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**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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**To cite this Article** Kim, Seon Jeong , Lee, Na Rae , Yi, Byung-Ju and Kim, Sun I.(2006) 'Synthesis and Characterization of Polymeric Acid-Doped Polyaniline Interpenetrating Polymer Networks', Journal of Macromolecular Science, Part A, 43: 3, 497 — 505

**To link to this Article: DOI:** 10.1080/10601320600575165

**URL:** http://dx.doi.org/10.1080/10601320600575165

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*Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry*, 43:497–505, 2006
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ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600575165

# Synthesis and Characterization of Polymeric Acid-Doped Polyaniline Interpenetrating Polymer Networks

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*Polyaniline (PANI)/poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) semi-interpenetrating network polymers (semi-IPNs) were prepared using the simultaneous method. The formation and properties of the interpenetrating PANI/PAMPS semi-IPNs were investigated using Fourier transform infrared spectroscopy, X-ray diffraction, solid-state $^{13}$C-NMR, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The interaction of PAMPS with PANI as a polymeric acid dopant was also investigated. These semi-IPNs had a different microstructure compared to that of pure PANI. Packing structures and several decomposition steps were ordered for each semi-IPN, while pure PANI exhibits a single amorphous peak and one decomposition step. The NMR spectra show that these peaks broaden and shifted downfield in the semi-IPNs. A thermal reaction between PANI and PAMPS was observed using DSC and TGA, and the data from the two techniques are in agreement.*

**Keywords** poly(2-acrylamido-2-methylpropane sulfonic acid), polyaniline, thermal properties, semi-IPN

## Introduction

There have been a number of studies on the synthesis, characterization, and use of conducting polymers such as polyaniline, polypyrrole, and polythiophene (1, 2). Many applications of conducting polymers have also been studied and developed, such as their use as biosensors, gas sensors, anti-corrosion agents, in batteries, as light emission diodes, in solar cells, and in electrochromic devices (ECDs) (3–6). The conducting polymer, polyaniline (PANI), has been extensively studied, because of its excellent thermal stability and unique electrochemical properties.

The properties of PANI depend on both the oxidation state of the polymer and its degree of protonation. Dopants are also important in determining the chemical, physical, and mechanical properties of PANI (7). The dopants usually added to PANI

Received March 2005; Accepted April 2005.

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are small molecule acids. These acid dopants can evaporate at room or higher temperatures and can be leached by ageing or by contact with water, leading to a decrease in the conductivity of the acid-doped PANI. This drawback can be overcome by using polymeric acid dopants, and polymeric acid-doped PANI has enhanced flexibility (8) and film processability (9). In addition, polymeric acid dopants can be used as a template for the oxidative polymerization of aniline, which results in a water soluble form of PANI (1). Typical polymeric acids that have been used as dopants are: poly(acrylic acid), poly(styrenesulfonic acid), poly(ethenesulfonic acid), and poly(2-acrylamido-2methylpropane sulfonic acid) (10).

The incorporation of polyelectrolytes is also of interest, in that the formation of structures with a high water content is possible, due to cation or anion exchange in an aqueous environment. These polyelectrolytes acting as a dopant can combine with PANI, either during chemical or electrochemical polymerization of aniline, or by doping it using aqueous or nonaqueous solutions. However, the stability of aqueous polyaniline is not satisfactory, and the release of water-soluble electrolytes in polyaniline composites in water can be a problem for practical applications. This is difficult to overcome when employing common blending methods. However, the semi-interpenetrating network (semi-IPN) technique may be useful for this purpose, because polyaniline can be confined in a crosslinked network.

The aim of this study was to find a convenient way to synthesize polyaniline semi-IPNs from aqueous solutions using the simultaneous method. For this purpose, 2-acrylamido-2methylpropane sulfonic acid (AMPS) was employed as a network material, as well as a polymeric acid dopant. The thermal properties of the resulting PANI/PAMPS semi-IPNs were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). We also studied the chemical structure and degree of PANI doping of the semi-IPNs using Fourier transform infrared spectroscopy (FTIR), solid-state $^{13}$C-NMR, and X-ray diffraction (XRD).

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## Experimental

### Materials

The AMPS monomer, N,N′-methylene-bis-acrylamide (MBAAm) crosslinker, and the potassium persulfate (KPS) initiator used were purchased from the Aldrich Chemical Co. (Milwaukee, WI). The polyaniline emeraldine EB (PANI EB) used, with an average molecular weight of $6.5 \times 10^4$ (undoped powder form, minimum assay = 99.5%) and NMP (1-methyl-2-pyrrolidone) as solvent were also purchased from Aldrich Chemical Co, (Milwaukee, WI).

### Preparation of the Semi-IPN Hydrogels

The PANI/PAMPS semi-IPN hydrogels were prepared using the simultaneous IPN method. The AMPS was fully dissolved in deionized water, while the PANI was dissolved in NMP (2 wt%). Each solution was then mixed using specific ratios, and stirred at room temperature for a period of 12 h. Different percentages of PANI (5, 10, and 15 wt%) were obtained in the presence of a fixed content of AMPS (9 wt%). The crosslinking polymerization reaction of the AMPS was carried out in solvent at 65°C for a period of 1 day in the presence of PANI, using MBAAm (5 wt% of the AMPS) and KPS (1 wt% of the AMPS) as the crosslinking agent and initiator, respectively.

The solutions containing PANI (5, 10, 15 wt%) and polymerized AMPS were then poured into Petri dishes and dried at 60°C for a period of 2 days. Two homopolymers, PANI EB (2 wt% in NMP) and crosslinked PAMPS (9 wt% in deionized water), were also prepared. The dried samples were then washed with distilled water to remove any unreacted materials that were not incorporated into the network, and then dried for a period of 1 day. The semi-IPN samples were referred to as: P-1, P-2, and P-3, with the numeric term relating to the initial PANI content of 5, 10, and 15%, respectively.

### *Measurements*

The FTIR spectra of the samples were recorded on a Nicolet 550 FTIR spectrophotometer using KBr pellets. The XRD scans for the samples were obtained using a D/MAX RINT Model 2000 diffractometer. The samples were scanned using a rate of $2\theta = 2^\circ/\mathrm{min}$ in the reflection mode over the range $5^\circ < 2\theta < 40^\circ$. Solid–state $^{13}$C-NMR spectra were obtained by using a Varian Unity Inova 200 spectrometer with a solids accessory. The experimental parameters used were: $^{13}$C ($f = 200\,\mathrm{MHz}$) with a zircon cell (length = 2 cm, internal diameter = 5 mm). The thermal properties of the samples were determined using DSC and TGA. The DSC data was obtained in a nitrogen atmosphere using a TA Instruments DSC Q100 (TA Instruments, USA) that contained in a refrigerator cooling system (RCS). An initial scan eliminated any residual water and solvent, and was carried out by equilibrating the sample at 150°C for 30 min. A second scan was then carried out at a heating rate of 10°C/min in the temperature range 35–350°C. Thermal decomposition was carried out using a TA Instruments SDT 2960 simultaneous DSC-TGA (TA Instruments, USA), by heating the samples from room temperature to 700°C using a heating rate of 10°C/min under flowing nitrogen.

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## Results and Discussion

### *FTIR Spectra*

The FTIR spectra of dried PANI (EB), semi-IPNs, and PAMPS (crosslinked) samples are shown in Figure 1. The spectrum of the PANI EB (Curve a) is consistent with the reported spectrum of the polyaniline EB, (11) where the characteristic absorption peaks are assigned to the quinone ring ($1600\,\mathrm{cm}^{-1}$) and the benzene ring ($1500\,\mathrm{cm}^{-1}$) stretches, the C-N stretch of a secondary aromatic amine ($1303\,\mathrm{cm}^{-1}$), and the C-H out-of-plane bending ($828\,\mathrm{cm}^{-1}$). The peak at $1166\,\mathrm{cm}^{-1}$ was assigned to an electronic band or a vibrational band of the nitrogen quinone (12).

The PAMPS spectrum (Curve c) shows absorption bands at $1230–1100\,\mathrm{cm}^{-1}$ and $1035\,\mathrm{cm}^{-1}$ that correspond to the asymmetric and symmetric stretching of the $SO_2$ groups in the PAMPS polymeric acid. The hydrogen-bonded N-H stretch of a noncyclic N-monosubstituted amide was observed close to $3300\,\mathrm{cm}^{-1}$, with a weaker band close to $3100\,\mathrm{cm}^{-1}$, i.e., the Fermi resonance-enhanced overtone of the strong infrared band at $1560\,\mathrm{cm}^{-1}$. The C=O stretch occurred near to $1660\,\mathrm{cm}^{-1}$.

The spectrum of the semi-IPN (Curve b) showed the presence of PANI from the aromatic double carbon bond stretch occurring at 1577 and $1496\,\mathrm{cm}^{-1}$. A peak that was shifted to lower wavenumbers was also observed from the vibrational band of nitrogen quinone ($1145\,\mathrm{cm}^{-1}$), which was broader than that of the PANI EB due to its overlapping with the S-O stretch of the sulfonic group of PAMPS. The band occurring at $1145\,\mathrm{cm}^{-1}$ was assigned to an electronic-like band, due to the doping of the PANI (13). This evidence

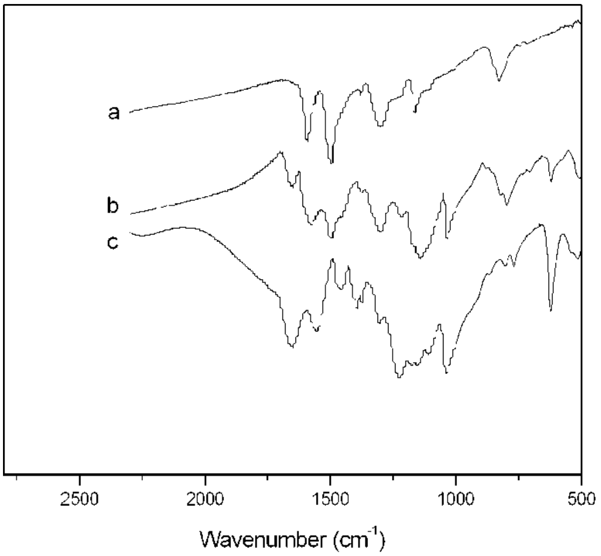

**Figure 1.** FTIR spectra of two homopolymers and their semi-IPN: (a) PANI, (b) semi-IPN, and (c) PAMPS.

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supports the assumption of the molecular incorporation of the PAMPS in the PANI through an interaction between $SO_3$ groups of the PAMPS and nitrogen atoms of the PANI.

### *X-Ray Diffraction Analysis*

XRD patterns of the PANI, PAMPS, and semi-IPN samples are shown in Figure 2. The PANI EB sample exhibited a single one broad, amorphous peak at $2\theta = 20^\circ$, which was ascribed to the periodicity of the parallel polymer chains. The PAMPS exhibited some diffraction shoulders at $2\theta = 8$, 14, and 20°. However, no diffraction shoulders at $2\theta = 8^\circ$ and 14° were identified in the XRD spectrum of the semi-IPN sample, indicating a relatively strong interaction between the PAMPS and the PANI chains. The XRD spectra of PAMPS-doped PANI have been reported by other researchers (15) However, these composites did not exhibit any pronounced diffraction peaks in their XRD patterns, while our PAMPS/PANI semi-IPNs did exhibit diffraction peaks at $2\theta = 15$ and 25°.

The peak at $2\theta = 25^\circ$ may be the result of a periodicity directed perpendicular to the polymer chain (14). This indicates that the PAMPS/PANI semi-IPNs had an ordered packing structure, despite the potential steric hindrance of the PANI polymeric acid dopant bulk amino methylpropane sulfonic acid groups. The structural difference between our semi-IPNs and that of the composites is due to the different material preparation methods used (15). By using the semi-IPN technique for polymerization, any doping occurs spontaneously during the polymerization, so that the PAMPS chains can both incorporate and grow along the PANI chains. This method allows PANI chains in the PAMPS networks to form relatively confined and rigid structures, which favors ordered packing. By using the solution blending method however, both the PAMPS and PANI chains have some conformational freedom in solution, so that are difficult to align. Doping occurs in a random manner among the large-size PAMPS chains, which in turn, makes ordered packing of the PANI chains difficult.

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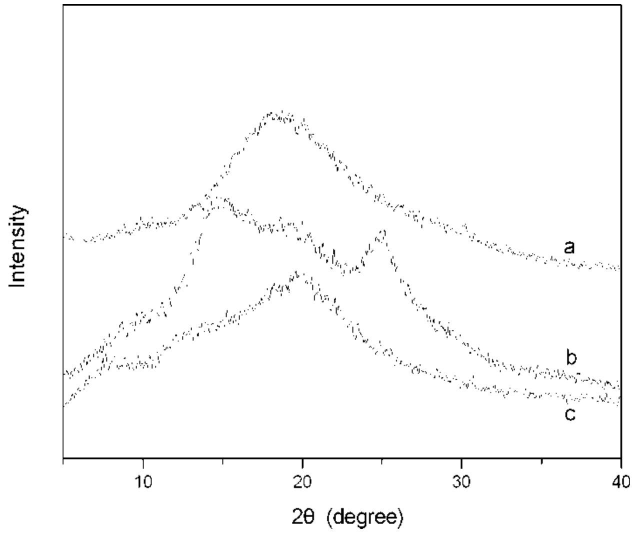

**Figure 2.** XRD spectra of: (a) PANI, (b) semi-IPN, and (c) PAMPS.

### *$^{13}$C-NMR*

The $^{13}$C CP/MAS NMR spectra of the PANI EB, PAMPS, and semi-IPN samples are shown in Figure 3. The spectrum of pure PANI consisted of the main signal at 122 ppm arising from the C-H groups of the quinoid rings, a shoulder at 135 ppm which was assigned to the benzenoid C-N carbons, and another at 157 ppm originating from the C=N quinoid bond.

Compared to the spectrum of pure PANI, the spectrum of semi-IPN (Curve b) exhibited very broad resonance signals, which is characteristic of a polymeric system.

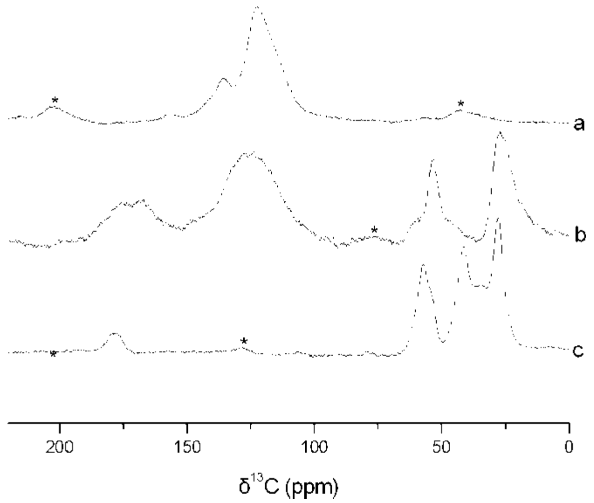

**Figure 3.** Solid-state $^{13}$C-NMR spectra of: (a) PANI, (b) semi-IPN, and (c) PAMPS. The asterisks denote spinning sidebands.

The broad peaks indicate some interactions occurred between the components in the solid state. Other inconspicuous peaks were also observed in semi-IPN, where the PANI and PAMPS components interacted with each other. This was due to the PAMPS sulfonic groups bonding to the benzene rings of the PANI, which affected the chemical shift of nearby carbon atoms. Curve b in Figure 3 shows the spectrum of the semi-IPN, in which the PAMPS acted as a polymeric acid dopant of the PANI. The semi-IPN spectrum exhibited a broad asymmetric peak that was shifted downfield at 127.27 ppm, whose signal is known to arise from the benzenoid carbons. The line broadening is due to the heterogeneity in charge distribution along the polymer chain, resulting from structural disorder of the polymer chains in the solid state (16). The signals in the PAMPS spectrum occurred at 177.97, 57.05, 41.12, and 27.89 ppm. The signal at 177.97 ppm has a contribution from two types of amide carbon: one from the PAMPS and the other from bisacrylamide, which acts as crosslinker binding the chains together. All the PAMPS peaks were shifted either downfield or upfield in the semi-IPN. The strong peak centered at 41.12 ppm, which was assigned to the sulfonic acid group of the PAMPS, disappeared in the semi-IPN spectrum. This result shows that there was an interaction between the PANI and the PAMPS. Some interaction between the PANI and PAMPS polymer chains in the solid state, operating over a distance comparable to that of a few bonds occurs, so that the electron clouds of individual components are disturbed.

### *Thermogravimetric-Differential Thermal Analysis*

The thermal stability of the PANI, semi-IPNs, and PAMPS was evaluated using TGA. From Figure 4, it can be seen that, the pure PANI EB compound showed good thermal stability up to 530°C, with a very small decomposition, which was due to evaporation of the solvent under a nitrogen atmosphere. The PAMPS sample showed a severe weight loss due to the loss of its sulfonic acid group between 200–350°C, followed by the broad mass loss from 400°C onwards. This mass loss was due to dehydration and from degradation of the crosslinked polymer network.

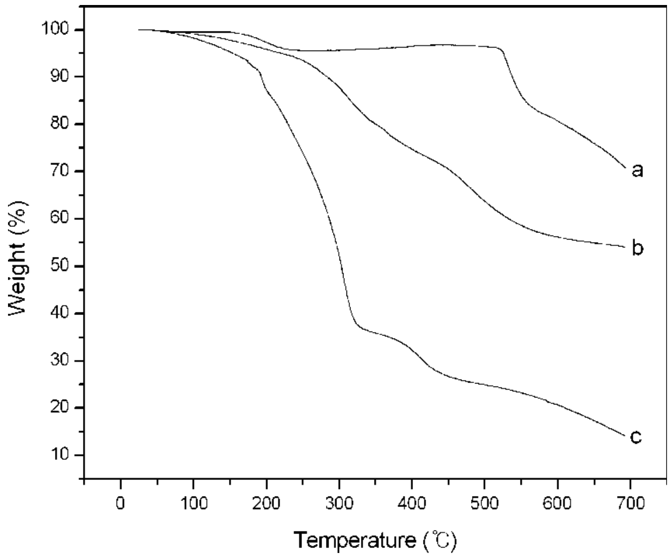

**Figure 4.** TGA curves of: (a) PANI, (b) semi-IPN, and (c) PAMPS.

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The semi-IPN composed of PANI and crosslinked PAMPS showed several weight loss processes. The first process was a slow initial weight loss in the temperature range 90–230°C due to the evaporation of moisture and solvent. The second weight loss process was for weight loss occurring at around 250°C, which was attributed to the loss of excess PAMPS sulfonic acid groups. This was followed by a broad, strong mass loss starting at around 300°C, which was due to the degradation of the PAMPS chains and the loss of bound PAMPS, which was bonded to the imine nitrogen groups on the PANI chains. A detailed temperature is shown in Figure 5. Weight loss was also observed in the final process occurring between 450 and 700°C, which arose from the decomposition of the PANI and crosslinked PAMPS network.

The TGA thermograms of the semi-IPNs contained several weight loss processes, with peaks occurring at different rates, as shown in the corresponding DTA thermograms. The DTA thermograms of the three semi-IPNs, P-1, P-2, and P-3, are shown in Figure 5 in the temperature range 200–350°C. As the PANI content of the semi-IPNs increased, the second exothermic peak shifted gradually to higher temperatures of 304–313°C, with a corresponding decrease in peak area. Sample P-3 was more stable than Sample P-1. In general, free sulfonic groups that would not have been bound (or interacted with) to the PANI would have been thermally active (17). However, when the sulfonic acid groups formed a complex with the imine nitrogen groups on the PANI chains, then they would have become more thermally stable. This indicates that the more interaction that occurs between the PANI and sulfonic acid groups of the PAMPS, the better thermal stability the semi-IPN.

### *Differential Scanning Calorimetry*

DSC thermograms of the PANI, PAMPS, and three semi-IPN samples are shown in Figure 6. The DSC thermograms of pure PANI showed a broad and shallow exothermic peak at 200–350°C, which was the result of the crosslinking reaction with the PANI

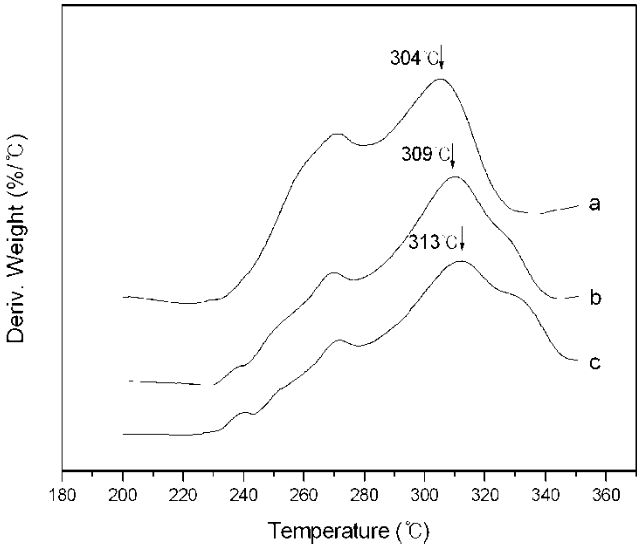

**Figure 5.** DTA curves of: (a) P-1, (b) P-2, and (c) P-3.

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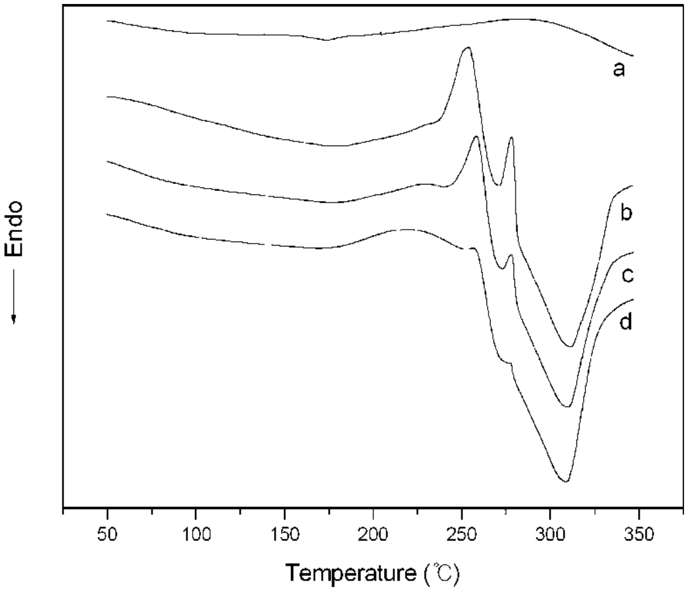

**Figure 6.** DSC curves of: (a) PANI, (b) P-1, (c) P-2, and (d) P-3.

chains. This crosslinking reaction is most likely to occur through linkages with the imine nitrogen and its neighboring quinoid ring.

Exothermic peaks caused by the thermal crosslinking reaction were also observed in the semi-IPNs at 280°C. This provides evidence that there was a plateau on the curves at 280°C, so that there was no degradation or decomposition of samples, as shown in Figure 5. The area of the exothermic peak increased as the PANI content in the semi-IPNs increased, as shown in Table 1.

Another exothermic peak at about 255°C was observed in the semi-IPNs. The relatively large exothermic peak, accompanied by a weight loss on the TGA trace (Curve b), indicates that this could be attributed to the degradation of the PAMPS. The area of this peak provides an indication of the magnitude of heat released during the degradation (or dehydration) of the PAMPS, and the breaking down of the hydrogen bonds between the solvent and the PAMPS networks. The large endothermic peak at 320°C, corresponding to the third weight loss process on the TGA trace, was due to the

**Table 1**
DSC thermogram data of PANI/PAMPS semi-IPNs

| | PANI content (%) | $T_{max}{}^{a}$ (°C) | $T_{max}{}^{b}$ (°C) | $Q_{exo}{}^{c}$ (J/g) |
|---|---|---|---|---|
| P-1 | 5 | 257.1 | 277.8 | 0.488 |
| P-2 | 10 | 259.02 | 278.39 | 2.188 |
| P-3 | 15 | 254.2 | 278.6 | 6.507 |

[a] Maximum temperature of the first exothermic peak.
[b] Maximum temperature of the second exothermic peak.
[c] Heat released during crosslinking of the PANI.

decomposition of the PAMPS, which was incorporated with the PANI as a polymeric acid dopant.

## Conclusions

Semi-IPNs composed of PANI and PAMPS were obtained using the simultaneous method. The incorporation of PANI in the PAMPS, which acts as a crosslinked network for PANI confinement and a polymeric acid dopant, was characterized using the FTIR and $^{13}$C-NMR methods. Moreover, XRD data showed that the semi-IPNs had an ordered packing structure, while the PANI has an amorphous structure. The $^{13}$C-NMR data verified the crosslinked network structure, and that a reaction between PANI and PAMPS were occurred in the semi-IPNs. The thermal properties of the semi-IPNs were investigated using TGA and DSC. The TGA data shows that IPNs with higher PANI content were more thermally stable than other IPNs with higher PANI content, which combined with the PAMPS as this is bonded to the imine nitrogen groups on the PANI chains. The DSC data shows several endothermic and exothermic peaks, and these are in agreement with the TGA data.

## Acknowledgement

This work is supported by the Korea Science and Engineering Foundation (KOSEF) under grant: R01-2005-000-10238-0.

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