Microstructure and Electrical Properties of Poly-*N*-isopropylacrylamide-*N*-vinylcarbazole Copolymers

R. Pierson, C. Basavaraja, Na Ri Kim, Eun Ae Jo, and Do Sung Huh*

Department of Chemistry and Institute of Basic Science, Inje University, Kimhae, Kyungnam 621-749, Korea
E-mail: chemhds@inje.ac.kr

Conducting poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) copolymers were synthesized via in situ deposition technique by dissolving different weight percentages of *N*-vinyl carbazole (10, 20, 30, and 40%). The structural morphology and FT-IR studies support the interaction between PNI and *N*-vinyl carbazole. The temperature-dependent DC conductivity of PNI-nvc was studied within the range of $300 \leq T \leq 500$ K, presenting evidence for the transport properties of PNI-nvc. The DC conductivity of PNI-nvc copolymers signifies the future development of new nanocopolymers that acts as a multifunctional material.

Introduction

In recent years, considerable research attention has been focused on hydrogels that are able to alter their volume and properties in response to environmental stimuli such as pH, temperature, ionic strength, and electric field. Poly-*N*-isopropylacrylamide (PNI) is one of the most interesting sensitive polymer microgels which have been extensively studied because its lower critical solution temperature (LCST) is close to room temperature. PNI can be dissolved by using a chelating agent that binds to the ions. Moreover, their size ranges typically from 50 nm to 5 µm. Recently, several types of colloids by silica, gold nanoparticles, and carbon nanotubes with polymer have been used for surface-modification with PNI to study thermal response of PNI in an aqueous medium.[1] The PNI microgels undergo volume phase transition around LCST, and they possess several advantages over bulk gels, for example, small size and volume, high surface area, faster response to stimuli, and high diffusivity.

Recently carbazole-based polymers have received much attention,[2-4] due to their electrical and photo-electrochemical properties. A great deal of attention has been given to *N*-vinylcarbazole (nvc) and its derivatives over the years because of its unusual electrical and photoelectrical properties. Its use has been suggested for a number of applications, i.e., photo active devices, sensors and electrochoromic devices.[5] The common usage of (nvc) material has been restricted due to the poor processibility and the lack of stability.[6] Surface modifications by chemical, electrochemical means and plasma treatments enhance the wetting properties of the surface,[7-9] and increase the possibility of forming attractive bonds (including polar interactions, hydrogen and of course covalent bonds) between the reinforcing fibers and the surrounding matrix polymer. Inclusion of acrylamide (AAm) into the polycarbazole (PCz) structure, even within a few percent range by electrocopolymerization, improved the thermal properties, the flexibility and the surface character of the resulting copolymer.[10]

The objective of this work is to synthesize conducting poly-*N*-isopropylacrylamide-*N*-vinyl carbazole (PNI-nvc) copolymers by dissolving different weight percentages of *N*-vinylcarbazole into PNI network. The morphology and structural characterization was studied by FT-IR. The temperature-dependent DC conductivity of PNI-nvc was studied to understand the transport properties of PNI-nvc. Since there is a chemical bonding between the two component networks, each network may retain its own property while the proportion of each network can be varied independently. Interpenetration of the two networks may also lead to a much higher mechanical strength with respect to the homopolymer network.

Experimental Sections

Materials and synthesis procedure. AR grade *N*-isopropylacrylamide (NIPAAm, backbone monomer), acrylic acid (AA), potassium persulfate (KPS, initiator), and *N,N'*-methylenebisacrylamide (MBA, crosslinker) were purchased from Sigma-Aldrich. All solutions were prepared in aqueous media using deionized water. Synthesis of PNI was carried out using the equivalent grade of NIAAm, AA, MBA, and KPS in deionized water in a three-necked flask at 70 °C under nitrogen atmosphere with vigorous stirring. In case of copolymer *N*-vinyl carbazole taken in a different molar % with respect to NIPAAm was dissolved completely in ethanol and added to the reaction mixture in a three-necked flask and all were stirred thoroughly till we get colorless homogeneous solution. The ratio of water to ethanol was 3:1. In the following paragraph PNI represents pure poly (NIPAAm), the copolymers PNI-nvc (20%) and PNI-nvc (40%) represents molar concentration of nvc in 20 and 40% respectively.

Characterization technique. The FT-IR spectra of the samples were measured by a Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. The surface morphology of these composite films was investigated by using Philips XL-30 ESEM scanning electron microscopy. Thermal properties were obtained by TGA (Perkin Elmer model TGA 7) and DSC by (Perkin Elmer model DSC 7) in the range 30 ~ 700 °C at 10

°C/min in nitrogen atmosphere. The measurements of complex impedance were performed over a temperature range 298 ~ 533 K using impedance/gain-phase analyzer (Hewlett-Packard LF4194A) at 100 Hz. The parallel surfaces of pressed pellets, 1.5 × 1.3 mm, 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 taken by varying the temperatures with heating and cooling during the measurements.

Results and Discussion

Structural characterization. Figure 1 shows the FT-IR spectra of PNI, PNI-nvc (20%), and PNI-nvc (40%). In the spectra of PNI, the absorption peak at 3330 cm^{-1} can be attributed to the stretch for the hydrogen bonded NH group. The antisymmetric stretching vibration of the CH$_3$ group can be formed at 2970 cm^{-1}. The C – O groups give rise to a strong band at 1658 cm^{-1}. The mixed vibration of CN and NH may appear at 1326 cm^{-1}, and the antisymmetric deformation of CH$_3$ is at 1455 cm^{-1}. After mixing with nvc there are shifts occurs in the vibrations as we can see from PNI-nvc (20%) and PNI-nvc (40%). The vibration for hydrogen bonded NH group in these copolymers has been approximately shifted to 3429 cm^{-1}. Whereas the band corresponding to C = O has been blue shifted to 1651 cm^{-1} in PNI-nvc (20%) and is disappeared in PNI-nvc (40%). The mixed vibration band of NH has been red shifted to 1320 cm^{-1}.[11,12] The above observations clearly indicate the composite formation during the synthesis process. Further FT-IR spectra also indicates the intensity of the band peaks at 749 and 1453 cm^{-1} are increased which are present in PVK which shows the polymerization process.

Surface morphology. Figures 2(a)-(c) represent the SEM images of PNI, PNI-nvc (20%) and PNI-nvc (40%) copolymer samples at 5 μm, respectively. As shown in the Figure 2(a) PNI forms a gel like membrane which appears like rigid structure. However with the addition of nvc during the synthesis, the polymer surface change into smooth reducing the formation of gel like structure as shown in the Figures 2(b) and (c) of PNI-nvc (20%) and PNI-nvc (40%), respectively. This may due to the formation of week link with the polymer backbone of PNI. The surface uniformity in terms of the distribution of features is significantly improved with the increase in the content of nvc.

Thermal characteristics. The TGA thermograms of the PNI, PNI-nvc (20%) and PNI-nvc (40%) copolymers recorded under N$_2$ atmosphere scanned in the range 10 ~ 600 °C at a heating rate of 10 °C/min are shown in Figure 3. The major stages of the decomposition processes are summarized in Table 1. The first weight loss between 20 ~ 120 °C is due to the elimination of water and other volatiles. The second stage in the temperature range 200 ~ 400 ° C is presumably due to the decomposition of excess dopant present in the composite. In the copolymers the bound nvc decomposes at about 400 °C and then the PNI itself decomposes. The TGA thermogram of the PNI-nvc (20%) and PNI-nvc (40%) copolymers show the similar weight loss.
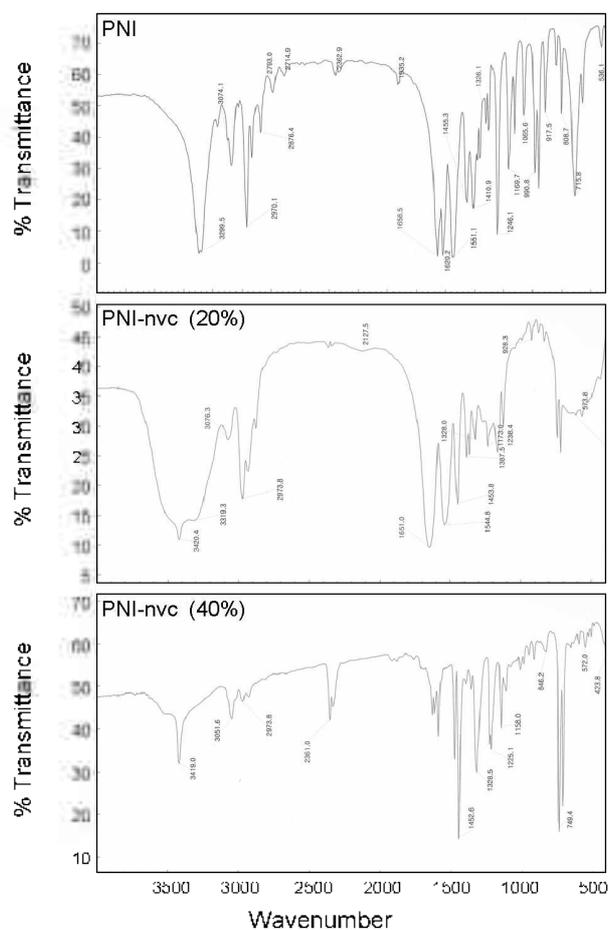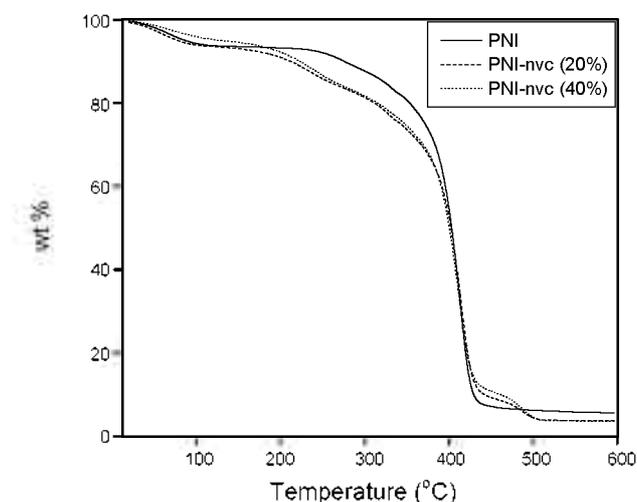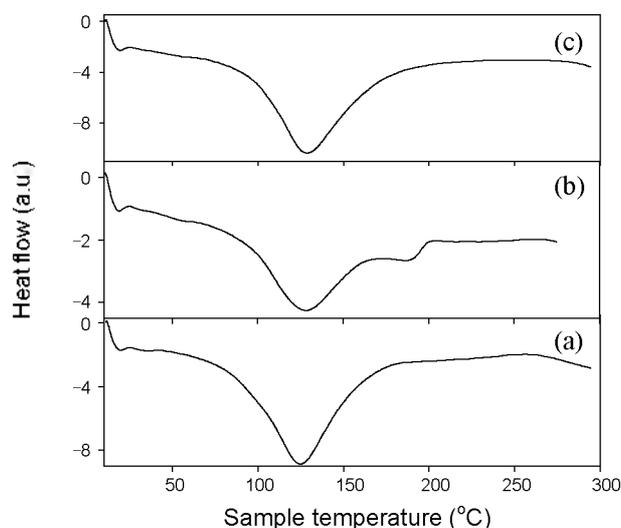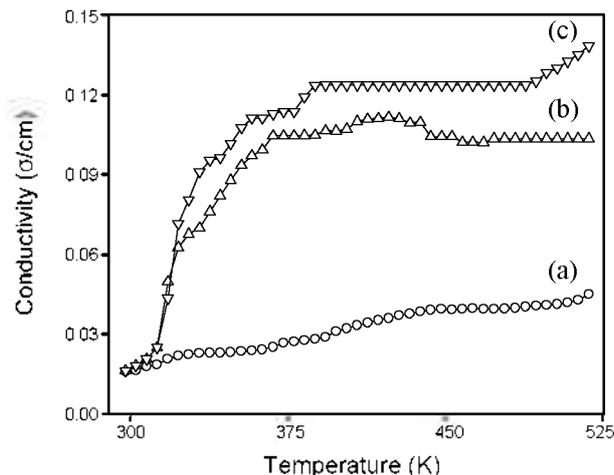
Figure 1. FT-IR spectra of PNI, PNI-nvc (20%), and PNI-nvc (40%) copolymers.
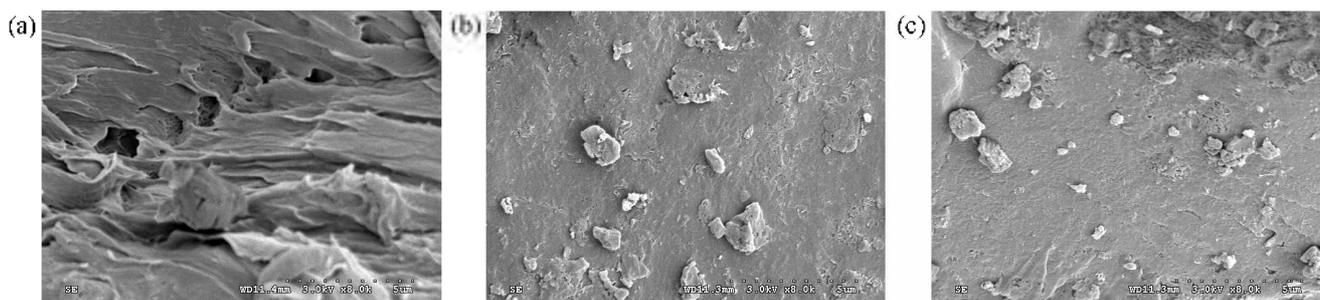
Figure 2. Scanning electron micrographs for (a) PNI, (b) PNI-nvc (20%) and, (c) PNI-nvc (40%).

Table 1. The major stages of decomposition process for PNI and the copolymers of PNI-nvc (20%) and PNI-nvc (40%)

Materials	Temperature (°C)	Weight loss (%)
PNI	20 ~ 120	6.3
	200 ~ 400	38.2
	400 ~ 600	55.2
PNI-nvc (20%)	20 ~ 120	5.8
	200 ~ 400	39.4
	400 ~ 600	47.25
PNI-nvc (40%)	20 ~ 120	4.43
	200 ~ 400	41.82
	400 ~ 600	48.72

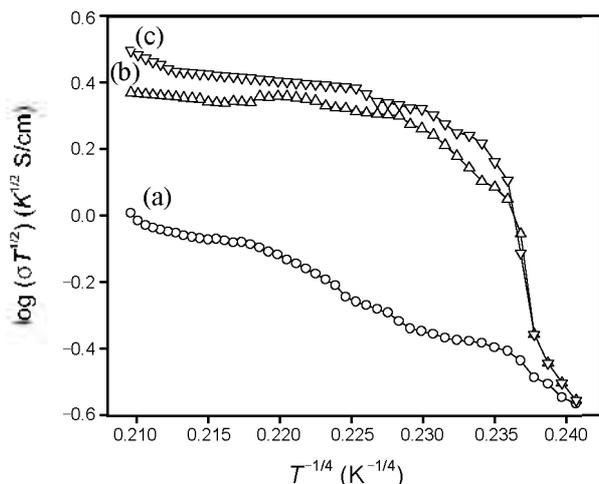**Figure 5.** Temperature-dependent DC conductivity of (a) PNI, (b) PNI-nvc (20%), and (c) PNI-nvc (40%) copolymers.

Figure 3. TGA curve of PNI, PNI-nvc (20%), and PNI-nvc (40%) copolymers recorded under N₂ atmosphere at a heating rate of 10 °C/min.

but the weight losses are lower in each major stage than that without nvc. and the decomposition temperature of excess dopant nvc increases by about 39% and 41%. respectively. relatively higher than the bulk PNI which is about 38%. This result indicates the PNI-nvc (20%) and PNI-nvc (40%) copolymers are thermally stable than PNI at lower temperatures. The decrease in weight loss at higher temperatures for PNI-nvc (20%) and PNI-nvc (40%) is due to complete volatilization of NVC or depression of heat resistance from dilution.

There are three endothermic peaks in the curves of Figure 4 which shows DSC thermograms for (a) PNI. (b) PNI-nvc (20%), (c) and PNI-nvc (40%) recorded in the range 10 ~ 300 °C with a heating rate of 10 °C /min. The first one is at 50 ~ 120 °C because of the removal of moisture. The second at 150 ~ 300 °C results from the removal of PNI backbone and the complete removal of chemically active organic molecules. Figure 3(c) for PNI (40%) differs significantly from Figures 3(a) and 3(b). since these endothermic peaks are minimized due to the higher content of nvc particles confirming the structural changes after the incorporation of nvc.

Electrical behavior of PNI-nvc copolymers. To investigate the charge transport mechanism in the PNI-nvc copolymers. temperature-dependent DC conductivity has been studied. Fig. 5 shows the relationship between DC conductivity and temperature within the range of 300 ~ 500 K for (a) PNI and. (b) PNI-nvc (20%) and (c) PNI-nvc (40%) copolymers. These values vary exponentially with temperature. From the Figure 5 it is observed that the conductivity values of PNI-nvc improved and the values are much greater than pure PNI. The results show that nvc has a positive influence on the temperature dependent conducting property of PNI, which may be caused by the mobility of nvc counter ions as the temperature was increased. This is attributed to the modification of bulk morphology of PNI by nvc.

Figure 6 presents the relation of log ($\sigma_v T^{1/2}$) versus $T^{-1/4}$ for PNI and the copolymers PNI-nvc. This figure does not show linear relation within the temperature range. So it is not possible to apply Mott's variable range hopping suggesting the conducting process may be complicated.[16] Overall the depen-

Figure 4. Differential scanning calorimetry thermograms for (a) PNI, (b) PNI-nvc (20%), and (c) PNI-nvc (40%) recorded with a heating rate of 10 °C /min.

Figure 6. Plot of log($\sigma T^{1/2}$) as a function of $T^{-1/4}$ of (a) PNI and the copolymers, (b) PNI-nvc (20%), and (c) PNI-nvc (40%).

dence on temperature of the DC electrical conductivity of the copolymers is similar to semiconducting behavior. The electrical conductivity of the copolymers PNI-nvc increases with temperature as the nvc concentration is increased. and this exhibits a thermal electron process (high-temperature region) and a hopping process (low-temperature region). This may be due to the increase in the apparent energy of activation with the increase in the content of PM with temperature. By our study of this report. the synthesized PNI-nvc copolymers are thermally more conducting than PNI and have a stable DC conductivity which varies with temperature.

Conclusion

PNI-nvc copolymers were synthesized by the chemical method using *N*-isopropylacrylamide in an aqueous media contain ing well dissolved *N*-vinylcarbazole. The structural and thermal characterization reveals nvc is dispersed into the polymer matrix of Poly-*N*-isopropylacrylamide. The DC conductivity was stu-

died within the temperature range of 300 ~ 500 K. The increase in conductivity suggests that the nvc acts as a suitable material for making PNI copolymers. This feature makes it a very promising material for futuristic applications. The method described here may be useful for developing new applications of these copolymers/composites in molecular electronics and other fields.

Reference

1. Zhang, J.; Nicholas A. P. *Macromolecules* **2000,** *33,* 102.
2. Morisihima, Y. *Prog. Polym. Sci.* **1990,** *25,* 949.
3. Morisihima, Y. *Adv. Polym. Sci.* **1992,** *5,* 104.
4. Novakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989,** *22,* 3903.
5. *Handbook of Organic Conductive Molecules and Polymer,* Nalwa, H. S., Ed.; Wiley: New York, 1997.
6. MacDiarmid, A.; Kaner, R. T. *Handbook of Conducting Polymers,* Skotheim, Ed.; Marcel Decker: New York, 1986; p 689.
7. Fitzer, E.; Jager, H. Z. *Werkstofftechn* **1985,** *16,* 215.
8. Yuan, L.J.; Shyu, S. S.; Lai, J. Y. *J. Appl. Polym. Sci.* **1991,** *42,* 2525.
9. Bismarck, A.; Kumru, M. E.; Song, B.; Springer, J.; Moos, E.; Karger-kocsis, J. *J. Composites A* **1999,** *30,* 1351.
10. Yavuz, O.; Berlouis, L. E. A.; Hitchmann, M. L.; Saraç, A. S. *Synth. Met.* **2000,** *110,* 165.
11. Sarac, A. S.; Bardavit, Y. *Progess in Organics* **2005,** *49,* 85.
12. Ling, Q. D.; Cai, Q. J.; Kang, E. T.; Neoh, K. G.; Zhu, F. R.; Huang, W. *J. Mater. Chem.* **2004,** *14,* 2741.
13. Basavaraja, C.; Pierson, R.; Vishnuvardhan, T. K.; Huh, D. S. *Eur. Poly. J.* **2008,** *47,* 1556.
14. Basavaraja, C.; Pierson, R.; Kim, J. H.; Huh, D. S. *Bull. Korean Chem. Soc.* **2008,** *29*(9), 1699.
15. Basavaraja, C.; Veeranagouda, Y.; Lee, K.; Pierson, R. Huh, D. S. *J. Polym. Sci. Part B: Poly. Phys.* **2009,** *47,* 36.
16. Basavaraja, C.; Veeranagouda, Y.; Lee. K.; Pierson, R.; Revanasiddappa, M.; Huh, D. S. *Bull. Korean Chem. Soc.* **2008,** *29*(12), 2423.