The Effect of Pyridine Ring Functionalization on the Conductivity of Crosslinked *CO*-Poly(styrene-4-vinylpyridine) Derivatives

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SYNOPSIS

The effect of pyridine ring functionalization in crosslinked *co*-poly(styrene-4-vinylpyridine) on electrochemical behavior was studied using impedance spectroscopy. The introduction of a substituent on the nitrogen atom increases conductivity from 10^{-14} to around 10^{-11} Scm^{-1} at room temperature, but the effect of the substituent becomes more evident at 64°C, at which the *n*-butyl derivative (*co*-poly[styrene-[4-vinyl(N-butylpyridinium bromide)]])-(3) has a higher conductivity ($\sigma = 7 \times 10^{-10}$ Scm^{-1}) than the hydrogen analog (*co*-poly[styrene-[4-vinyl(pyridinium bromide)]])-(2) ($\sigma = 4.3 \times 10^{-10}$ Scm^{-1}), while the iodo derivative (*co*-poly[styrene-[4-vinyl(N-iodopyridinium bromide)]])-(6) has a conductivity ten times lower. Further increase in the conductivity was observed upon the substitution of the bromine anion with the three-bromide anion (Br$_3$)$^-$, but the effect depends on the substituent on the nitrogen atom: 4.4 times higher conductivity was found for the hydrogen pyridinium salt (4) in comparison with sample (2), and the conductivity increases 30-fold for the N-butyl derivative (5) compared with sample (3). The conductivity increased exponentially with temperature and the activation energy values vary from 0.76 to 1.01 eV. Impedance responses for dried samples of pyridinium salts (2), (3), (4), (5), and (6) suggested electron-type conductivity. The conductivity of crosslinked polymers depends very much on the conditions, and increases by several orders of magnitude when water or methanol is present in the atmosphere during measurement. The conductivity also depends on the structure of the substituent attached to the nitrogen atom: $\sigma = 5 \times 10^{-4}$ Scm^{-1} and $\sigma = 2 \times 10^{-4}$ Scm^{-1} for hydrogen bromide (2) and N-butyl bromide derivative (3), but the conductivity of the N-iodo derivative (6) changed very little. In contrast, the impedance responses for samples stored in the presence of water or methanol suggested ion conductivity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Electroactive polymers have gained an important position in polymer science. This "new" class of conductive materials includes electronic and ionic conducting polymers and polymers which are mixed electronic/ionic conductors. Their properties make them attractive for use in batteries, chemical sensors, electrochromic displays, and in other electrochemical devices.[1-3] In the quest for improved electrical conductivity and mechanical properties, both electronically conductive polymers and polymer electrolytes, either in solvent-free or solvent-swollen form, have been prepared and studied in many laboratories.[1] A large number of investigations have been performed on ion-conducting polymer electrolytes based on alkali metal salt complexes with poly(ethylene oxide) or poly(propylene oxide),[1,4,5] whereas much less attention has been paid to other types of polymer conductors.

Poly(vinylpyridinium) salts are polyelectrolytes in which positive charged groups are bound to the polymer (polycations) and small counterions, as halides, are associated with the fixed ionic charges on

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the polymer, thereby maintaining the electroneutrality of the polyionic substance. The nature of the current carriers and the mechanism of conduction in poly(vinylpyridinium) salts are still not clear.[6] Commonly, most anhydrous polyelectrolytes are hard materials with a high T_g, and exhibit very low conductivity[1,7,8] due to ion pairing and ion clustering, which significantly reduce the mobility of charge carriers.[9] On the other hand, some solvent-swollen polyelectrolytes have been identified as excellent protonic conductors.[1,10] It has been suggested[11] that this type of material is ideal for humidity sensors, as its conductivity increases linearly with ambient humidity. To increase the conductivity of dry solid polyelectrolytes, plasticizers are added[7] or different salts are used,[12,13] while Watanabe et al.[14] synthesized complexes of polypyridinium halide, pyridinium halide, and aluminum chloride, which exhibited high ionic conductivity.

It is well known that crosslinked polystyrene, crosslinked copolymers between styrene and 4-vinylpyridine, and crosslinked poly(4-vinylpyridine) have very low conductivity and can be used as insulators.[2,3] On the other hand, several chemical transformations of crosslinked poly(4-vinylpyridine) and crosslinked co-poly(styrene-4-vinylpyridine) were published, but their derivatives were mainly used as reagents or catalysts.[15-17]

In previous publications the authors reported chemical modifications of crosslinked polymers and the effect of chemical modification on the properties of polymers.[18-20] In the present work an investigation of the effect of nitrogen atom functionalization in crosslinked co-poly(styrene-4-vinylpyridine) on the electrochemical properties using impedance spectroscopy is (the ratio between benzene and pyridine rings is 3 : 2 and 2% crosslinking degree) undertaken.

EXPERIMENTAL

Crosslinked co-poly(styrene-4-vinylpyridine)[21] was functionalized with hydrogen bromide, butyl bromide, or iodine bromide, and the pyridinium bromide conversions using bromine were done according to literature procedures.[22-25] The numbering of the samples is given in Scheme 1.

Preparation of Samples for Impedance Measurements

All samples were ground using an achate pestle and mortar with chloroform into granules of diameter 10–100 μm, then pressed into cylinders under pressure of 30 MPa. The sample diameter and thickness were 8 and 2–3 mm, respectively. Drying was carried out at about 60°C under vacuum for at least 24 h. Samples prepared in such a way were sandwiched between a pair of identical electrodes made of conductive carbon cement (CCC) or copper foil pressed on a pellet previously sputtered with a thin layer of gold. They were then placed in an Ar-filled hermetically sealed desiccator-like glass cell with metallic leads, which were connected to the impedance analyzer. Dry samples were stored and measured in a Braun Ar-filled dry box facility (less then 1 ppm H_2O). The influence of atmosphere on conductivity was studied; dry samples were stored at different concentrations of water or methanol in the desiccator for 24 h.
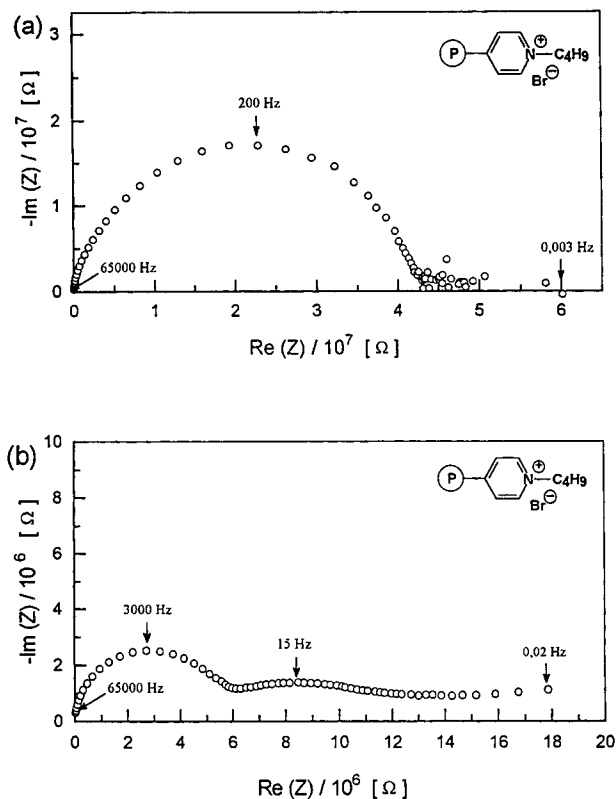
Impedance Measurements

The high-frequency impedance measurements were performed using a Hewlett-Packard 4284A impedance analyzer with a frequency range from 1 MHz to 20 Hz, while for the low-frequency impedance response measurements a Solartron 1250 Frequency Response Analyzer and a 1286 Electrochemical Interface with a frequency range of 65 kHz to 10 mHz were used. The amplitude of the AC voltage excitation was 1 V. Impedance responses were obtained as a function of temperature in the range of 25°C to 130°C. The temperature was measured using a Fe-Constantan thermocouple and controlled by a 4843 PARR regulator. The bulk resistance was evaluated from the impedance plot by fitting, using Voigt circuits with distributed C elements.[26]

RESULTS AND DISCUSSION

Chemical transformations of PVP (1) are shown in Scheme 1. Crosslinked polymer beads (1) were transformed with hydrogen bromide or n-butyl bromide to the corresponding hydrogen bromide salt (2) and N-butyl bromide salt (3), while the corresponding reaction with iodine bromide in chloroform yielded the N-iodo bromide salt (6). To study the effect of the size of the anion in the polymer matrix on conductivity, the anionic component of pyridinium salts was enlarged and three-bromide salts (4) and (5) were prepared by reactions of (2) and (3) with bromine.

Typical impedance spectra of dry samples are shown in Figure 1. It is well known that the type of electrode used may have a substantial effect on the measured impedance response.[27,28] Regarding solid

(a)

200 Hz

65000 Hz

0,003 Hz

-Im (Z) / 10^7 [Ω]

Re (Z) / 10^7 [Ω]

(b)

3000 Hz

15 Hz

0,02 Hz

65000 Hz

-Im (Z) / 10^6 [Ω]

Re (Z) / 10^6 [Ω]

Figure 1   The effect of electrode material on the impedance response of sample *3* at 128°C: (a) copper foil pressed on sputtered gold (b) conductive carbon cement.
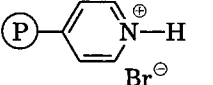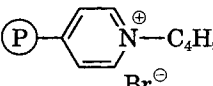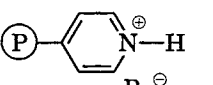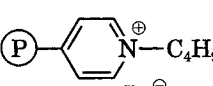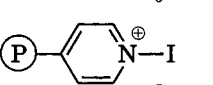
state samples, one of the requirements for a relevant impedance response measurement is that good physical contact is established between the electrode and the sample.[27,29] If the contrary is true, the so-called bulk impedance arc splits into two coupled arcs, of which one represents the true bulk sample properties, while the other represents the response of the region of poor contact. In this work several electrode types were tested with respect to the quality of contact. Figure 1(a) shows the impedance response of (*co*-poly[styrene-[4-vinyl(*N*-butylpyridinium bromide)]])-(*3*) measured using (a) a copper foil pressed against sputtered gold electrodes, and (b) electrodes made of conductive carbon cement (CCC). A detailed analysis using Voigt equivalent circuits with a variable number of elements shows that the apparent single arc in Figure 1(a) in fact consists of two closely coupled arcs with resistance values of 2.8 × 10^6 Ω and 3.9 × 10^7 Ω, whereas both capacitances have values of approximately 10^{-11} F/cm², i.e., the order of magnitude typically found for bulk sample response. On the other hand, the high-frequency arc in Figure 1(b) is a true single arc with a resistance of 5.0 × 10^{-6} Ω

and a capacitance of 10^{-11} F/cm². It is possible to conclude that in the former case there was poor contact between the electrodes and the sample, while in the latter measurement the contact area was practically 100% of the geometrical electrode surface area. A common characteristic of both measurements is that at low frequencies the phase angle [tan($Im(Z)/Re(Z)$)] tends to 0 degrees, which indicates the nonblocking character of the electrodes. Hence, it is assumed that under given experimental conditions (*co*-poly[styrene-[4-vinyl(*N*-butylpyridinium bromide)]])-(*3*), and due to analogy of impedance responses, other dry samples are also predominantly electronic conductors.

In order to compare the electrical properties of investigated compounds, the impedance responses of dry samples *2*, *3*, *4*, *5*, and *6* were studied at the same (room) temperature. Conductivities were calculated from impedance responses, and the effect of the structure of the polymer on conductivity is presented in Table I. It is evident that the conductivities of samples *2* and *3* are almost the same at room temperature and have values of approximately 10^{-11} Scm⁻¹, while the conductivity of sample *6* was out of the range of equipment and was estimated to be less than 10^{-11} Scm⁻¹. It is also evident from Table I that the substitution of the bromine anion in the polymer matrix with the much larger three-bromide anion $(Br_3)^-$ increases the conductivity of the copolymer, effect being more pronounced in cases in which butyl is bonded to the pyridine ring ($\sigma_{(5)}$ = 8.4 × 10^{-9} Scm⁻¹—30 times higher than $\sigma_{(3)}$) than in the hydrogen salt ($\sigma_{(4)}$ = 6.7 × 10^{-11} Scm⁻¹—4.4 times higher than $\sigma_{(2)}$). Obviously the conductivity at constant temperature is affected by the substitute attached to the pyridine ring as noticeably as by the size of the anion.

The effects of temperature and polymer structure on the conductivity of dry samples of functionalizate polymers *2*, *3*, *4*, *5*, and *6* were further investigated. With increasing temperature the conductivity of all five samples exponentially increases according to the Arrhenius relation $\sigma = \sigma_0 \cdot \exp(-E_a/kT)$ (Figs. 2–4). The reproducibility of impedance responses as a function of temperature and, indirectly, the temperature stability of the chemical composition of samples were investigated, and it was found that samples *2*, *3*, and *6* exhibit relatively good stability and the measurements of conductivity are reproducible, as can be seen in Figure 2. Conversely, three-bromide compounds *4* and *5* exhibit poor reproducibility and stability. A significant decrease in conductivity was observed during heat treatment. An Arrhenius plot for completely dry three-bromide
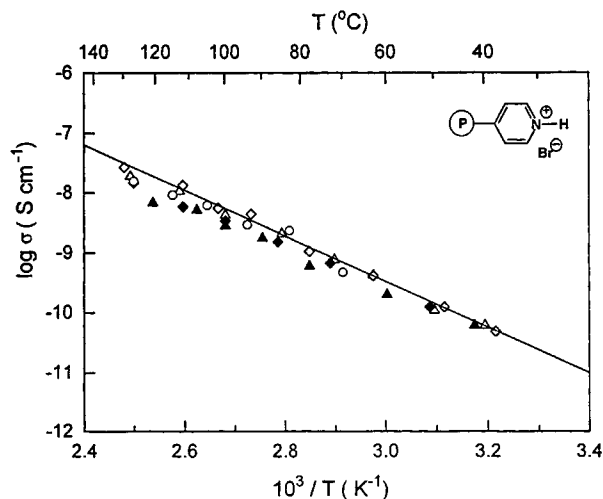
Table I **The Effect of Polymer Structure and Temperature on the Conductivity of Various Crosslinked co-Poly(styrene-4-vinylpyridine) Derivatives**

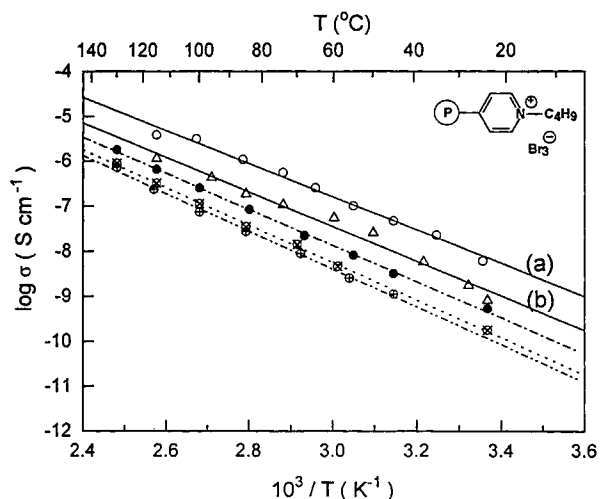| Samples | $\sigma(\text{Scm}^{-1})^a$ | | | E_{act} (eV)[b] | $\log(\sigma_0/\text{Scm}^{-1})^c$ |
	26°C	64°C	123°C		
ⓅN—H Br⊖ (2)	$\approx 1 \times 10^{-11}$	4.3×10^{-10}	2.1×10^{-8}	0.76	1.96
ⓅN—C_4H_9 Br⊖ (3)	$\approx 1 \times 10^{-11}$	7.0×10^{-10}	7.3×10^{-8}	0.91	4.38
ⓅN—H $Br_3^⊖$ (4)	6.7×10^{-11}	1.9×10^{-9}	9.9×10^{-8}	0.76	2.76
ⓅN—C_4H_9 $Br_3^⊖$ (5)	8.4×10^{-9}	2.1×10^{-7}	9.1×10^{-6}	0.73	4.29
ⓅN—I Br⊖ (6)	$< 10^{-11}$	3.1×10^{-11}	5.3×10^{-9}	1.01	4.55

^{a} $\sigma(1 \pm 0.3)$.
^{b} $E_{act}(1 \pm 0.06)$.
^{c} $\log \sigma_0(1 \pm 0.2)$.

sample 5 (heated at 55°C for 1 d) is shown in Figure 3 (straight line (a)). A decrease in conductivity occurs after each subsequent heating to 130°C (interrupted lines in Fig. 3), and also for the pellet heated
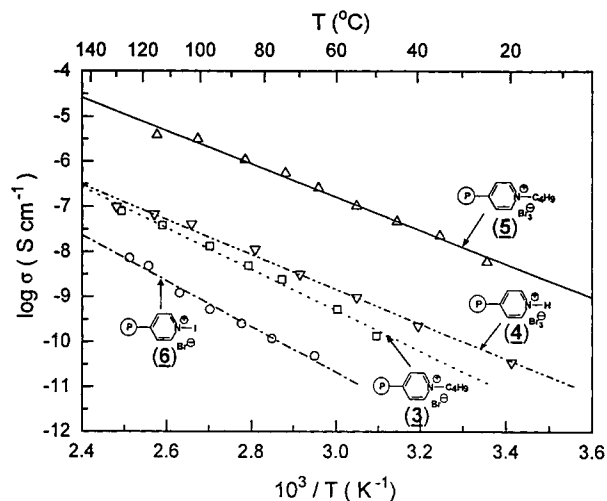
at 55°C for longer—7 days (line (b) in Fig. 3). The fall in conductivity may be explained by irreversible elimination of bromine in the Ar atmosphere. After

Figure 2 The effect of temperature on the conductivity of sample 2. Pellets were dried for various times under vacuum at 60°C: (△) 40 h, (○) 70 h, (◇) 80 h; solid signs correspond to a second measurement after cooling of samples to room temperature.

Figure 3 The effect of temperature on the conductivity of sample 5. Open signs belong to two different pellets dried at 55°C under vacuum for (a) (○) 1 d, (b) (△) 7 d. Signs (●) shows a second, (⊗) a third, and (⊕) a fourth measurement of pellet (a). After each heating the pellet was cooled to room temperature.

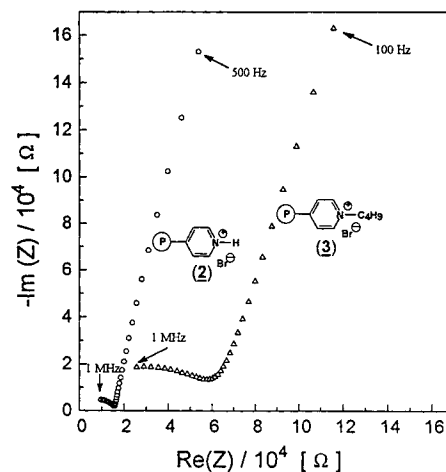**Figure 4** The effect of polymer structure and temperature on the conductivity of dry samples: (□) (*3*), (∇) (*4*), (△) (*5*), (○) (*6*).
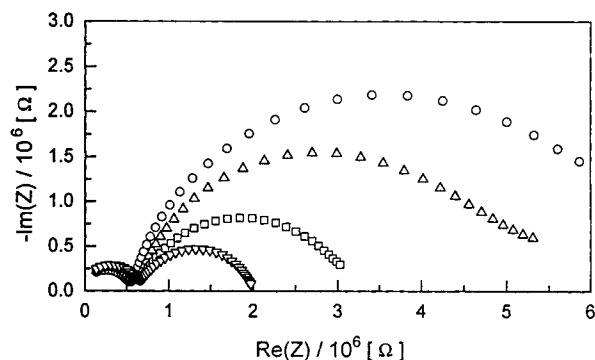
drying the bromine complex the amount of bromide salt in the sample increases (it is evident from Figure 4 that the bromide salts are much less conductive), and it is therefore thought that the ratio A : B (Scheme 2) is changing. The effect of temperature on conductivity for polymers *3*, *4*, *5*, and *6* is shown in Figure 4, while numerical values of the bulk electrical conductivities of all five samples for three temperatures, activation energies, and log σ_0 are given in Table I. It is obvious that the increase in conductivity with temperature depends on the substituent on the nitrogen atom. Comparison is more discernible at highest temperatures due to the limitations of the equipment used, which does not enable measurement of conductivities smaller than 10^{-11} Scm^{-1}. At 123°C the conductivity of the hydrogen derivative (*2*) ($\sigma = 2.1 \times 10^{-8}$ Scm^{-1}) is almost four times lower than the conductivity of the *N*-butyl compound (*3*) ($\sigma = 7.3 \times 10^{-8}$ Scm^{-1}) and four times higher than the conductivity of the *N*-iodo sample (*6*), which reaches 5.3×10^{-9} Scm^{-1} at 123°C. Calculated values of activation energy for samples *2*, *3*, and *6* vary from 0.76 to 1.01 eV, while for the resin bearing three-bromide anion (*4* and *5*) values between 0.76 and 0.73 eV were determined, which are very similar to the activation energy for *co*-poly[styrene-[4-vinyl(pyridinium bromide)]]-(*2*). The activation energy of samples (*4*) and (*5*) is lower, probably due to the elimination of bromine, but the reason why sample (*2*) differs from the first group is not clear.

Finally, the effect of the atmosphere on the conductivity of polymeric samples was investigated be-

cause it was found that a water or methanol environment greatly affected the increase of the conductivity of some samples. It is known from literature[1,2,8,11] that the conductivity of polyelectrolytes increases drastically on exposure to moisture. Very likely the hydration of the backbone charge takes place and the counterions behave as simple ions in an aqueous solution.[2,8] Higher conductivity could also be attributed to protonic conduction.[1,10] The impedance responses of wet samples *2* (exposed to 57% relative humidity, percentage of increase of weight of pellets during exposure to humidity— $\Delta m/m \times 100 = 6\%$) and *3*, ($\Delta m/m \times 100 = 5.5\%$) as shown in Figure 5, have a different shape to those obtained for dry samples (Fig. 1). A typical impedance response of a wet sample consists of a high frequency "arc" and a low frequency "tail." The first

Figure 5 The effect of polymer structure on the impedance response for wet samples: ($\Delta m/m \times 100 = 6\%$ for *2* and $\Delta m/m \times 100 = 5.5\%$ for *3*).

Figure 6 The effect of the dc voltage bias applied on the impedance response for sample *3* exposed to methanol atmosphere ($\Delta m/m \times 100 = 5.1\%$), where (○) shows impedance response without DC voltage bias, while (△) indicates DC voltage bias of 0.5 V, (□) 1V, and (∇) 1.5 V.
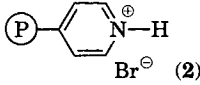
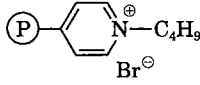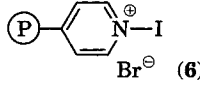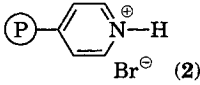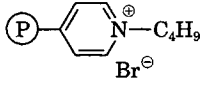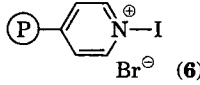is unaffected by the DC voltage bias, while the tail alters significantly with increasing DC bias (Fig. 6). From the impedance spectra it can be concluded that the high frequency arcs of the response belong to the bulk, while the low frequency tails belong to the interface between the bulk sample and the CCC. At low frequencies the phase angle of the imaginary part of the impedance response progressively increased. It is evident that the incorporation of solvent (water or methanol) not only increased the conductivity, but a change also occurred in the type of conduction (Figs. 1 and 5). The behavior of wet samples during impedance measurements could indicate ionic-type conductivity. In Table 2 the effect of water content on the conductivities of samples 2, 3, and 6 is shown. In a typical experiment a dry pellet with CCC electrodes was left for 24 h in an Ar atmosphere with a known amount of water or methanol. The change in the weight of the pellet and the impedance were measured at 29°C in a dry

Ar atmosphere. The weights of samples 2 and 3 and their conductivities increase linearly with water or methanol content (Fig. 7), while the conductivity of sample 6 remains almost constant (Table II). When kept at 57% relative humidity the conductivities of samples 2 and 3 increase by approximately six orders of magnitude ($\approx 10^{-5}$ Scm^{-1}), while at 100% relative humidity values of 5×10^{-4} Scm^{-1} and 2×10^{-4} Scm^{-1} were established for sample 2 and sample 3. The effect of water on conductivity is reversible. All pellets under vacuum reach the same low conductivity after drying as before exposure to methanol or water atmosphere.
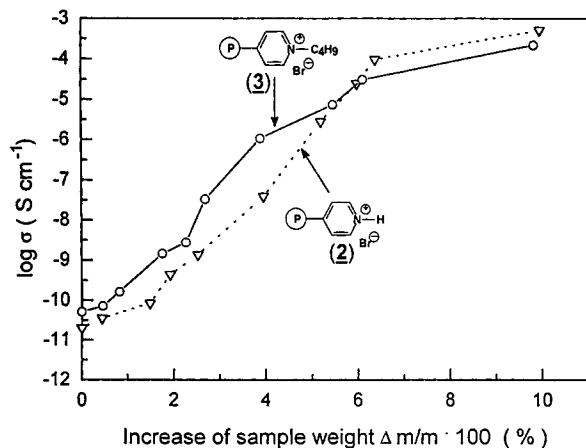
CONCLUSION

The conductivity of crosslinked co-poly(styrene-4-vinylpyridine) was increased by functionalization of the nitrogen atom in the pyridine ring, and was de-

Table II The Effect of Polymer Structure and Water or Methanol Contents in Atmosphere on the Conductivity of Samples (2), (3) and (6) at 29°C
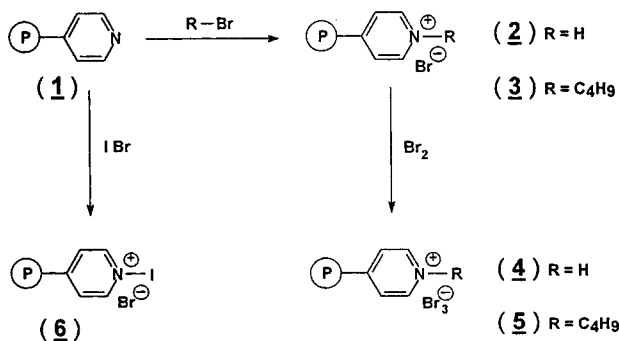
(a) H₂O Atmosphere	P—$N^{\oplus}$—H Br$^{\ominus}$ (2)		P—$N^{\oplus}$—C₄H₉ Br$^{\ominus}$ (3)		P—$N^{\oplus}$—I Br$^{\ominus}$ (6)	
Percentage relative humidity at 29°C (%)	$\frac{\Delta m}{m} \times 100$ (%)	log(σ/Scm^{-1})	$\frac{\Delta m}{m} \times 100$ (%)	log(σ/Scm^{-1})	$\frac{\Delta m}{m} \times 100$ (%)	log(σ/Scm^{-1})
0	0	< -10.5	0	-10.30	0	< -10.5
5	0.5	-10.45	0.5	-10.15	0	< -10.5
14	1.5	-10.09	0.8	-9.80	0	< -10.5
22	1.9	-9.364	1.8	-8.84	0	< -10.5
27	2.5	-8.867	2.3	-8.56	0	< -10.5
40	4.0	-7.413	2.7	-7.48	0	< -10.5
49	5.2	-5.551	3.9	-5.96	0	< -10.5
57	6.0	-4.609	5.5	-5.13	0	< -10.5
70	6.4	-4.017	6.1	-4.51	0	< -10.5
100	9.9	-3.291	9.8	-3.67	1.4	-9.95

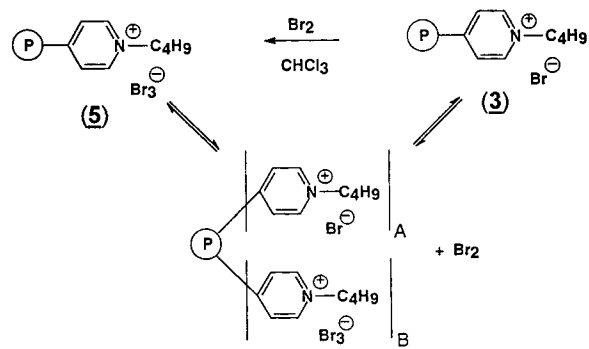| (b) Methanol Atmosphere	P—$N^{\oplus}$—H Br$^{\ominus}$ (2)		P—$N^{\oplus}$—C₄H₉ Br$^{\ominus}$ (3)		P—$N^{\oplus}$—I Br$^{\ominus}$ (6)	
Percentage saturated concentration of methanol at 29 (%)	$\frac{\Delta m}{m} \times 100$ (%)	log(σ/Scm^{-1})	$\frac{\Delta m}{m} \times 100$ (%)	log(σ/Scm^{-1})	$\frac{\Delta m}{m} \times 100$ (%)	log(σ/Scm^{-1})
0	0	< -10.5	0	-10.30	0	< -10.5
10	1.3	-9.86	1.8	-9.16	0	< -10.5
20	2.3	-8.55	4.0	-7.83	0	< -10.5
30	3.2	-7.70	4.5	-7.07	0	< -10.5
40	3.7	-6.91	5.1	-6.40	0	< -10.5
55	4.5	-5.91	6.3	-5.58	0	< -10.5
63	5.3	-5.72	8.0	-5.44	0.4	-10.5
75	6.6	-5.51	9.0	-5.39	0.8	-10.4
100	—ᵃ	—	—	—	1.4	-9.9

ᵃ Pellets swollen and declined.

Figure 7 The effect of water content on conductivity of co-poly[styrene-[4-vinyl(pyridinium bromide)]]- *2* and co-poly[styrene-[4-vinyl(*N*-butylpyridinium bromide)]]- *3* at 29°C.

pendent on the substituent attached to the pyridinium ring as well on anion size. Differences in conductivity were perceived at room temperature, but became more evident at 64°C, when co-poly[styrene-[4-vinyl(*N*-butylpyridinium bromide)]]-*3* exhibits a higher conductivity (σ = 7.0 × 10^{-10} Scm^{-1}) than co-poly[styrene-[4-vinyl(pyridinium bromide)]]-*2* (σ = 4.3 × 10^{-10} Scm^{-1}) and co-poly[styrene-[4-vinyl(*N*-iodopyridinium bromide)]]-*6* (σ = 0.3 × 10^{-10} Scm^{-1}). The substitution of the bromine anion with the larger three-bromide anion additionally contributes to an increase in the conductivity of the crosslinked copolymer, while the magnitude of this increase depends on the substituent on the nitrogen atom. At 64°C the conductivity of hydrogen three bromide derivative *4* increased more than fourfold (σ = 1.9 × 10^{-9} Scm^{-1}), while the *N*-butyl three-bromide salt *5* has a conductivity 30 times higher (σ = 2.1 × 10^{-7}

(P).... crosslinked copolymer styrene-4-vinylpyridine

Scheme 1.

Scheme 2.

Scm^{-1}) than the bromine analog. The conductivity varies with temperature according to the Arrhenius relation and the corresponding activation energies of dried polymers vary from 0.76 to 1.01 eV. Water or methanol presence in the atmosphere increases the conductivity of co-polymers by several orders of magnitude. The conductivities of the hydrogen bromide (*2*) and the *N*-butyl bromide derivative (*3*) reach the values 2.5 × 10^{-5} Scm^{-1} and 7.4 × 10^{-6} Scm^{-1} at average humidity, and 5 × 10^{-4} Scm^{-1} and 2 × 10^{-4} Scm^{-1} at 100% relative humidity, while the conductivity of the iodine derivative (*6*) is almost unaffected. The incorporation of solvents into pellets is reversible. The shape of impedance responses indicated that dried polymers exhibit predominantly electronic conductivity, while the samples exposed to a water or methanol environment become predominantly ionic conductors.

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