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Formation of polyelectrolyte complexes based on pendant type imidazolium organosilicon polymer with poly(sodium styrene sulfonate)

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Two novel polyelectrolyte complexes (PEC) have been synthesized using pendant type imidazolinium organosilicon copolymers with poly(sodium styrene sulfonate). These PEC dissolved in a ternary solvent system and displayed high thermal stability. Turbimetry and conductometry measurements showed PEC formation to be a stoichiometric reaction. The formation of PEC was decreased with increasing polyion concentration and organic solvent, but decreased with decreasing dielectric constant of the solvent. © 1998 Elsevier Science Ltd. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polyelectrolyte complex; imidazolium organosilicon polymer; poly(sodium styrene sulfonate))

INTRODUCTION

The study of polyelectrolyte complexes (PEC) formed by the electrostatic interaction of oppositely charged polyelectrolytes is of great importance both from a scientific and a practical point of view[1–6]. PEC have been applied extensively in advanced technologies such as medicine, pharmaceutical, semi-permeable membranes and electrographic print[7–10]. Until now there has been little investigation of the preparation and characterization of PEC using organosilicon polymer. Recently, there was a report about the formation of complexes of *N*-organosiloxane poly-2-methyl-5-vinylpyridiniums with polyacrylic acid[11]. We have reported on the preparation and characterization of PEC formed using copolymer of imidazolinium organosilicon-bisphenol A with poly(styrene sulfonic acid)[12]. In the present paper the preparation of PEC using two species of pendant type imidazolinium organosilicon polymers with poly(sodium styrene sulfonate) is described. The products formed were studied using turbimetry and conductometric titration. In addition, thermal characterization of the PEC and phase diagrams of the interpolymer complex–solvent system were investigated.

EXPERIMENT

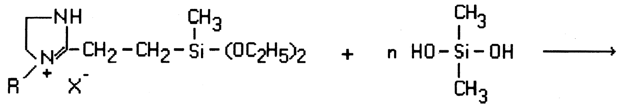
Materials

β-(*N*-Ethyl-2-imidazolinium bromide) ethyl methyl diethoxy silane (I) and β-(*N*-benzyl-2-imidazolinium chloride) ethyl methyl diethoxy silane (II) were synthesized as described previously[12]. Dimethyl silandiol (III) was prepared (white needles, m.p. 66–67°C). Sodium styrene sulfonate was purchased and used without further purification.

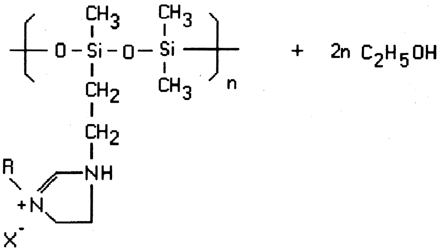
Polymer synthesis

Poly(sodium styrene sulfonate) (NaPSS), used as polyanion, was obtained in aqueous solution using $K_2S_2O_8$–$NaHSO_3$ redox as initiator. A 25% solution of NaPSS (0.24 mol) was prepared, and dry nitrogen bubbled through with vigorous stirring. $K_2S_2O_8$ (5×10^{-2} mmol) and $NaHSO_3$ (2.5×10^{-2} mmol) were added to the solution, and polymerization was carried out at 45°C for 5 h. The polymer solution was neutralized with aqueous NaOH to adjust the pH to 7. Then the polymer was precipitated by pouring it into a large excess of ethanol and purified by repeated precipitation. It was then dried under vacuum for 24 h at 30°C. Its intrinsic viscosity, determined viscometrically in 0.1 M NaCl corresponded to a molecular weight of 3.46×10^4 ($[\eta] = 1.78 \times 10^{-3}$ $[M]^{0.68}$)[13].

Imidazolinium polysiloxane (IV) and (V), used as polycations, were prepared by melting polycondensation of various quaternary ammonium halides of β-(2-imidazolinyl) ethyl methyl diethoxy silane (I) (II) with dimethyl silandiol (III). The synthetic route for the condensation polymer is as follows:



(I) (II) (III)



(IV) (V)

(I) (IV) : R=C_2H_5 X=Br

(II) (V) : R=$C_6H_5CH_2$ X=Cl

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Preparation of condensation polymer was carried out as follows. A 100 ml three-necked round-bottom flask was charged with 9.2 g (0.1 mol) dimethyl silandiol and 33.9 g (0.1 mol) β-(N-ethyl-2-imidazolinium bromide) ethyl methyl diethoxy silane. The mixture was stirred and heated at 100°C for 16 h, under reduced pressure (0.009 kPa), and ethanol was successively distilled. The resulting polymer ranged from viscious liquid to brown gel and was dissolved in 75% ethanol and reprecipitated into absolute ethanol to give a yellowish-brown brittle solid. Elemental analyses and molecular weight of condensation polymers are summarized in *Table 1*.

Table 1 Condensed polymerization of imidazolinium organosilicon with silanediol

Polymer	Halogen (%)		$M_w \times 10^{-3}$
	Calc.	Found	
(IV)[a]	23.53	23.69 (Br)	5.97
(V)[b]	9.94	10.22 (Cl)	5.79

[a]Copolymer of compound (I) with dimethyl silanediol
[b]Coplymer of compound (II) with dimethyl silanediol
M_w was measured by g.p.c.

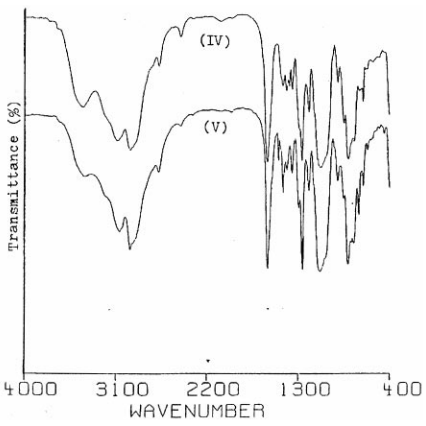

Figure 1 I.r. spectrum of copolymers (IV) and (V)

Preparation of PEC

Diluent solutions of polycation (0.1 M) and polyanion (0.1 M) were made up. Polycation solution was added dropwise to a polyanion solution while stirring for 2 days. The polyelectrolyte complex precipitate was separated by centrifugation, washed and dried in vacuum.

Solubility of PEC

The solubility of the PEC formed was determined using a three-component solubility diagram consisting of inorganic salt, organic solvent and water. All measurements were carried out in a 100 ml electric conductance cell at 30°C with magnetic agitation. Then, 15 mg of PEC was added in 10 g inorganic salt–H_2O mixed solution at various ratios of weight per weight (g/g). The organic solvents were added slowly dropwise into this mixed solution while the solution was vigorously stirred until it appeared transparent (i.e. lower limit of solubility), then the organic solvents were added in a continuous stream until the solution became turbid (i.e. upper limit of solubility). The solubility diagram was completed by connecting each limit.

Yields of PEC

Dilute solutions of polycation (V) (0.1 M) and polyanion NaPSS (0.1 M) were made up. Then, 3 ml of 0.1 M polycation (V) solution was added to each of eight weighted centrifugal tubes. Varying amounts of polyanion NaPSS solution were added to the centrifugal tubes. The reaction was conducted at 25°C for 0.5 h with stirring and allowed to

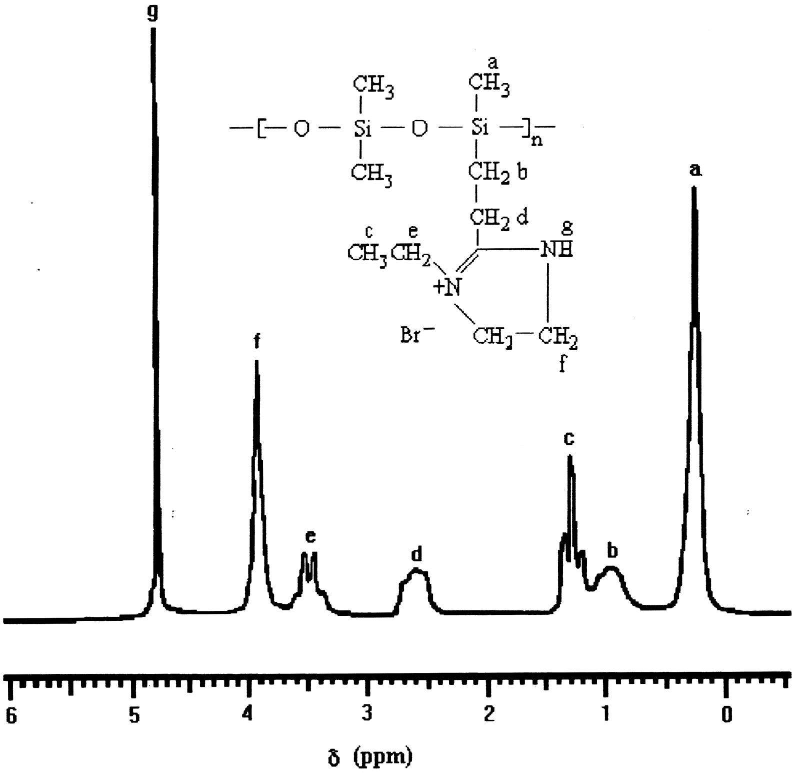

Figure 2 ^1H n.m.r. (90 MHz: D_2O) spectrum of copolymer (IV)

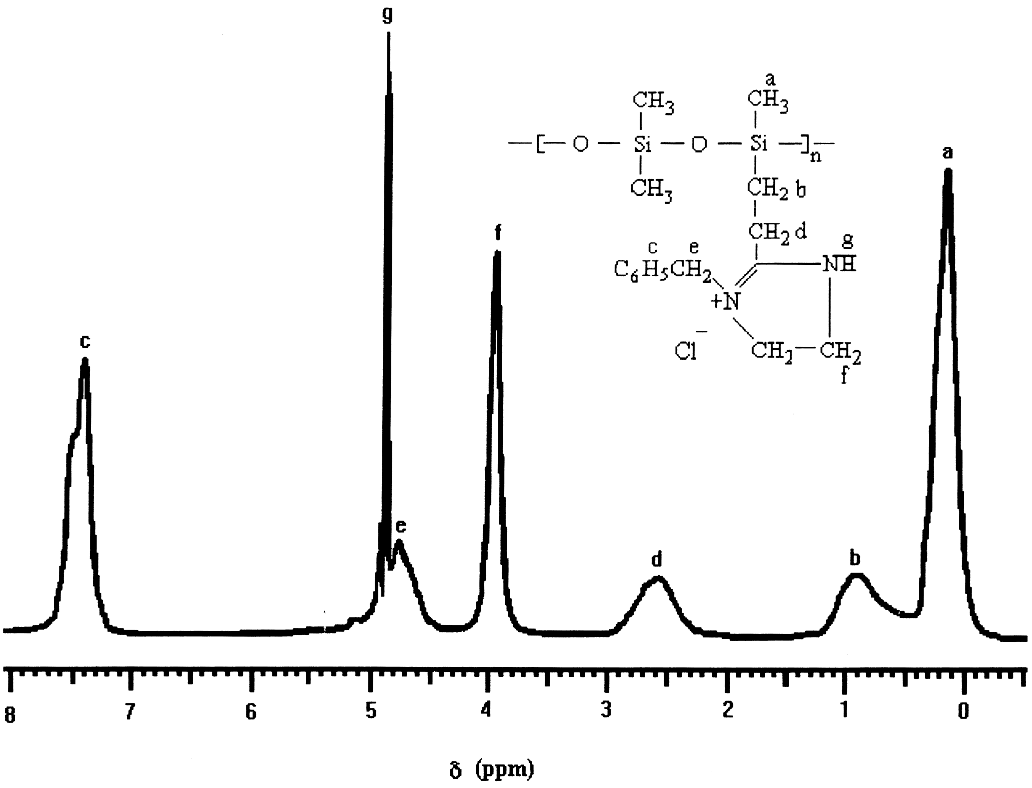

Figure 3 ^1H n.m.r. (90 MHz: D_2O) spectrum of copolymer (V)

react for 2 days at room temperature. The PEC precipitate was separated by centrifugation, washed several times with water and dried in vacuum.

The percent complex yield was calculated by:

$$\text{Yield (\%)} = \frac{\text{Sample (g)}}{3 \times 0.1 \times 10^{-3} \times M} \times 100$$

where M is the mass of segment unit of PEC.

Measurements

The molecular weight of the copolymers was estimated by gel permeation chromatography (GPC) with a Linear Ultrahydrogel Column (Waters Associates) calibrated with PEO standards. The flow rate of the aqueous fluent was maintained at 0.7 ml/min.

I.r. spectra were recorded on a NICOLET FT-20 SX spectrometer as KBr pellets.

^3H n.m.r. spectra were conducted with a FX-90 Q (90 MHz) spectrometer using D_2O as solvent.

Differential scanning calorimetry (d.s.c.) was conducted with RigaKu standard type. Nitrogen was used as purge gas and Al_2O_3 as reference.

The turbidity of the mixed solution at various molar ratios was measured after 2 min at 20°C using a 72-type photoelectric colorimeter at 500 nm.

The conductivities were measured with platinum–platinum (black) electrodes (DDS-11 type) at 25°C in high frequency. The concentration of a dilute polyion solution is 0.01 M and the supernatant of the mixed solution was measured after 2 days. In addition, the degree of stoichiometry attained was assessed by a comparison of the conductivity of the reaction mixture with that of a contrast solution made up to the composition expected for stoichimetric reaction and complete counterion release (NaBr or NaCl solution).

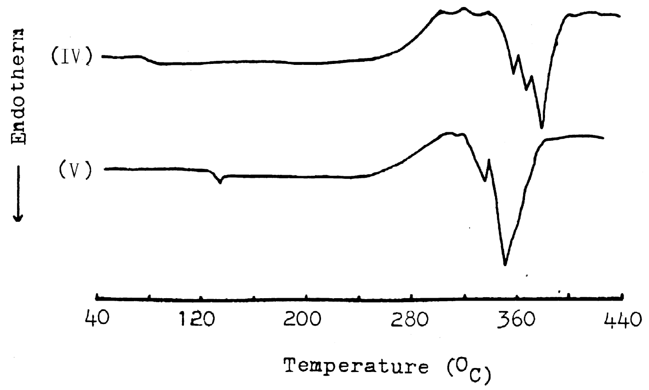

Figure 4 D.s.c. traces displayed during the first heating scan (heating rate: 10°C/min) for copolymers (1) (IV) and (2) (V)

RESULTS AND DISCUSSION

Figure 1 shows the infrared spectra of copolymers (IV) and (V), all of which exhibit absorptions at 1607, 3415 and 1080 cm^{-1}, characteristic of C=N, N–H and Si–O–Si bonds of imidazolinium organosilicon copolymer. However, the i.r. spectrum of copolymer (V) showed a phenyl group absorption peak at 1499 cm^{-1}. The ^3H n.m.r. spectra of copolymers (IV) and (V) with peak assignments are shown in *Figures 2* and *3*, respectively.

Figure 4 shows the d.s.c. curves of copolymers (IV) and (V). The glass transition temperature (T_g) increased successively: (IV), 73°C; (V), 128°C.

Polyanion (NaPSS) and polycation (V) are water soluble. The PEC prepared from these oppositely charged polyelectrolytes were insoluble in water, but dissolved in a ternary solvent system consisting of water, a strongly ionized microsalt, and a water-compatible organic solvent. *Figures*

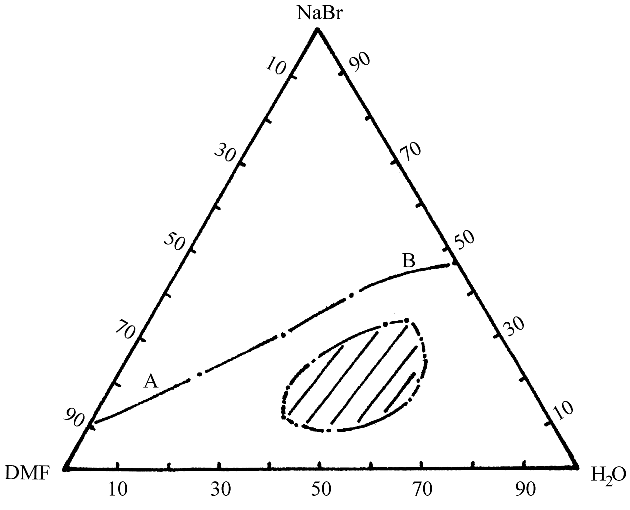

Figure 5 Solvent system of NaPSS–(V). H_2O–DMF–NaBr, 30°C

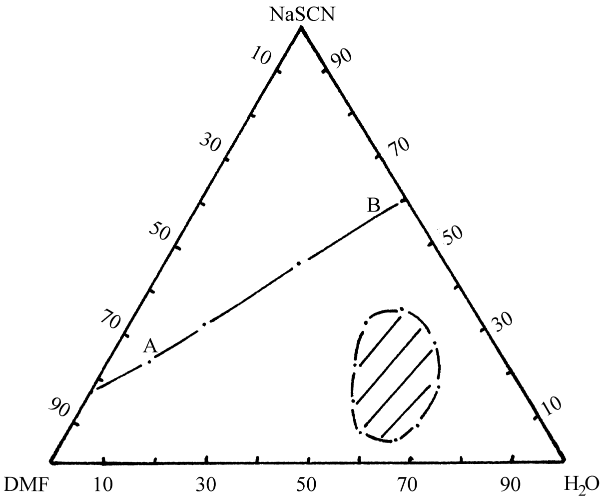

Figure 7 Solvent system of NaPSS–(V). H_2O–DMF–NaSCN, 30°C

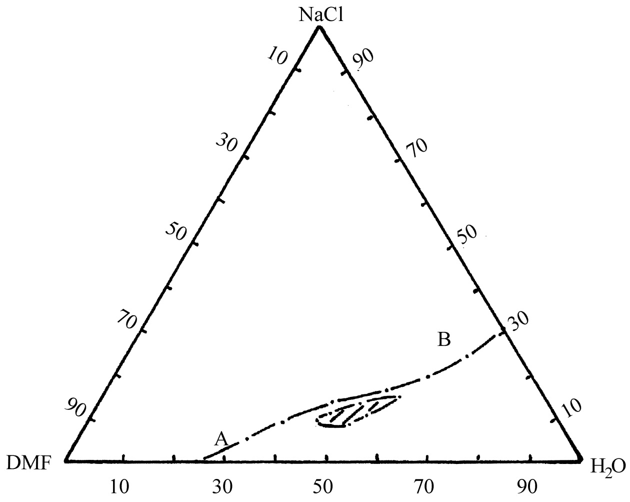

Figure 6 Solvent system of NaPSS–(V). H_2O–DMF–NaCl, 30°C

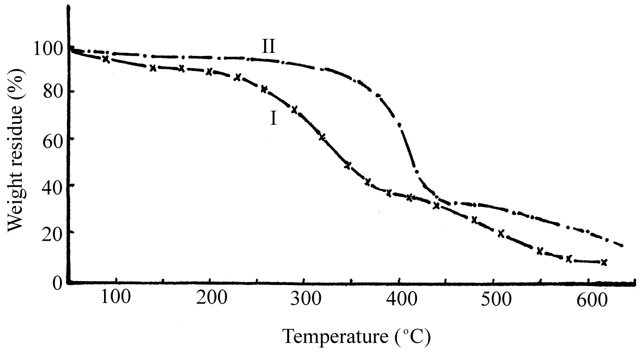

Figure 8 Thermogravimetric curve of PEC and the NaPSS–(V) mixture at a heating rate of 10°C/min in nitrogen

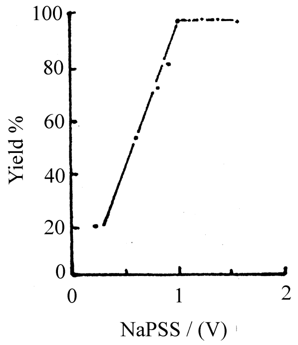

Figure 9 Relation between complex yield and mixing ratio. [NaPSS] = [(V)] = 0.1 M

5–7 depict a series phase diagram for a ternary solvent system consisting of H_2O–DMF–NaBr, H_2O–DMF–NaCl and H_2O–DMF–NaSCN of PEC of NaPSS-(V) at 30°C, respectively. The A–B curve shows the miscibility limit of a ternary solvent system. The shadow region denotes the range of solvent compositions that gives homogeneous, transparent and viscous solutions of PEC. *Figures 5–7* show that the solubility regions of this PEC are different for various ternary solvent systems. The solubility region of NaPSS–(V) is narrow in the H_2O–DMF–NaCl system, but broad in H_2O–DMF–NaBr and H_2O–DMF–NaSCN. The results indicate that the difference is dependent on dissociation energy and the size of the ionic radius of the microsalt. The solubilizing activity of the ternary solvent system is believed to result from the shielding activity of the microsalt, which weakens the electostatic interactions between macromolecules. Moreover, the solvating action of organic solvent on backbones of the polyelectrolytes may weaken hydrophobic interactions. The special solubility of PEC confirmed that the polyanion–polycation electrolyte pairs formed a network structure by the electrostatic interactions of the two oppositely charged polyelectrolytes.

In *Figure 8*, curve I is a thermogravimetric curve relating to the NaPSS–(V) mixture. It can be seen that there are two weight loss steps: the first located at 220°C (referable to (V)) and the second at 420°C (referable to NaPSS). Curve II is the TG curve of PEC of NaPSS–(V), there is only one weight loss step at 378°C (wt% loss 6.1). This indicates that the thermal stability of the PEC is higher than that of the NaPSS–(V) mixture. It was confirmed that the oppositely charged polyelectrolytes, when brought together in an aqueous solution, formed an intermolecular complex by chemical bonding rather than a mixture.

Figure 9 shows PEC yields *versus* various mixing ratios for a polyion NaPSS-(V) solution. It was found that in spite of the difference in molecular weight between polyanion

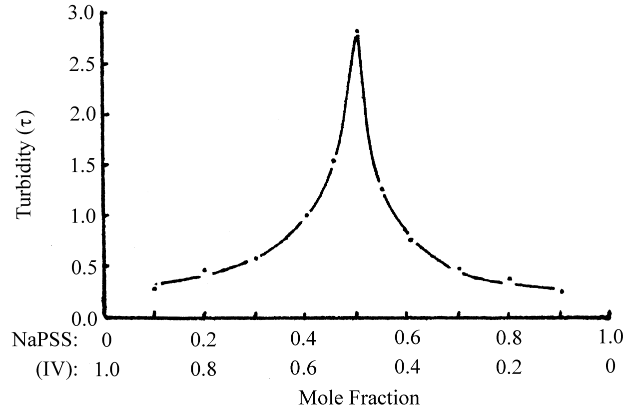

Figure 10 Effect of mole fraction of NaPSS–(IV) system on turbidity. 1×10^{-2} mol/L [NaPSS]–1×10^{-2} mol/L [(IV)]

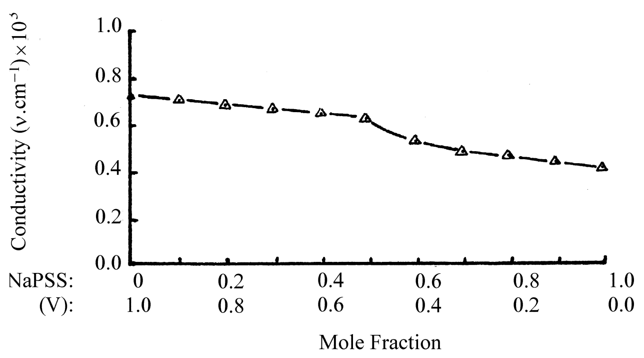

Figure 12 Conductances of NaPSS–(V) system and contrast solution. 1×10^{-2} mol/L [NaPSS]–1×10^{-2} mol/L [(V)]; 25°C; pH 7.0. △, NaPSS–(V) system; ●, contrast solution

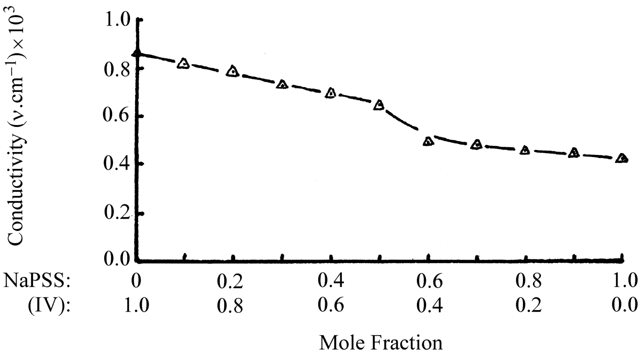

Figure 11 Conductances of NaPSS–(IV) system and contrast solution. 1×10^{-2} mol/L [NaPSS]–1×10^{-2} mol/L [(IV)]; 25°C; pH 7.0. △, NaPSS–(IV) system; ●, contrast solution

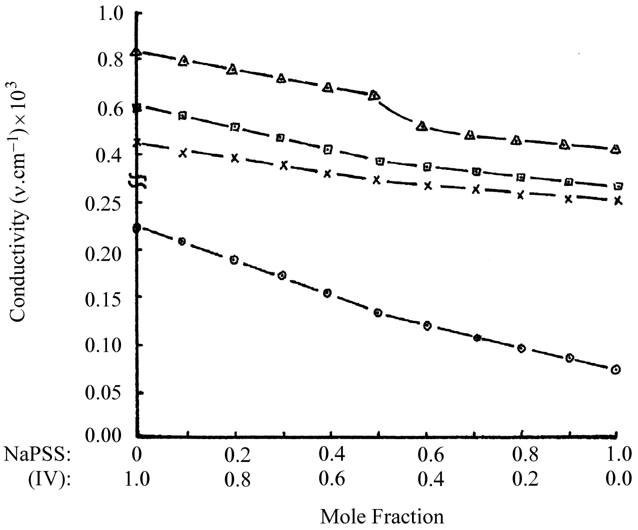

Figure 13 Effects of NaPSS–(IV) system concentration on conductance. △, 1×10^{-2} mol/L [NaPSS]–1×10^{-2} mol/L [(IV)]; □, 0.75×10^{-2} mol/L [NaPSS]–0.75×10^{-2} mol/L [(IV)]; ×, 0.5×10^{-2} mol/L [NaPSS]–0.5×10^{-2} mol/L [(IV)]; ○, 0.25×10^{-2} mol/L [NaPSS]–0.25×10^{-2} mol/L [(IV)]; 20°C, pH 7.0

NaPSS ($M_w = 3.46 \times 10^4$) and polycation (V) ($M_w = 5.79 \times 10^3$), PEC yields increased with increasing concentration of NaPSS. The maximum PEC yields attained 100% at NaPSS/(V) = 1, which was described as a stoichiometric reaction (composition 1:1). The excess of polyanion NaPSS did not influence formation of the PEC.

Such formation of PEC can also be studied by the turbidimetric method. The dependence of the turbidity of the NaPSS-(IV) reaction system on mole fraction is shown in *Figure 10*. The turbidity of the NaPSS–(IV) reaction system increased rapidly with increasing the mole fraction of NaPSS. At a concentration 0.01 M, the maximum turbidity attained 2.8 at 0.5 mole fraction of NaPSS, which was also described as a stoichiometric reaction (composition 1:1).

The mixing of oppositely charged polyelectrolytes leads to the formation of PEC and the release of microsalt, which has an effect on the conductivity of the reaction mixture system. As a result, the formation of PEC can also be illustrated by conductometric studies. *Figures 11* and *12* show the conductivity of NaPSS–(IV) and NaPSS–(V) reaction systems compared with that of the contrast solution, respectively. The conductivity of the NaPSS–(IV) and NaPSS–(V) reaction systems decreased gradually with an increase in the mole fraction of NaPSS and was identical with that of the contrast solution. There was a turning point at 0.5 mole fraction of NaPSS, which was also described as a stoichiometric reaction (composition 1:1). Comparing *Figures 11* and *12*, the conductivity of the NaPSS–(IV) reaction system was greater than that of NaPSS–(V) because the conductivity of the released microsalt (NaBr) was greater than that of NaCl. *Figure 13* shows the dependence of the conductivity of the NaPSS–(IV) reaction mixture on mole fraction at various concentrations of a polyion pair solution. All the conductivity curves are the same in that the conductivity decreased with the concentration of the polyion pair in the solution.

The possibility of the formation of PEC was observed not only in water, but also in some organic solvent[14,15]. Since the component polyelectrolytes are difficult to dissolve in organic solvent, only few studies on the organic solvent effect on the formation of PEC are reported. The conductivity curves of the NaPSS–(IV) system in C_2H_5OH–H_2O, CH_3COCH_3–H_2O and DMF–H_2O are shown in *Figure 14*. These indicate that the conductivity of these reaction systems also decreases with increasing mole fraction of NaPSS. All the conductivity curves deviate from that of the contrast solution, and the deviation of the conductivity curves of these systems is in this order: DMF–H_2O>CH_3COCH_3–H_2O>C_2H_5OH–

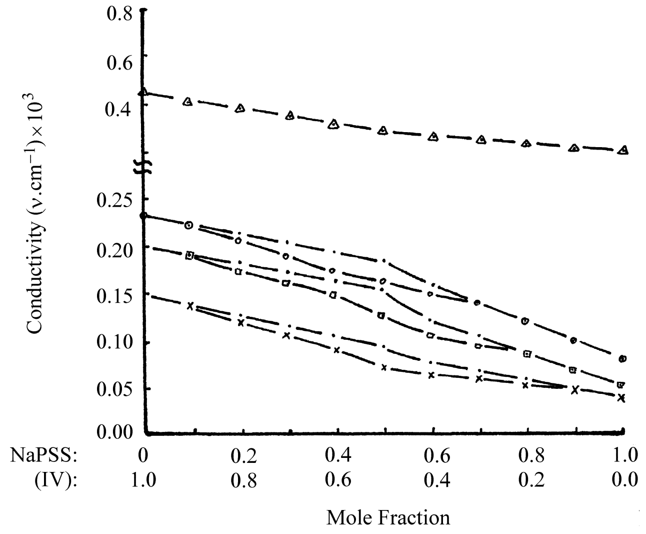

Figure 14 Effects of various organic solvents on conductance. △, 1×10^{-2} mol/L [NaPSS]–0.5×10^{-2} mol/L [(IV)] aqueous solution; ○, 1×10^{-2} mol/L [NaPSS]–0.5×10^{-2} mol/L [(IV)] in C_2H_5OH–H_2O (20:80); □, 1×10^{-2} mol/L [NaPSS]–0.5×10^{-2} mol/L [(IV)] in CH_3COCH_3–H_2O (20:80); ×, 1×10^{-2} mol/L [NaPSS]–0.5×10^{-2} mol/L [(IV)] in DMF–H_2O (20:80); 20°C, pH 7.0

H_2O. *Figure 15* shows the effect of C_2H_5OH concentration on the conductivity of the NaPSS–(IV) system, the deviation of the conductivity curve increased with increasing concentration of C_2H_5OH solution. The above mentioned results illustrate that the degree of dissociation of the polyelectrolyte component decreases with a decrease in the dielectric constant (ε) of the solvent (ε: $H_2O > C_2H_5OH > CH_3COCH_3 >$ DMF) and with an increase in the concentration of organic solvent. In addition, hydrophobic interactions stabilize the complex, but they were considerably weakened in organic solvent.

CONCLUSION

PEC based on two imidazolinum silicone polymers with poly(sodium styrene sulfonate) were synthesized. The PEC were studied using turbimetry and conductometric titration. It was shown that the compositions of NaPSS–(IV) and NaPSS–(V) were 1:1. Conductometric titration showed that polycation structure, polyion concentration, organic solvent, and the organic solvent concentration affected PEC formation.

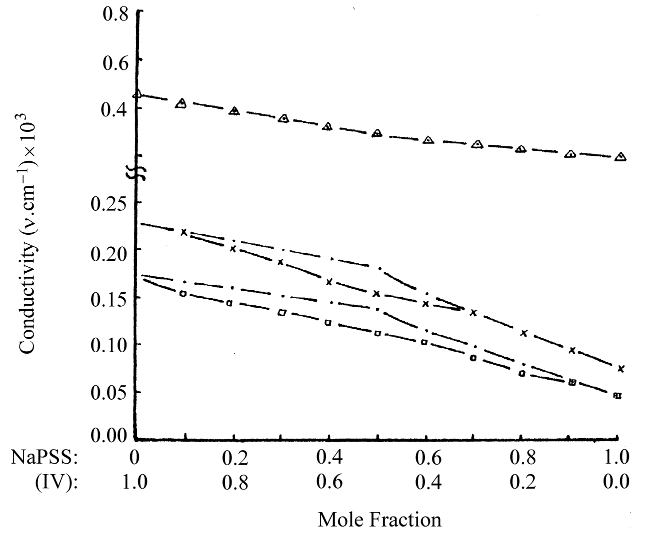

Figure 15 Effects of C_2H_5OH concentration on conductance. △, 1×10^{-2} mol/L [NaPSS]–0.5×10^{-2} mol/L [(IV)] aqueous solution; ×, 1×10^{-2} mol/L [NaPSS]–0.5×10^{-2} mol/L [(IV)] in C_2H_5OH–H_2O (20:80); □, 1×10^{-2} mol/L [NaPSS]–0.5×10^{-2} mol/L [(IV)] in C_2H_5OH–H_2O (40:60); 20°C, pH 7.0

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