Ionic Conductivity Studies on Salt–Polyzwitterion Systems

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ABSTRACT: In this work, the results for the ionic conductivity properties on zwitterionic polymers of the sulfobetaine type are presented. The polymers include various structures of the inner-salt kind resulting from chemical modification of precursor nonionic polymers. Measurements performed on pure polymer samples and polymer–salt mixtures are carried out by the ac spectroscopy technique, and the analysis of the results is made through complex impedance curves. Salts used include sodium iodide, lithium perchlorate, and sodium tetraphenylborate at several concentrations (0–1 M). Variations of conductivity with temperature follow an Arrhenius behavior, with values found within the range from 10^{-6} to 10^{-4} S cm^{-1}. The highest values correspond to the pure polymer samples and also to the equimolar mixture. Dielectric relaxation studies included analyses of the real and imaginary parts of the impedance as a function of frequency in the range from 5 Hz to 13 MHz. The results show a Debye-type behavior within 0.2–0.8 M salt concentration and significant deviations for the pure polymer and the equimolar mixture.

1. Introduction

Polymers of the sulfobetaine type have been extensively studied by Galin and co-workers.[1,2] These materials present interesting properties, which include their ability to be dissolved in mineral salts at high proportions. For instance, the system polysulfobetaine/lithium perchlorate showed no substantial segregation up to ratios of the order of 1:1 M, and extensive phase segregation occurred only at 1.25 M salt per mole of monomer.

Ionic conductivity polymer systems have been given considerable attention, due to their potential value as solid electrolytes for high-energy density batteries. Polyether–alkali metal salt complexes have been by far the more widely studied systems, owing to their high conductivity values.[3,4]

The ion transport in these systems has been observed to occur primarily within the amorphous region of the polymer, where cooperative interactions of neighboring polar groups and ions may generate many ion carriers. Simultaneously, high segmental mobility corresponding to low glass transition temperature (T_g) may enhance the mobility of these carriers.

In most of these studies, the general dependence of the conductivity on the salt content is found to increase within a short range of small salt proportions, and this trend is followed by a pronounced decrease for higher salt contents. Homogeneous solid solutions of these systems are observed only at low salt proportions.

The observed decrease in conductivity at high salt concentrations in the polyether–alkali metal salt systems is attributed to several factors. On the one hand, the extent of solvation of the salt by the polymer to form free ions decreases as the salt concentration increases,[5] indicating a low dissociation of the salt and high crystallinity of the system. On the other hand, it is found that the production of ion carriers is favored when the glass transition temperature difference (ΔT_g) between the polymer–salt system and the pure polymer is large. In these systems, T_g increases monotonically with added salt, but saturation is found for high salt fractions. At this point, ionization diminishes and leads to a decrease in conductivity.

Numerous analyses on ionic conductivity made on polymeric materials conclude that high conductivity at ambient temperature may be obtained in systems that present a large concentration of highly polar groups and low glass transition temperature.[6] The zwitterionic systems studied in this work present highly polar groups, where strong dipoles of lateral pendant structures are likely to contribute to fast ionic transport. The polymers include zwitterionic pendant groups whose general structure is shown in Figure 1. Here, three variations of this structure are possible, depending on the chain length between the backbone and the nitrogen atom and on the length between this atom and the SO_3 group. These systems may provide new evidence of the influence of molecular structure on conductivity, in addition to improve the understanding of ionic conductivity in polymeric materials.

2. Experimental Section

Synthesis of the Polymeric Systems. Polymers were synthesized by aqueous solution polymerization from monomers provided by Aldrich, according to the technique used by Monroy and Galin.[1] The general structure of the corresponding polymers is shown in Figure 1.

Characterization. The structure of the materials was verified by FTIR (Nicolet FTIR 5MX) and NMR (Varian EM-360). Figure 2 shows two spectra corresponding to the expected structure. The chemical composition was also verified by elemental analysis (Perkin-Elmer 250C), and the molecular weights were determined by GPC in aqueous solution, using sodium poly(styrene sulfonate) as the standard. An Ultrahydrogel column was used at 40 °C in a Waters-150C chromatograph linked to a microprocessor. Intrinsic viscosities were determined in an Ubbelohde viscometer.

Polymer–Salt System Preparation. Solid blends were prepared by freeze-drying of the corresponding aqueous solutions at −198 °C and under vacuum at 10^{-2} Torr for 24 h. The structure and formation of the homogeneous solution were verified by X-ray diffraction (Siemens refractometer D-500) using the powder method. The experimental conditions included a sweep from 2 to 70° at 1 deg/min, under Cu Kα radiation. Samples were also analyzed by a scanning microscope with polarized light, and the thermal behavior was determined by differential scanning calorimetry on a Perkin-Elmer DSC II.

Dielectric Measurements. Powder samples were pressed at 3 ton/cm^2 for 25 min, to obtain disk-shaped pellets of less than a millimeter thick and with 12-mm diameter. Silver paste was applied to both sides, and gold foil electrodes were attached and dried at 70 °C for 1 h to harden the paste. The resulting arrangement had the structure silver/polymer electrolyte/silver.

Samples were encased in a Pyrex glass cell, and this was placed inside a temperature-controlled furnace with a 150-W electric bulb as the heating source. The temperature was monitored (±1 °C) by a thermocouple placed adjacent (10 mm) to the sample

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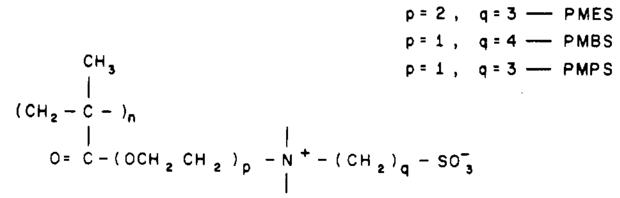

$$\left(CH_2-\overset{CH_3}{\underset{|}{C}}-\right)_n \quad O{=}C-(OCH_2CH_2)_p-N^+-(CH_2)_q-SO_3^-$$

Figure 1. Molecular structure of the zwitterionic polymers. For example PMPS: [(methacryloyloxy)ethyl][1-(3-sulfopropyl)]ammonium inner salt.

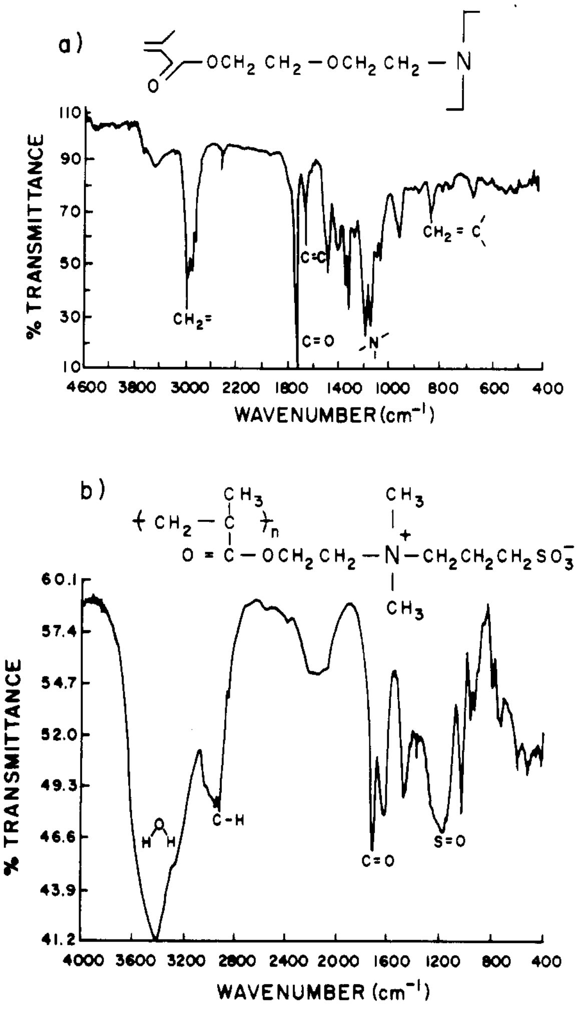

Figure 2. Infrared spectra of the precursor polymer (a) and those of the quaternized polymer (b), indicating the chemical groups associated with the corresponding intensity bands.

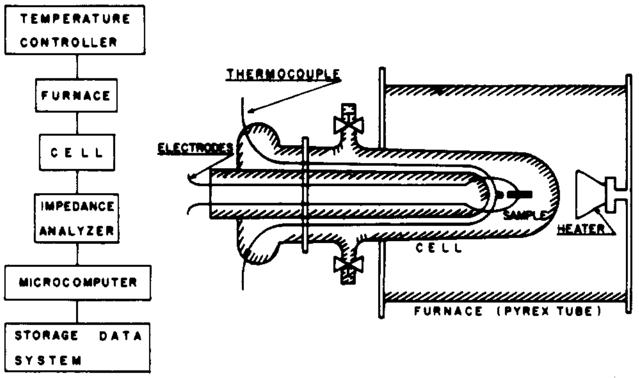

Figure 3. Experimental apparatus.

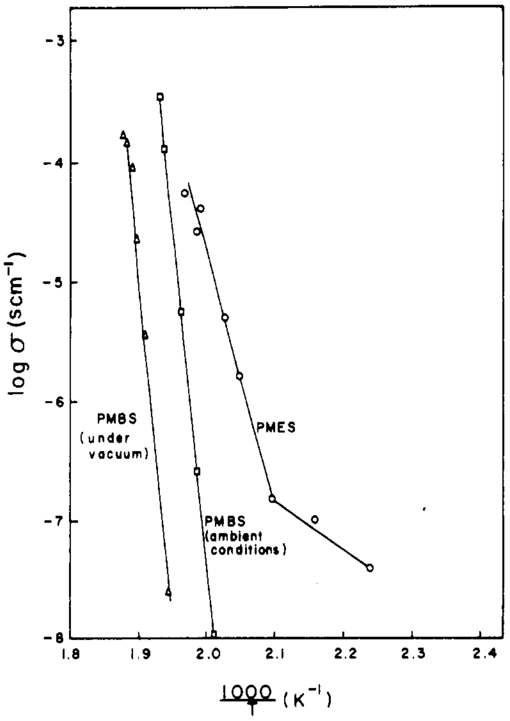

Figure 4. Arrhenius plots of conductivity vs inverse temperature for two polymer samples.

(see Figure 3). To eliminate any trace of water, samples were previously placed in the furnace at 50 °C for 12 h.

Alternating current conductivity measurements were made by using a Hewlett-Packard 4192A impedance analyzer controlled by a HP-85 microcomputer. Measurements were made under vacuum after a sufficient time had been allowed for temperature equilibration (20–30 min) and with an applied voltage of 0.5 V. They covered the range from 5 Hz to 13 MHz.

3. Results and Discussion

A particular characteristic of zwitterionic systems, i.e., the presence of ionic groups containing two charges of opposing sign joined by covalent bonds, induces very interesting ionic conductivity properties. Among them is their ability to be ionic conductors without the presence of inorganic salts. As an example, Figure 4 shows the variation of ionic conductivity with reciprocal temperature for two polymer systems (PMES and PMBS; see Figure 1). In addition, this figure exhibits the effect of ambient conditions upon the conductivity, showing two PMBS samples under vacuum and atmospheric conditions, respectively.

These systems reach high conductivity values (of the order of 10^{-4} S cm^{-1}), and a substantial increase is observed within a small range of temperature. In the PMES sample (T_g = 140 °C), high values are observed at lower temperatures and with lower activation energies than in the PMBS sample (T_g = 257 °C). The most substantial effect is observed in the sample under ambient conditions, where humidity affects the water content of the polymer sample. As indicated by Galin,[2] the depression in T_g due to bound water in polysulfobetaine systems is very large, which reflects the strong water–polyzwitterion interaction, showing evidence of the hygroscopic characteristics of these systems.

The strong depression in T_g induced by bound water produces a very large increase in the ionic conductivity (about 3 decades) for a given temperature and also a substantial increase in the activation energy. This is clearly observed in the corresponding Arrhenius curves for the PMBS system in Figure 4. These results confirmed the expectations about the influence of molecular mobility on the ionic transport mechanism.

In the absence of salt, the observed conductivity exhibits specific dipole–dipole interactions in the zwitterionic

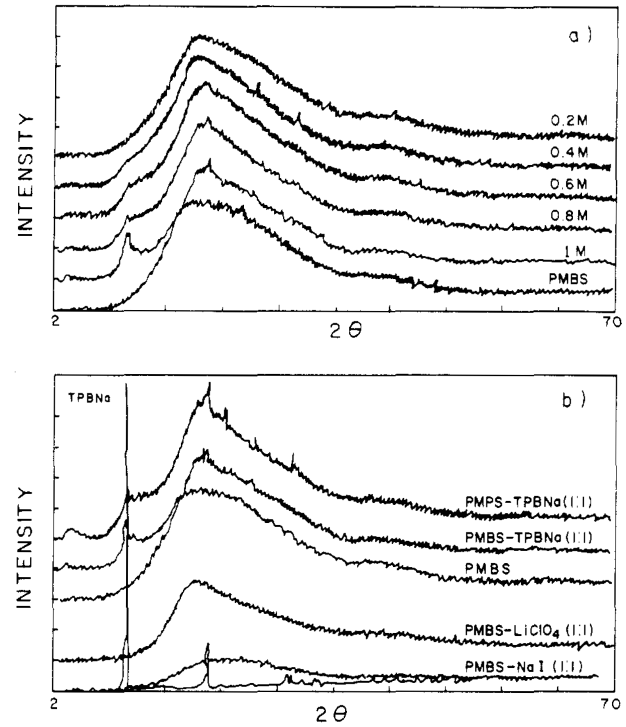

Figure 5. X-ray diffraction patterns showing the intensity variation with angle for (a) the PMBS–TPBNa system at several concentrations and (b) Equimolar mixtures of PMPS and PMBS with various salts.

polymers studied. These interactions induce a level of conductivity comparable with that of the more traditional salt–polyether systems. A more detailed study on the molecular mechanism provided by the analysis on the dielectric properties of these systems is presented later.

The high conductivity observed in zwitterionic systems is particularly interesting. However, the temperature range where these values are observed is quite narrow. A definite improvement is observed after salt is dissolved in the polymer matrix.

The ionic conduction of salts dissolved in polymeric materials requires the formation of a homogeneous mixture with an amorphous structure. This is based on the fact that ionic transport within the amorphous regions is an important condition to obtain high conductivity systems.[7]

Mixtures of the zwitterionic polymers shown in Figure 1 were prepared with three different salts, namely sodium iodide, lithium perchlorate, and sodium tetraphenylborate (TPBNa). Sample preparation was made according to the method described in the Experimental Section. The structures of the resulting mixtures were verified by X-ray diffraction studies.

Figure 5 shows X-ray diffraction patterns obtained from powder samples. In Figure 5a, the results for the PMBS–TPBNa system are presented for several salt concentrations (0–1 M) per mole of monomer. At low salt concentrations, crystalline structures are absent, whereas for higher concentrations (1 M) a diffraction peak appears at $2\theta = 11°$, which corresponds to crystalline TPBNa.

Figure 5b provides further evidence showing equimolar mixtures of the same salt with two polymers (PMPS and PMBS). In both systems, a peak located at the same position is clearly observed. The width of this peak increases with salt concentration, exhibiting the presence of the crystalline phase, which corresponds to salt domains dispersed in the polymeric matrix (crystallinity content ~5%). The presence of the crystalline phase inhibits the ionic transport in these systems for temperatures lower

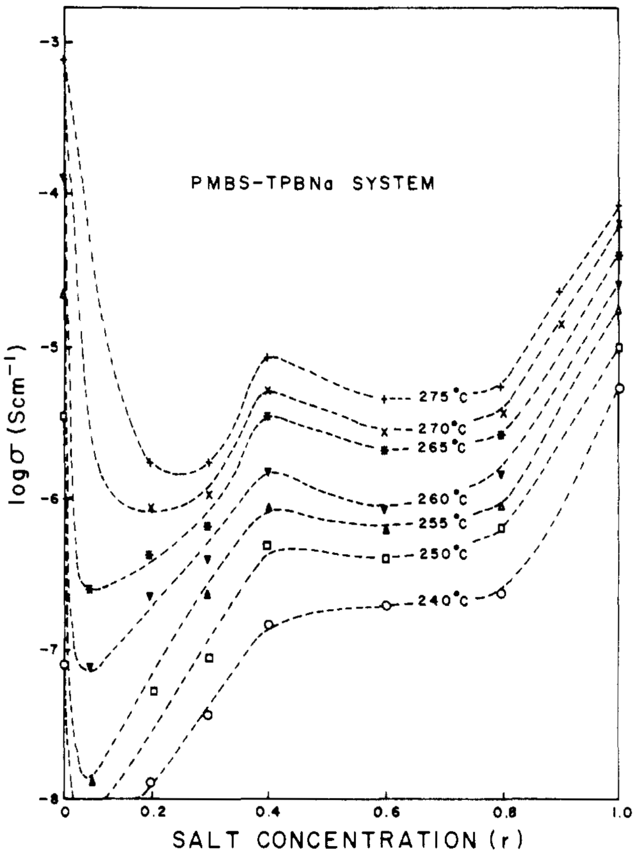

Figure 6. Variation of ionic conductivity with salt concentration (r) for the PMBS–TPBNa system, at several temperatures. r is defined as the ratio of molar concentration of salt to molar concentration of the monomer.

than 230 °C. For higher temperatures, crystalline domains melt and the salt is subsequently dissolved in the polymer, inducing a measurable level of conductivity. This observation has also been reported by Sorensen and Jacobsen[8] in the poly(ethylene oxide)–$LiCF_3SO_3$ system.

The influence of the mixture morphology on the conductivity properties in polymer–salt systems has been given special attention by many authors.[5-12] An increase in the ion's mobility is generally observed as soon as the degree of crystallinity of the sample lowers. Crystalline regions inhibit this mobility by acting as potential barriers.

The variation of ionic conductivity with salt concentration for the system PMBS–TPBNa at several temperatures (240–275 °C) is shown in Figure 6. The behavior of conductivity shows a pronounced decrease from the pure polymer value down to $r = 0.2$ (r is the ratio of molar concentration of salt to molar concentration of the monomers). This decrease is followed by a continuous rise with a small maximum located at $r = 0.4$ for temperatures higher than 240 °C. Following a quasi-plateau region, the conductivity increases sharply for mole fractions exceeding 0.8, up to a value close to the pure polymer level. As mentioned, the ionic conductivity is proportional to the number of ionic carriers times the ionic mobility. The region around $r = 0.4$ manifests a competition between the buildup of ion carriers due to increased salt content and the increase in T_g, which inhibits ion mobility as the polymer matrix becomes more rigid. The upturn at high salt concentrations exhibits behavior that is in contrast to that of more familiar polyether–salt systems, where conductivity actually decreases with salt content for high salt fractions.[5]

As some authors have suggested, the conductivity in polymer–salt systems may be correlated with the glass

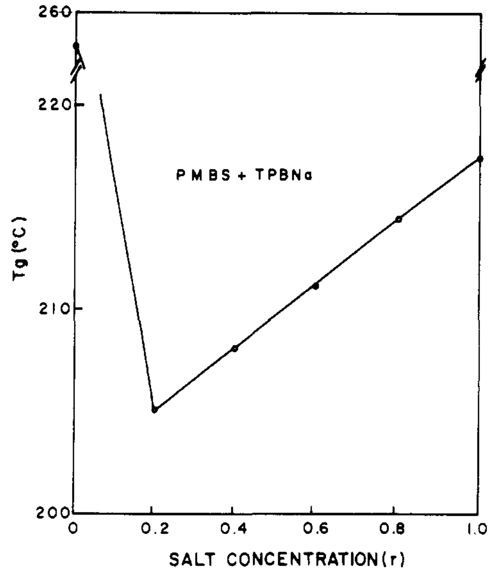

Figure 7. Variation of the glass transition temperature of the mixture with salt concentration (*r*), for the system PMBS–TPBNa. The pure polymer value is 257 °C.

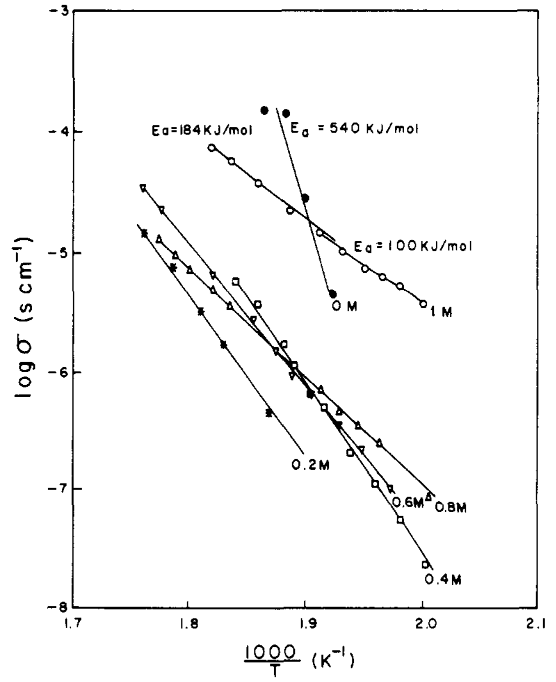

Figure 8. Arrhenius plots of ionic conductivity vs reciprocal temperature for the PMBS–TPBNa system at several salt concentrations.

transition temperature difference between the polymer–salt system and that of the polymer itself. In Figure 7, the glass transition temperatures of the mixture are plotted with the salt fraction for the system PMBS–TPBNa.

A steep decrease from the pure polymer value followed by a linear trend for salt fractions exceeding 0.2 is observed. T_g for the pure polymer was difficult to determine, and its value was estimated to be 257 °C. In this context, additional evidence is provided by the results shown in Figures 8 and 9, where the onset for conductivity in the systems studied shows up for temperatures just above T_g. In Figure 8, the conductivity is detected for temperatures higher than 257 °C in the pure polymer sample, exhibiting a large activation energy, 540 kJ/mol, within a narrow temperature range where high values are observed.

The observed strong decrease in T_g of the pure polymer indicates the change in molecular conformation brought about by the addition of salt. The depression in T_g manifests a strong salt–polyzwitterion interaction, similar to that observed with water. With further addition of salt, the trend reverses, showing a small increase in T_g with increasing salt concentration.

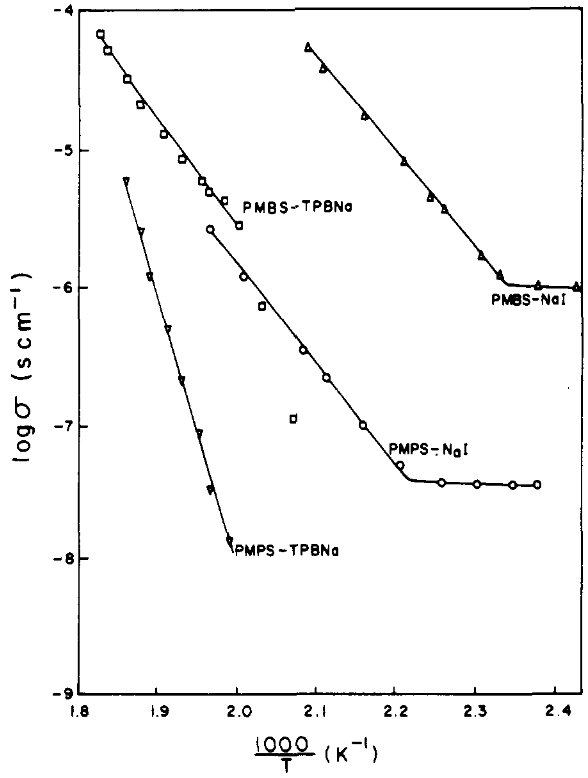

Figure 9. Arrhenius plots showing the effect of molecular structure of the polymers upon conductivity.

As shown in Figure 7, the magnitude of the increase in T_g due to increasing salt concentration is rather small (14 °C, up to 1 M). A small ΔT_g is associated with a weak interaction between the salt ions and the polymer ionic groups, and its magnitude cannot account for the substantial change in the observed conductivity at high salt contents. Hence, in these systems, a correlation between conductivity and ΔT_g does not hold, and the high ionization levels responsible for the upturn in conductivity manifest a more complex interaction between the salt ions and the zwitterionic groups. The strong dipole of the ionic side groups may induce the formation of a solvation layer, with regions of strong interaction and weak interaction. The steep decrease in T_g from the pure polymer value may be caused by increased flexibility, due to a strong interacting solvation region that shields the polymer ionic groups. This state may promote an ion-pair coupling between the salt ions and these ionic groups, the so-called site binding, with low production of ion carriers.

As the salt concentration increases, the capability for further site binding is reduced, leading to "atmospheric binding", an external effect that may produce a delocalized ionization of the salt by the polymer dipoles, inducing the observed high mobility of the ion carriers. The increase in T_g is therefore associated with weak interactions of the salt ions and the polymer ionic groups within this external solvation layer.

Evidence of strong dipole effects of the ionic side groups is the unusual ability of these polymers to complex salts up to stoichiometric ratios and the observed large generation of ion carriers. This high conductivity was also observed by Galin et al.[2] on similar zwitterionic materials in stoichiometric mixtures. However, it is in contrast with

Table I
Glass Transition Temperatures (T_g)

system (1:1)	T_g DSC, °C
PMPS–TPBNa	222
PMPS–NaI	157
PMBS–TPBNa	217
PMBS–NaI	131

the behavior exhibited by ionomers, where conductivity actually decreases with the neutralization degree of the ionic groups.

According to the X-ray diffraction studies mentioned above, a small phase separation occurs for salt concentrations around 1 M in the PMBS system, where the presence of a crystalline phase is apparent. In a equimolar mixture, the balance of charges implies a proportion of the ionic groups of the molecule and those of the salt. This configuration of charges promotes an interaction of the dipoles comparable to that observed in the pure polymer sample. A consequence of this interaction is the observed departure from the Debye behavior, which is discussed later in the dielectric studies of this paper.

Figure 8 shows the variation of conductivity of the PMBS–TPBNa system with reciprocal temperature, for several salt concentrations. Activation energies of such systems are calculated in accordance with the Arrhenius expression

$$\sigma = \sigma_0 e^{-E_a/kT} \tag{1}$$

where σ is the ionic conductivity, σ_0 is a preexponential factor, k is the Boltzmann constant, T is the absolute temperature, and E_a is the apparent activation energy. These results show a pronounced decrease of the activation energy with increasing salt content, leveling off for values larger than $r = 0.8$. At equimolar proportions, the conductivity displays two regions with different activation energies, corresponding to the glass-rich phase (100 kJ/mol) and amorphous phase (184 kJ/mol), respectively. As expected, the amorphous phase displays the higher conductivities.

Similar behavior is found in the zwitterionic systems studied by Galin et al.,[2] namely the PMES–$LiClO_4$ mixture, but with smaller conductivity values than those presented here.

Figure 9 shows the effect of the molecular structure of the polymers on conductivity. Equimolar mixtures of two polymers (PMPS and PMBS) with two different salts (TPBNa and NaI) are considered. The differences in the molecular structure of the polymer lies in the number of carbon atoms or chain length between the nitrogen atom and the sulfur atom. These molecular characteristics influence the glass transition temperature of the mix and hence the conductivity. For instance, Table I shows that T_g values for the PMPS–NaI system are 26 °C higher than the corresponding values for the PMBS–NaI mixture (157 vs 131 °C). The system PMBS–NaI presents larger lateral groups with higher chain flexibility, and these properties are manifested in a lower T_g value. Ionic conductivity has been shown to be highly dependent on these properties, i.e., mobility of the chain and the presence of an amorphous structure. Consequently, conductivity values are expected to be larger in the system with lower T_g. This is clearly shown in Figure 9, with values of 6.7×10^{-6} S cm^{-1} for PMPS–NaI and 4×10^{-4} S cm^{-1} for PMBS–NaI, at 200 °C. In the systems PMPS–TPBNa and PMBS–TPBNa, the difference in T_g is quite small (5 °C), and, hence, the difference in conductivity values of the two systems is smaller than in the previous case.

Figure 9 also shows the influence of the salt type on conductivity. Systems with NaI present higher conductivities at lower temperatures. These results show a possible influence of the salt ionic radii upon conductivity, as suggested by Munshi and Owens.[13,14]

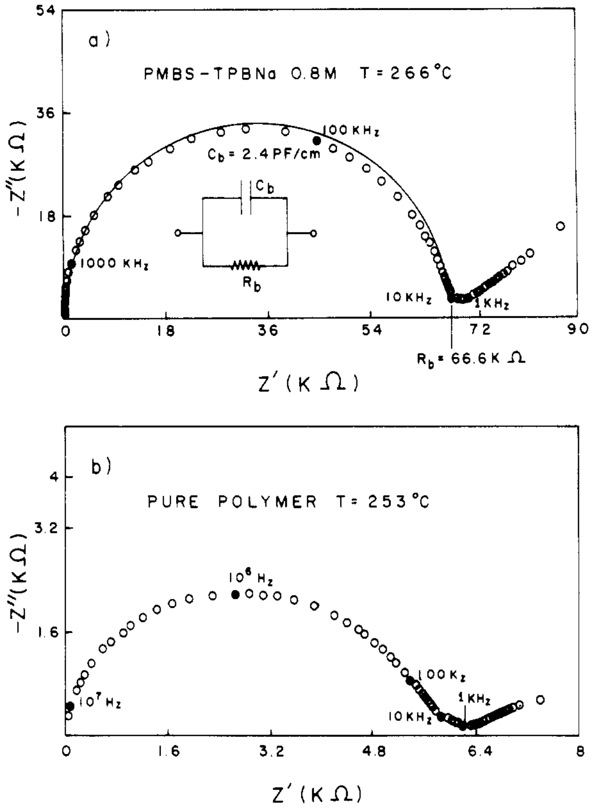

Figure 10. Complex impedance diagrams. (a) PMBS–TPBNa system for $r = 0.8$. The circles indicate experimental values, and the continuous line shows the simulation according to eq 2. (b) PMBS sample. The semicircle center lies below the horizontal axis.

Dielectric properties of the systems are analyzed in terms of complex impedance curves. Figure 10 shows the Cole–Cole diagrams where the imaginary part (Z'') is plotted as a function of the real part (Z') of the complex impedance, for PMBS and also for the PMBS–TPBNa system with 0.8 M fraction. A complete diagram should comprise two semicircles, one for the bulk polymer sample and the other one representing the electrode contribution. The contribution due to the bulk sample may be simulated by the following expression

$$Z^* = R_b\left(\frac{1}{1 + (wR_bC_b)^2}\right) - iR_b\left(\frac{wR_bC_b}{1 + (wR_bC_b)^2}\right) \tag{2}$$

where w is the angular frequency, i is the imaginary unit, and R_b and C_b are the bulk resistance and capacitance, respectively. Conductivity values were obtained from the Z' vs Z'' plots of the samples at several temperatures within the measuring range. In Figure 10a, the experimental results are plotted together with the simulation of eq 2 shown as a continuous line, with values of R_b = 66.6 kΩ and C_b = 2.4 pF/cm at 266 °C. Because the semicircle may be simulated with a capacitance of the order of pF/cm in all cases, this indicates that the values obtained are due to the bulk response of the sample. Equation 2 also may be expressed by the equivalent RC circuit shown in Figure 10a.

The imaginary component of the impedance (Z'') at low frequencies shows behavior corresponding to blocking electrodes, and this implies that the samples are ionic conductors. Typical values of the capacitance in the low-frequency region of the Z'', Z' plots were of the order of 1 μF.

Figure 5b depicts the dielectric behavior of the pure polymer sample. The semicircle has its center below the real axis, corresponding to values of the Cole–Cole β parameter lower than 1 ($\beta = 1$ represents the Debye limit), in the expression

$$Z^* = \frac{R_b}{1 + (i\omega R_b C_b)^\beta} \quad (3)$$

A deviation from this limit shows the level of interaction among the dipoles in the molecule. It also corresponds to a superposition of a group of Debye-like relaxation processes with a range of relaxation times symmetrically distributed about the main relaxation time, $\tau = RC$.

The smaller magnitude of β observed in the polymer sample without salt shows that the dipole interaction is stronger in the polymer system than in the mixture. This is reflected in a larger conductivity, according to values given in Figure 6. On the other hand, the samples with salt (with the exception of the equimolar mixture) show an interesting Debye behavior, which actually corresponds to noninteracting dipoles. This effect is associated with the solvation of the polymer ionic groups by the salt ions, in such a way that the solvation layer prevents a level of interaction among the dipoles of the polymer. This behavior is manifested in a lower conductivity.

As previously mentioned, in the case of equimolar mixtures, the balance of charges induces increased interaction of dipoles. This situation leads to a departure from the Debye behavior and, hence, to the onset of high conductivity. Further experimental evidence concerning with the dielectric behavior of these systems is provided in ref 16.

4. Conclusions

Ionic conductivity studies performed on zwitterionic polymers dissolved in different salt types by means to the ac spectroscopy technique show that conductivity is highly dependent on the molecular structure of the polymer. High conductivity values are found in the pure polymer sample and at high salt contents. Dielectric measurements have shown that dipole–dipole interaction leads to a cooperative effect that is actually manifested in a departure from the Debye limit, corresponding to a high conductivity. Within the region between 0.2 and 0.8 M salt content, solvation of the ionic groups by the salts results in a Debye behavior, which indicates a diminishing dipole interaction and lower conductivity. Although high values in conductivity in the pure polymer samples are interesting in the context of possible applications, however, those systems present a narrow temperature range where the conductivity is high. This problem may be actually overcome by dissolving the salt systems in these polymers.

Further studies on the dielectric properties of these systems are currently under investigation in this laboratory.

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Registry No. PMES, 132980-94-0; PMBS, 133008-40-9; PMPS, 41488-70-4; TPBNa, 143-66-8; NaI, 7681-82-5; $LiClO_3$, 7791-03-9.