacrylamide and poly-*N*-isopropylacrylamide-*N*-vinyl carbazole polymers. The electrical resistance decreases exponentially with temperature, which is similar to the semi-conducting behaviour and it rises with the increase in the content of *N*-vinyl carbazole. The temperature coefficient of resistivity (TCR) is determined from the variation of electrical resistivity with temperature using the following relation[24]:

$$TCR = \left(\frac{1}{\rho(T_1)}\right)\left(\frac{\Delta\rho}{\Delta T}\right) \qquad (1)$$

where $\Delta\rho = \rho(T_1) - \rho(T_2)$ and $\Delta T = T_2 - T_1$. Table-1 shows the calculated TCR values for the different polymers. The TCR values of poly-*N*-isopropylacrylamide are all negative. The poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (20 %) shift occurs from negative to positive, while poly-*N*-isopropyl-acrylamide-*N*-vinyl carbazole (40 %) shows a mixed trend of positive and negative values. Fig. 6 shows the relation of the DC conductivity *versus* the temperature of polymers with different concentration of *N*-vinyl carbazole. These values vary exponentially with temperature. The DC conductivity of the poly-*N*-isopropylacrylamide-*N*-vinyl carbazole polymers is significantly higher than the bare polymer poly-*N*-isopropyl-acrylamide. The results show that *N*-vinyl carbazole has a
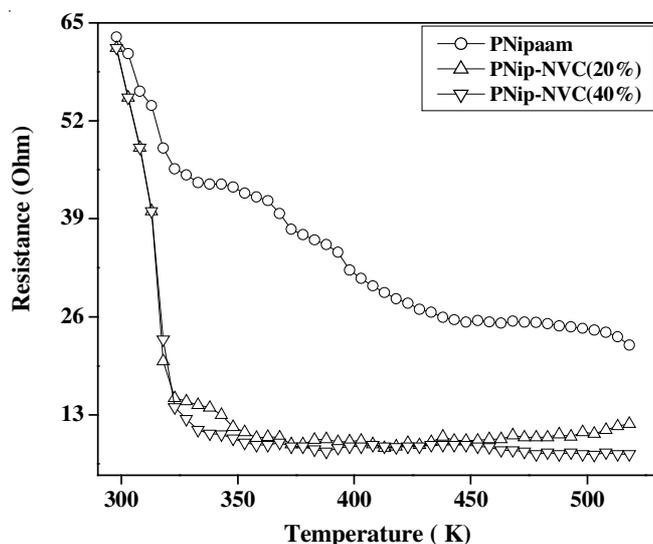
Fig. 5. Electrical resistance *vs.* temperature for (a) poly-*N*-isopropyl-acrylamide and polymers (PNIpaam) (b) poly-*N*-isopropylacrylamide -*N*-vinyl carbazole (PNI-nvc) (20 %) and (c) poly-*N*-isopropyl-acrylamide -*N*-vinyl carbazole (PNI-nvc) (40 %)

TABLE-1
CALCULATED VALUES OF THE TEMPERATURE
COEFFICIENT OF RESISTIVITY (TCR) FOR PNI AND
THE COPOLYMERS PNI-nvc (20 %), PNI-nvc (40 %)

Temp. (K)	Temperature coefficient of resistivity (TCR)		
	PNI	PNI-nvc (20 %)	PNI-nvc (40 %)
300-350	-0.00598	-0.01630	-0.01680
350-400	-0.00509	-0.00330	-0.00213
400-450	-0.00428	-0.00021	0.00045
450-500	-0.00067	0.00044	-0.00260
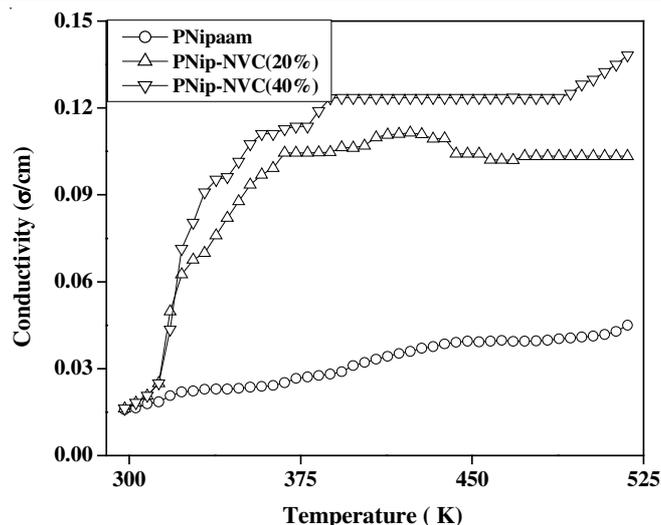
Fig. 6. Temperature-dependent DC conductivity of (a) poly-*N*-isopropyl-acrylamide (PNIpaam) and (b) poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) (20 %) and (c) poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) (40 %) polymers

positive influence on the temperature-dependent conducting property of poly-*N*-isopropylacrylamide, which may be caused by the mobility of the counterions of *N*-vinyl carbazole at a higher temperature.

The conductivity behaviour depending on temperature can be ascribed by two mechanisms for electrical conduction in the composites. The reason for the increase in the conductivity is attributed to the thermal energy at higher temperature to excite the electrons in the conduction band (thermal process). Such behaviour can be expressed by the Arrhenius equation[25]:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \qquad (2)$$

where σ is the DC conductivity; σ_0 is the constant for a material; k_B is the Boltzmann constant; T is the absolute temperature and E_a is the activation energy.

The other mechanism takes place in the low-temperature region and it is attributed to the hopping process, in which the excited electrons in this region lose their transition ability to the conduction band with lowering temperature. Thus, the electron attempts to find a state of similar energy by tunneling beyond its nearest neighbors to hop into more distant sites. This hopping leads to a greater selection of possible energy levels of electrons. The behaviour of DC conductivity in this region is called variable range hopping (σ_v), which is expressed in Mott's theory as follows[25,26]:

$$\sigma_v = \frac{\sigma_0}{T^{1/2}}\exp(-AT^{-1/4}) \qquad (3)$$

where A is the Arrhenius constant. The values of E_a is determined from the slopes of the fitted lines as in Fig. 7 (best fit of Arrhenius curves) and they are indicated in Table-2 at different temperature ranges. These values show the dependence of the thermal rate process of electron transport within these tempe-rature ranges. The difference in the values of the apparent activation energy (Table-2) for the three temperature ranges shows different electrical mechanisms taking place in the bulk of these composites.
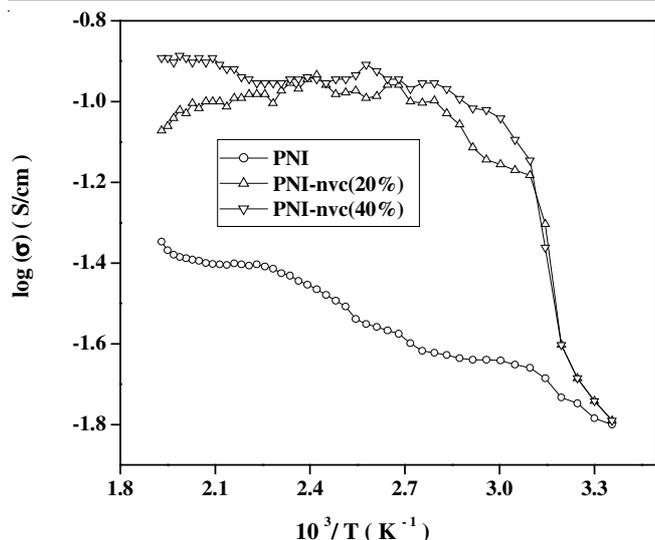
Fig. 7. Inverse of temperature dependence of conductivity in logarithm for poly-*N*-isopropylacrylamide (PNI), poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) (20 %) and poly-*N*-isopropyl-acrylamide-*N*-vinyl carbazole (PNI-nvc) (40 %)

TABLE-2
CALCULATED VALUES OF THE ACTIVATION ENERGY FOR
PNI AND THE COPOLYMERS PNI-nvc (20 %), PNI-nvc (40 %)

Temp. (K)	Activation energy (kcal/mol)/(10^3)		
	PNI	PNI-nvc (20 %)	PNI-nvc (40%)
300-400	1.125	2.189	2.379
400-450	2.892	3.495	3.776
450-500	5.746	6.357	4.786

Fig. 8 presents the relation of log ($\sigma_v T^{1/2}$) *versus* $T^{-1/4}$ for the three different composites. This figure shows a nearly linear relation within the temperature range, which supports the assumed mechanism. This observation is consistent with Mott's variable range hopping process[24-26]. The electrical conductivity of these composites increases with temperature in all the composites as the *N*-vinyl carbazole concentration is increased and this exhibits a thermal hopping process. The apparent activation energy shows a pronounced effect with the increase in the *N*-vinyl carbazole content with temperature.
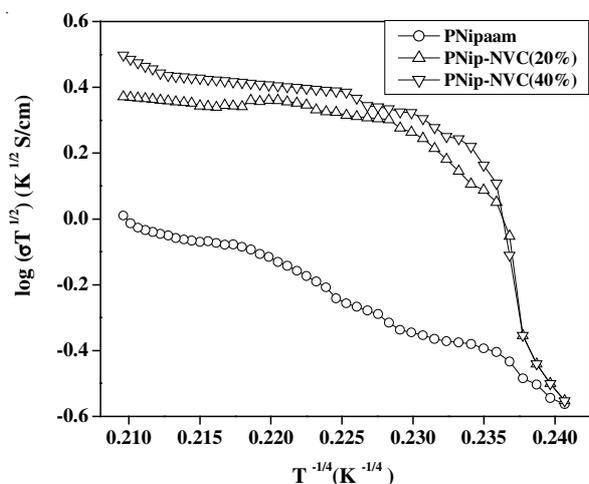
Fig. 8. Plot of log ($\sigma T^{1/2}$) as a function of $T^{-1/4}$ of (a) poly-*N*-isopropyl-acrylamide and the copolymers (PNIpaam) (b) poly-*N*-isopropyl-acrylamide-*N*-vinyl carbazole (PNI-nvc) (20 %) and (c) poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) (40 %)

Conclusion

Conducting poly-*N*-isopropylacrylamide-*N*-vinyl carbazole copolymers were synthesized by dissolving different weight percentages of *N*-vinyl carbazole (10, 20, 30 and 40 %) during the polymerization of *N*-isopropylacrylamide. The surface uniformity was significantly improved with the increase in the concentration of poly-*N*-isopropylacrylamide, as well as in the electronic interaction between poly-*N*-isopropylacryl-amide and the *N*-vinyl carbazole electrons in the skeleton poly-*N*-isopropylacrylamide-*N*-vinyl carbazole with an increase in conjugation length. The DC conductivity versus temperature of poly-*N*-isopropylacrylamide-*N*-vinyl carbazole with different wt % of *N*-vinyl carbazole studied in the temperature range of 300-525 K showed that *N*-vinyl carbazole had a positive influence on the temperature-dependent conducting property of poly-*N*-isopropylacrylamide, which could be caused by the mobility of the counterions of the *N*-vinyl carbazole at a higher temperature. Further, the conduction mechanism was explained with the help of Mott's theory; Mott's parameters were determined and compared. The method described here may be useful for developing new nanomaterials, which are very useful in molecular electronics and other fields.

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