

# Synthesis and Characterization of Proton-Conducting Copolymers on the Basis of Vinylpyrrolidone and Acrylamido Sulfonic Acid

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**ABSTRACT:** Free-radical copolymerizations of 1-vinyl-2-pyrrolidone with 2-acrylamido-2-methyl propane sulfonic acid at different feed ratios were investigated. The copolymers were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FTIR. The copolymer composition was determined from the elemental analysis. The molecular weights ( $M_w$ ,  $M_n$ ) and dispersities of the copolymers were determined by gel permeation chromatography. Thermogravimetric analysis indicated that copolymers are stable at least up to 200°C.

Temperature dependency of the alternating current (ac) conductivities was investigated by means of impedance spectroscopy. The direct current (dc) conductivities of the samples were obtained from the ac conductivity data. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3347–3353, 2003

**Key words:** copolymerization; thermal properties; proton-conducting copolymers; poly(vinylpyrrolidone); poly(acrylamido sulfonic acid)

## INTRODUCTION

The synthesis of novel proton-conducting polymer electrolytes with a variety of properties has been the focus of polymer research for many years for “high-tech” applications such as proton-exchange membranes (PEM) for fuel cells. Hydrated perfluorosulfonic polymers such as NAFION® is the most widely studied ionomer that has high proton conductivity at moderate temperatures.<sup>1</sup> However, there is a strong demand for water-free polymer membranes that may be applicable above 100°C. In this context, several blends of polymers and phosphoric acid have already been reported in the literature, among which are poly(ethylene oxide)–H<sub>3</sub>PO<sub>4</sub> and polybenzimidazol “doped” with H<sub>3</sub>PO<sub>4</sub>.<sup>2–5</sup> We previously reported on blends consisting of a cationic polyelectrolyte and phosphoric acid with reasonable conductivity.<sup>6,7</sup> Several single-ion conductive polymers have already been prepared by polymerization of sulfonated monomers.<sup>8</sup> Although these polymer electrolytes were designed to operate at higher temperatures, the conductivity of these materials remains low probably because of a high degree of ion pairing between cation and the immobilized anion.<sup>9</sup> Another approach for anhydrous proton-conducting polymer electrolytes is the substitution of water by heterocycles as proton-solvating species in the host polymer.<sup>10</sup>

Recently, proton conductivity in polymers based on proton solvents covalently bound by flexible spacers was demonstrated.<sup>16</sup> Also proton-conducting copolymers based on 2-acrylamido-2-methyl propane sulfonic acid (AMPSA) and 2-hydroxyethyl methacrylate were produced and their conductivity results were reported.<sup>17</sup>

Previously, the synthesis and solution properties of *N*-vinylpyrrolidone with different comonomers (i.e., *N,N*-dimethylacrylamide, sulfonate monomers) were discussed.<sup>11–13</sup>

In this work, proton-conducting polyelectrolytes were synthesized by free-radical copolymerization of AMPSA as a proton donor with 1-vinyl-2-pyrrolidone (VP) as a proton acceptor. Copolymers with different compositions were obtained and their thermal and conductivity properties are discussed.

## EXPERIMENTAL

### Chemicals

AMPSA (Merck, Darmstadt, Germany) was used as received. VP (Merck) was purified by distillation under nitrogen before use. Potassium persulfate was used as obtained from Merck with 99% purity.

### Synthesis of polyelectrolytes

Poly(2-acrylamido-2-methyl propane sulfonic acid) (PAMPSA) was synthesized in deionized water in which 1 mol % of potassium persulfate was used as an

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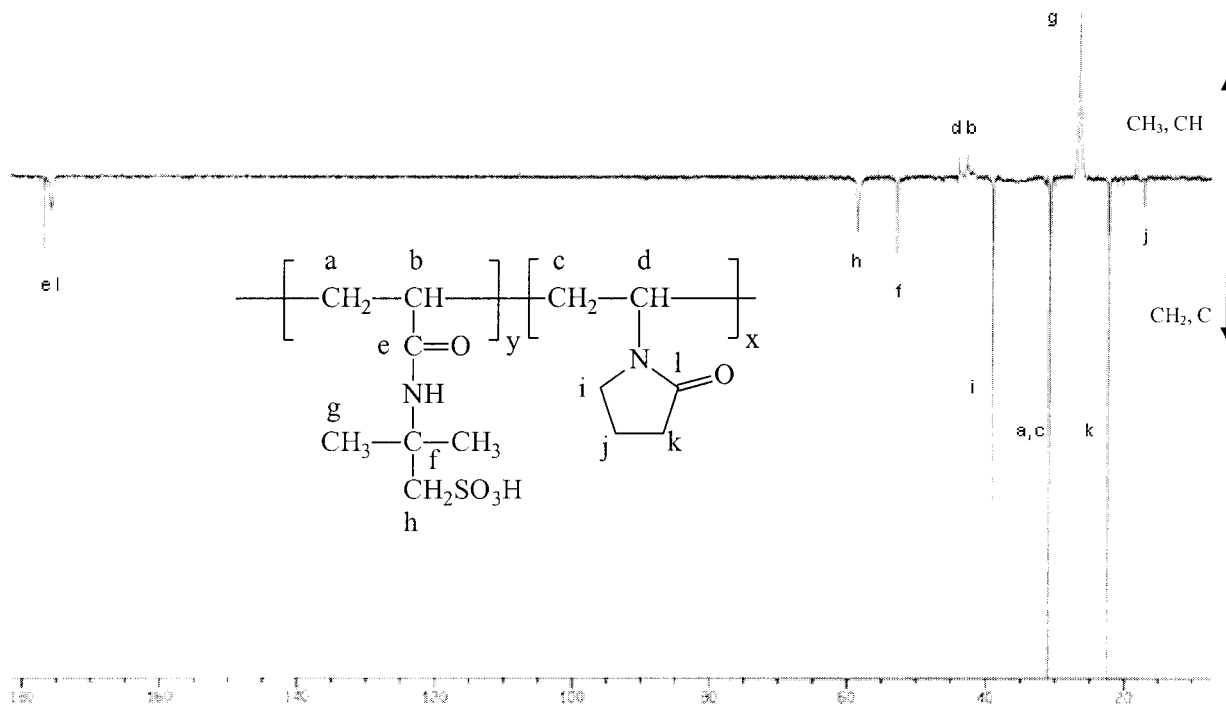


Figure 1  $^{13}\text{C}$ -NMR spectrum of copolymer X5 (250 MHz,  $\text{D}_2\text{O}$ ).

initiator. Polymerization of AMPSA was carried out at  $70^\circ\text{C}$  for 48 h, after which the homopolymer was purified by dialysis.

Copolymerization of AMPSA with VP was carried out with various monomer feed ratios: 1 : 16, 1 : 7, 1 : 4, 2 : 5, 1 : 2, and 5 : 3 (mol : mol) of the two monomers. The procedure for the synthesis of the copolymer of 1 : 2 (mol : mol) VP and AMPSA was as follows: 18 mmol VP, 9.2 mmol AMPSA, and 0.15 mmol potassium persulfate (1 mol % relative to the number of moles of the monomers) were dissolved in deionized water. The reaction mixture was stirred under nitrogen atmosphere at  $70^\circ\text{C}$  for a period of 48 h. After the polymerization, the copolymer was precipitated in excess THF (3 : 1, THF :  $\text{H}_2\text{O}$ ) and the residue was redissolved in distilled water and dialyzed with a 2000 MWCO membrane. The aqueous solution of the copolymer was freeze-dried.

### Characterizations

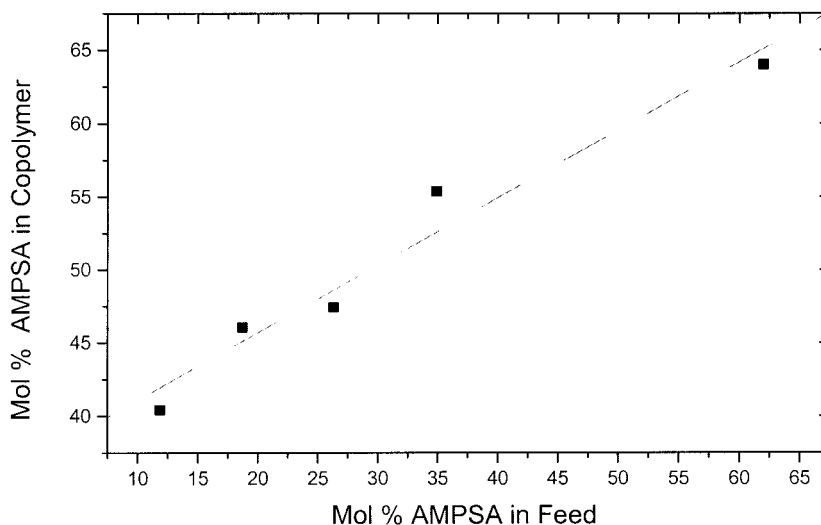
$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the samples were recorded with a Bruker (Rheinstetten, Germany) AC 250 spectrometer in  $\text{D}_2\text{O}$ . FTIR spectra of the polymers are recorded by depositing a thin film of the sample on a silicon wafer. The IR spectra were recorded with a Mattson Galaxy 2020 series spectrometer.

Elemental analysis data were determined by Prof. Dr. H. Melissa and G. Reuter GmbH Analytic Laboratories in Germany. GPC measurements were carried out using a UV S-3702 (Soma) detector. The eluent, 0.1M  $\text{NaNO}_3\text{-H}_2\text{O}$  solution was used with a flow rate of 1 mL/min. Calibration was carried out using a series of poly(ethylene oxide) (PEO) standards.

Thermogravimetric analyses of the homopolymers and copolymers were investigated with a TGA Mettler TG50 (Greifensee, Switzerland). The samples ( $\sim 10$

TABLE I  
Monomer VP ( $x$ ) and AMPSA ( $y$ ) in the Feed and Composition of the Copolymers

Sample	Feed ratio $x : y$ (mol : mol)	Elemental analysis data					Mol % $y$ in copolymer
		%C	%H	%N	%O	%S	
X1	16 : 1	45.60	7.58	9.29	28.50	8.9	42.1
X2	7 : 1	44.91	7.42	9.34	29.55	8.63	40.4
X3	4 : 1	44.83	7.55	9.20	29.03	9.49	46.1
X4	3 : 1	43.09	7.56	8.73	31.04	9.69	47.4
X5	2 : 1	41.78	7.50	9.38	30.56	10.8	55.5
X6	3 : 5	42.6	6.96	6.52	32.10	11.68	62.4



**Figure 2** Relationship of the feed monomer ratio and copolymer composition for the copolymerization of AMPSA and VP (70°C, 48 h, H<sub>2</sub>O).

mg) were heated at a rate of 10°C/min from room temperature to 600°C under inert atmosphere. The samples were dried 2 days under vacuum at 70°C before the measurement.

DSC data were obtained between -100 and +200°C using a Mettler DSC TA 3000 scanning calorimeter. The samples were weighed (10–15 mg) and loaded into aluminum pans and slowly cooled from room temperature to the starting temperature. Samples were then heated to the desired temperature at a scan rate of 10°C/min. The second heating curves were evaluated.

The ac conductivities of the copolymer samples were determined with a Novocontrol (Hundsangen, Germany) impedance spectrometer in the frequency range 10<sup>-2</sup>–10<sup>7</sup> Hz. The samples were placed between Au-coated steel plates and their conductivities were measured in the cooling cycle at 10-K intervals as a function of temperature and frequency. The temperature change was controlled with a Novocontrol cryo-system applicable between -150 and 500°C with a precision of 0.01°C. Before conductivity measurements the samples were dried under vacuum at 70°C for 2 days to minimize the content of moisture.

## RESULTS AND DISCUSSION

In this work six copolymerizations were conducted with different feed ratios of AMPSA and VP. Solution-cast copolymer films were transparent, pale yellow, and very hygroscopic. If the AMPSA content was too great (>45 mol %) brittle films would result, whereas the other samples were soft gels.

The copolymer structure was assigned on the basis of the high-resolution <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra. Figure 1 shows the <sup>13</sup>C-NMR spectrum of sample X5

in D<sub>2</sub>O as an example. Around 180 ppm two signals appear that can be assigned to both, the carbonyl carbons of VP and AMPSA. Signals corresponding to the methyl and methylene carbons appear between 17 and 60 ppm.

The compositions of the copolymers, calculated from the elemental analysis, are summarized in Table I. When AMPSA feed mol % is varied from 12 to 60 the AMPSA mol % in the copolymer changed from 42 to 62 (Fig. 2). A copolymer composition closer to an alternating one was observed even in the presence of the lowest content of AMPSA in the feed.

The number-average ( $M_n$ ) and weight-average molecular weights ( $M_w$ ) and polydispersity index of the copolymer samples were determined by gel permeation chromatography and are given in Table II. The polydispersity index is very close to unity for X1, which may be attributable to the low molecular weight of the copolymer at low AMPSA : VP feed ratio. It increases gradually for other compositions, reaching to 2.7 for X5.

Figure 3 shows the IR spectrum of copolymers X2 and X5 (see Table I). The CH<sub>2</sub> and CH<sub>3</sub> absorption peaks corresponding to both monomer-units are ob-

**TABLE II**  
Number-average ( $M_n$ ) and Weight-average Molecular Weights ( $M_w$ ) and Polydispersity Index ( $M_w/M_n$ ) of the Copolymer Samples

Sample	$M_n$ (g/mol)	$M_w$ (g/mol)	$M_w/M_n$
X1	4,876	6,568	1.347
X2	6,629	10,630	1.603
X3	10,660	20,260	1.901
X4	7,263	20,010	2.75
X5	24,500	67,460	2.7

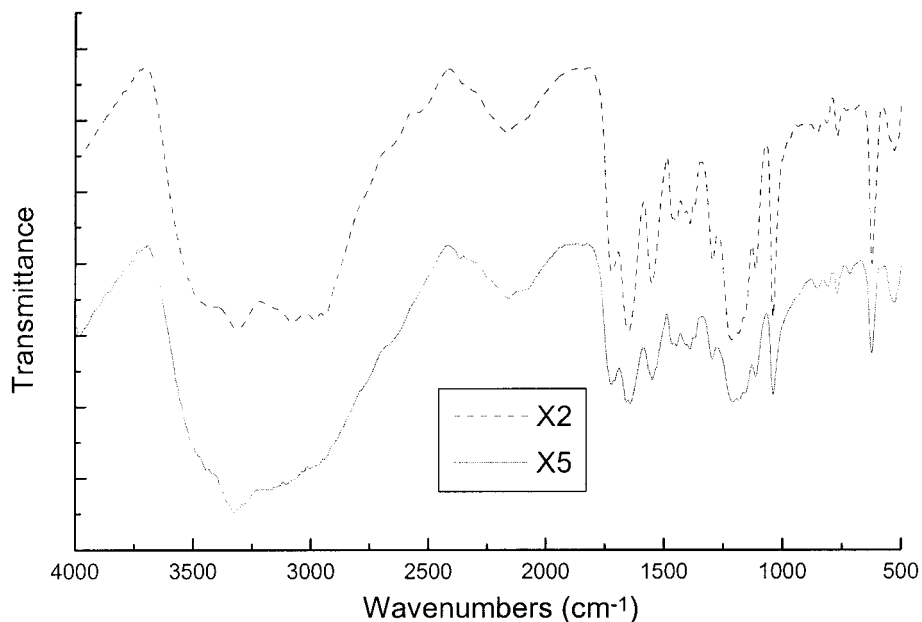


Figure 3 FTIR spectra of copolymers X2 and X5.

served at 1457, 1400, and 1037  $\text{cm}^{-1}$ . A medium absorption band of the C—N group of both monomers appears near 1550  $\text{cm}^{-1}$ . A strong absorption peak at 1035  $\text{cm}^{-1}$  belongs to  $-\text{SO}_3^-(\text{H}^+)$  and a broad band near 1200  $\text{cm}^{-1}$  is attributed to  $-\text{SO}_2$  stretching of the same group. The N—H asymmetric and symmetric absorptions of the AMPSA units are situated near 3100 and 3300  $\text{cm}^{-1}$ . The C=O stretching vibrations of amide groups of VP and AMPSA units of

the copolymer are placed near 1720 and 1647  $\text{cm}^{-1}$ , respectively. Broadening of these peaks at higher AMPSA-containing samples indicated the protonation C=O units. Previously, we described the protonation of the carbonyl groups in poly(vinylpyrrolidone).<sup>2</sup> The broad peak that expands toward higher wavenumbers (2500–3340  $\text{cm}^{-1}$ ) may be attributed to the formation of a hydrogen-bonding network.

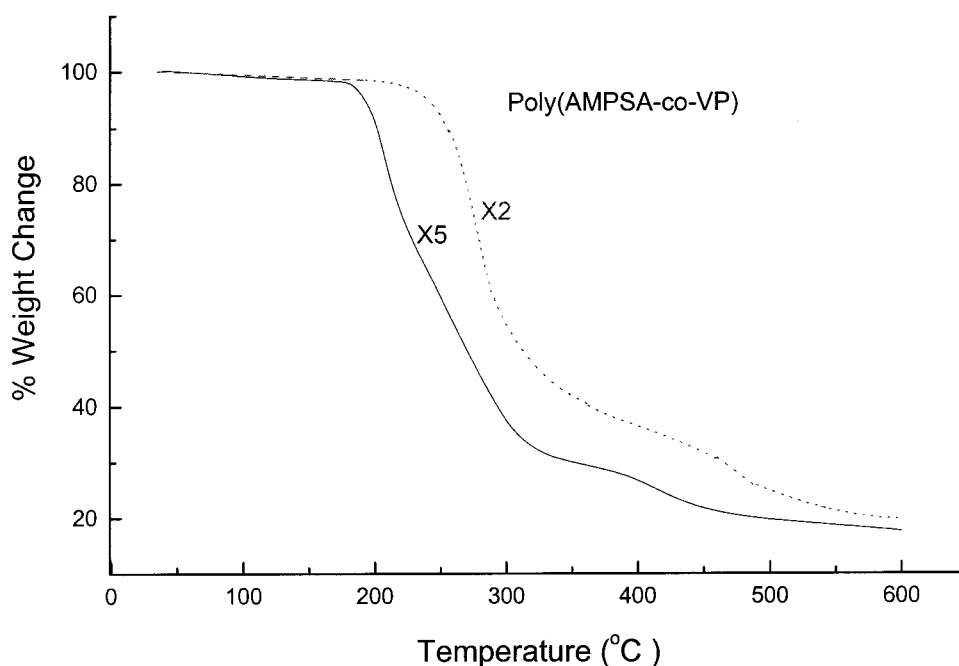
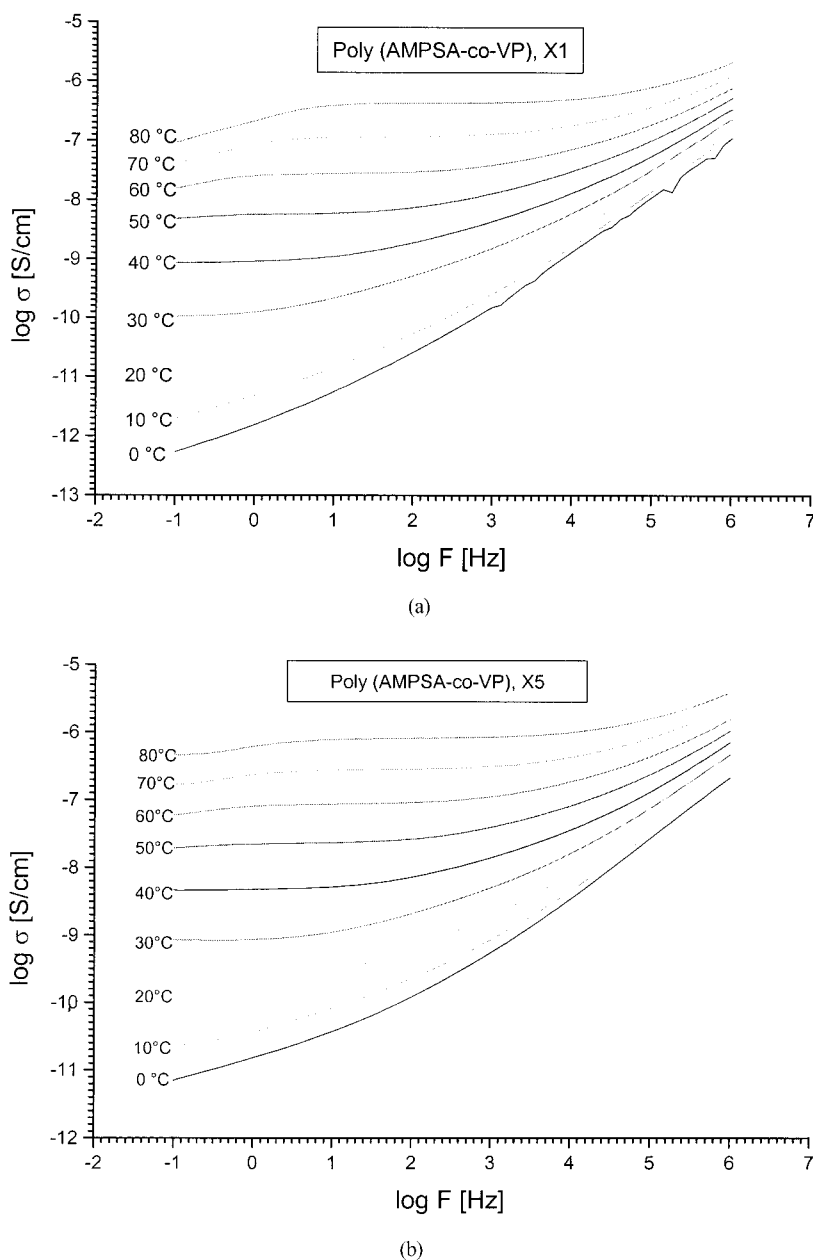


Figure 4 TGA curve of copolymers X2 and X5 recorded under  $\text{N}_2$  atmosphere at a heating rate of 10 K/min.



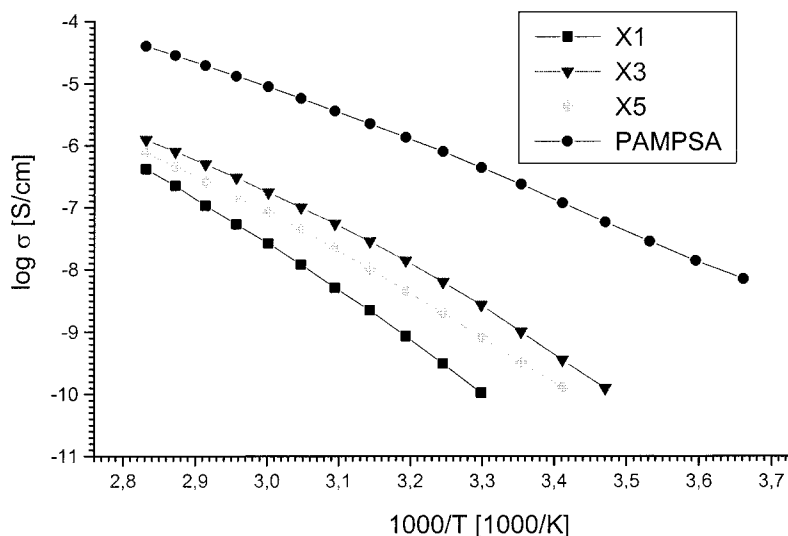
**Figure 5** (a)  $\sigma_{ac}$  (ac conductivity) versus frequency for copolymer X1 with temperature as parameter; (b)  $\sigma_{ac}$  versus frequency for copolymer X5 with temperature as parameter.

The TG curves of copolymers samples X2 and X5 are shown in Figure 4. The thermograms indicate that decomposition of the copolymers occurs in a single step (i.e., decomposition temperature of copolymer): X5 starts near 180°C and that of X2 is 250°C. TGA results indicate that the thermal stability of the copolymers increases with VP content.

The glass-transition temperatures ( $T_g$ ) of the homopolymers and copolymers were measured with DSC. The  $T_g$  values of PVP and PAMPSA were found to be 180 and 108°C, respectively. For copolymer X5, no traces of first-order (melting) or glass transition were detected up to its decomposition temperature.

This is probably a result of the restrictions of segmental motions in AMPSA because of hydrogen bonding.<sup>14</sup> However, for copolymers X1 and X2 a large shift of the glass-transition temperature relative to that of PVP homopolymer was observed (for X2 the  $T_g$  was near 33°C). The reason for such a shift may be attributed to the low molecular weights of the copolymers (Table II).

Conductivities of the copolymer samples were determined by an ac impedance spectrometer. Samples were placed between Au electrodes and conductivities were obtained at 10-K intervals within the frequency range  $10^{-2}$ – $10^7$  Hz.



**Figure 6** Temperature dependency of the dc conductivities of the homopolymer, PAMPSA, and copolymers X1, X3, and X5.

The ac conductivity  $\sigma_{ac}$  was obtained using the following equation:

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega \varepsilon_0 \quad (1)$$

where  $\sigma'(\omega)$  is the real part of conductivity, angular frequency  $\omega = 2\pi f$ , and  $\varepsilon_0$  is the vacuum permittivity ( $\varepsilon_0 = 8.852 \times 10^{-14}$  F/cm).

Figure 5 exhibits the ac conductivities of the X1 and X5 copolymers as a function of angular frequency in a log scale. At low temperatures (0–20°C),  $\sigma_{ac}$  increases strongly with frequency. Such a conductivity increase can be attributed to the “normal” dispersion in polymers.<sup>14</sup> At higher temperatures, a conductivity plateau is developed, the frequency range of which increases from low to higher frequencies with increasing temperature. The conductivity drop at the low-frequency edge of the plateau may be the result of the electrode polarization (blocking electrodes).

The dc conductivities ( $\sigma_{dc}$ ) of the samples were estimated from the conductivity plateaus. The plateau values in the medium frequency range coincide quite well with the  $\sigma_{dc}$  values obtained from the  $Z''$  minimum in the plot of imaginary part versus real part of the impedance ( $Z''/Z'$ ), so that  $\sigma_{dc}$  values could be taken from the extrapolation of the ac conductivity plateaus.

Figure 6 displays the  $\log \sigma_{dc}$  data versus  $1000/T$  for copolymers X1, X3, and X5, compared with that of the homopolymer PAMPSA. Clearly, the proton conductivity of the copolymers is more than one order of magnitude lower than that of PAMPSA. This may be the evidence of a smaller charge carrier concentration in the copolymers attributed to the number of pyrrolidone units in the backbone. At low temperatures the

$\sigma_{dc}$  conductivities of the copolymers are very low, so that no significant proton transport can be expected. However, the conductivities of these materials increase gradually with temperature. The dc conductivity in the measured temperature range is between  $10^{-6}$  and  $10^{-10}$  S/cm. For comparing the conductivity results one has to take into account that the charge carrier concentration of copolymer X5 is higher than that of X3, assuming that the number of charge carriers is determined by the number of sulfonic acid moieties only. However, the conductivity regimes are reversed. The higher conductivity of copolymer X3 may be attributed to a lower  $T_g$  compared to that of X5. FTIR confirmed the protonation C=O groups attributed to the solvation of  $-\text{SO}_3\text{H}$  units in the copolymer. The proton exchange may occur between protonated and nonprotonated units in the copolymer (structural diffusion).

## CONCLUSIONS

Novel proton-conducting copolymers were produced by immobilizing acidic and basic monomers in the backbone by radical copolymerization. Copolymers were characterized by FTIR,  $^{13}\text{C}$ -NMR spectroscopy, and elemental analysis. Molecular weights and polydispersities of the copolymers depend on the AMPSA : VP content. The thermal stability depends on the copolymer composition; however, most of the copolymers are stable at least up to 200°C. The dc conductivities of the dry copolymers are between  $10^{-6}$  and  $10^{-10}$  S/cm in the temperature range between 0 and 80°C. From the copolymer composition, FTIR, and  $\sigma_{dc}$  data, it can be concluded that the Grotthuss mechanism (struc-

tural diffusion) is the possible pathway for the proton transport.

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