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Morphology-conductivity correlations in salt-polysulfobetaine systems

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Summary

Polysulfobetaine polymers present highly polar lateral groups with zwitterionic structures and such molecular characteristics are highly desirable in the production of ionic conductive systems. The extent of their conductive properties is significantly dependent on the morphological changes which take place in their mixtures with salts when temperature is varied. As soon as the salt melts and dissolves in the polymer matrix, conductivity increases sharply for unusually high salt proportions, attaining a level similar to that observed in the pure polymer. Microscopic observations of these systems reveal interesting morphological changes associated with the onset of high conductivity.

Introduction

Ionic conductivity in polymeric materials mixed with salts is highly dependent on properties such as low glass transition temperature of the system, a large concentration of highly polar groups, the presence of amorphous regions with low crystallinity and the formation of homogeneous polymer-salt mixtures.

Analyses on the morphology of polymer-salt systems have been conducted mostly to obtain high ionic conductivity at ambient temperature [1,2]. Technological applications of these studies are focused on the production of high energy-density solid batteries.

Zwitterionic polymers have been the subject of recent studies (c.f. Galin et al. [3]). We have conducted analyses on polysulfobetaines, in particular with respect to their thermal and dilute solution properties [4], their special molecular and dipole characteristics [5] and their ionic conductivity properties [6]. The present work provides a detailed study on the morphology of sulfobetaine polymers mixed with salts and its influence on the mechanism of ionic conductivity. These systems present a large concentration of highly polar groups, where dipoles of the ionic pendant structures may contribute to fast ionic transport. A major effect of the strong dipole of the zwitterionic structure is the ability to dissolve salts up to stoichiometric ratios, with the formation of homogeneous solid solutions. This is an important aspect in the conductive properties of these systems.

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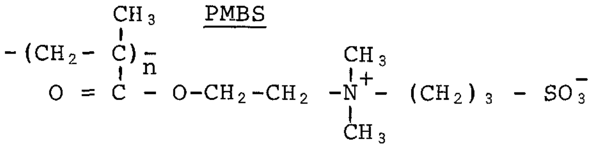
EXPERIMENTAL PART

The synthesis of the sulfobetaine polymers has been described elsewhere [3,4,6]. The resulting molecular structure is the following:



$$-(CH_2-\underset{O=C-O-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{N^+}}-(CH_2)_3-SO_3^-}{\overset{CH_3}{C}})_n-$$

PMBS

[Methyl methacryloxiethyl 1-(3-sulfobutyl)ammonium] inner salt.

Solid blends were prepared by freeze drying of the corresponding aqueous solutions at -198°C and with a vacuum of 10^{-2} torr for 24 hours. Structure and formation of the homogeneous solutions was verified by X-Ray diffraction (Siemens Refractometer D-500) and evaluation of the crystallinity content was made. Experimental conditions included a sweep from 2° to 70° at 1°/min, under Cu K_α radiation. Samples were also analyzed by a scanning polarizing microscope (Olympus) equipped with a heating device (Leitz 350) controlled within ±1°C. Experiments were performed in powder samples in the range 50°C - 250°C. Scanning electron microscopy (Joel T20) was also used. In this case, samples were prepared by gold deposition using the sputtering technique. The thermal behavior of the systems was determined by differential scanning calorimetry on a Perkin-Elmer DSC II-C.

RESULTS AND DISCUSSION

As previously mentioned, an important condition to obtain high ionic-conductive systems is the homogeneity of the solid solution with low crystallinity content. In figure 1, X-Ray spectra of the PMBS-TPBNa (tetraphenyl boron sodium) system with various salt contents are shown. At low salt proportions, characteristic peaks corresponding to crystalline regions are absent, whereas for higher salt contents a characteristic band located at $2\theta = 11°$ is observed. This peak corresponds to the diffraction patern of the salt, depicting the presence of a crystalline phase, which increases with salt proportion. From these data, the degree of crystallinity is quantified by using the diffraction-intensity vs. diffraction-angle curves. Refer-

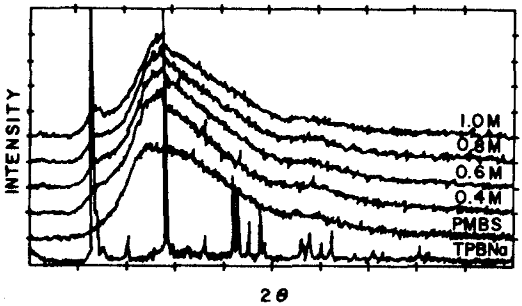


Figure 1. X-Ray diffraction patterns showing the intensity variation with angle for the PMBS-TPBNa system at several concentrations.

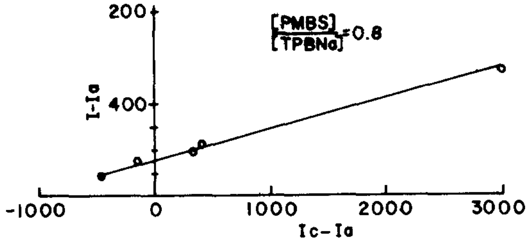
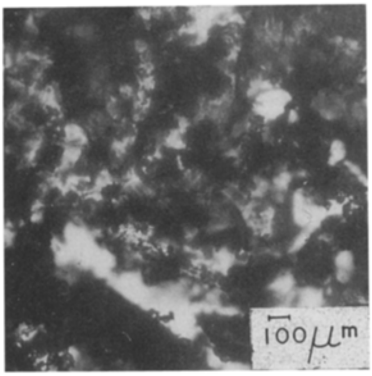
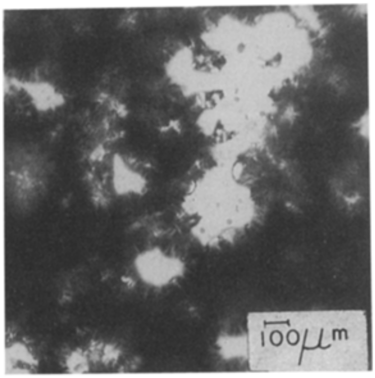
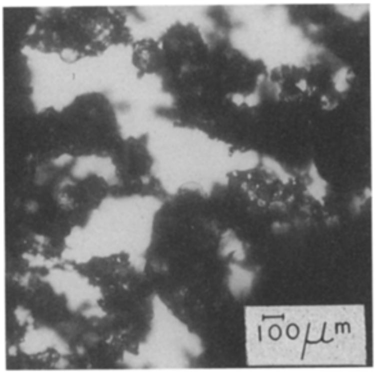


Figure 2. Diffraction intensity values provided by the X-Ray spectra of figure 1. Ia and Ic are the intensities of the amorphous polymer and the crystalline salt, respectively.





(b)



(c)

Figure 3. Series of micrographs showing the morphological changes produced on the polymer-salt system with increasing temperature (r=0.8) . (a) T=185°C, (b) T=232°C and (c) T=246°C.

ence samples included the pure polymer (amorphous) and the pure salt (TPBNa). According to this analysis technique, the X-ray data is plotted in the form I-Ia vs. Ic-Ia. Ia and Ic correspond to the diffraction intensity of the amorphous polymer and the crystalline salt, respectively (see figure 2). The degree of crystallinity (X_C) can be calculated from

$$X_C = \frac{(I-Ia) - K}{(Ic-Ia)}$$

where I is the scatter intensity from the unknown sample and K is a constant which can be calculated from the referred curve. Results for the degree of crystallinity vs. the ratio of molar concentration of salt to molar concentration of the monomer (r) show a value of 3.9% for r=0.4 and 5% for r=1, respectively. These low values of crystallinity content indicate that the salt is indeed dissolved in the amorphous regions of the polymeric matrix, up to ratios of the order of 1M. This results also shows that the strong dipole of the ionic side groups in the zwitterionic structure leads to the unusual ability to form homogeneous solid solutions up to stoichiometric ratios. This observation is in contrast to those of other systems, such as the polyether-alkali metal salts, where phase segregation is observed at lower salt contents.

Further observations of the phase behavior of zwitterionic salt systems are shown in figure 3. A succession of micrographs using transmission optical microscopy were taken for the system PMBS-TPBNa (r=0.8) with increasing temperature. No morphological change is observed in the range from ambient temperature up to 220°C, and for example, figure 3a shows the structure at T = 185°C. As soon as the temperature reaches 220°C, an apparent change in the morphology is observed, corresponding to a slow fusion process. In figure 3b (T=232°C) small droplets are detected immediately after the fusion of the salt is completed. As soon as the crystalline phase melts, it is subsequently dissolved into the amorphous phase, indicating the formation of an homogeneous mix with amorphous tridimensional structure. (See figure 3c, T = 246°C). The melting and absorption of the salt in other systems have also been observed by Sorensen et al. [7] on the PEO-$LiCF_3SO_3$ system. At this point, conductivity increases steeply, manifesting an enhanced ionic mobility previously limited by the potential barriers in the crystalline phase. (see figure 4).

Additional evidence of the melting of the crystalline phase is provided by differential scanning calorimetry. The PMBS-TPBNa sample (r=0.9) presents an endothermic peak located at 228°C, with an enthalpy of 1.25 cal/g. To verify the melting of salt, a second temperature sweep was carried out.

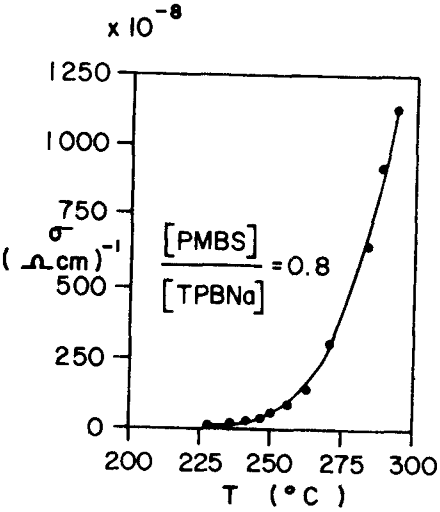


Figure 4. The onset of ionic conductivity for temperatures higher than 246°C.

Results show (see figure 5) that the peak disappears and the Tg of the sample can be evaluated. Consequently, because the salt is the only ingredient to present a first order transition, it is concluded that the salt melts and it is subsequently dissolved in the polymer matrix. Unfortunately, it is not possible to calculate the degree of crystallinity from the DSC data to compare it with the X-ray analysis. For this, it would be necessary to use the salt as the standard, a material 100% crystalline and to determine its heat of fusion. However, the salt decomposes before melting, a fact that does not occur in the polymer-salt system. This is due to the decrease in the melting point of the salt brought about by the increase in salt content of the solid solution.

Different behavior is shown in the case of the polymer without salt, where no apparent change is observed up to 260°C. Figure 6 depicts the morphology when the temperature is 253°C, revealing larger size agglomerates than the ones observed in the polymer-salt system. This observation is verified by the electron microscopy studies shown below.

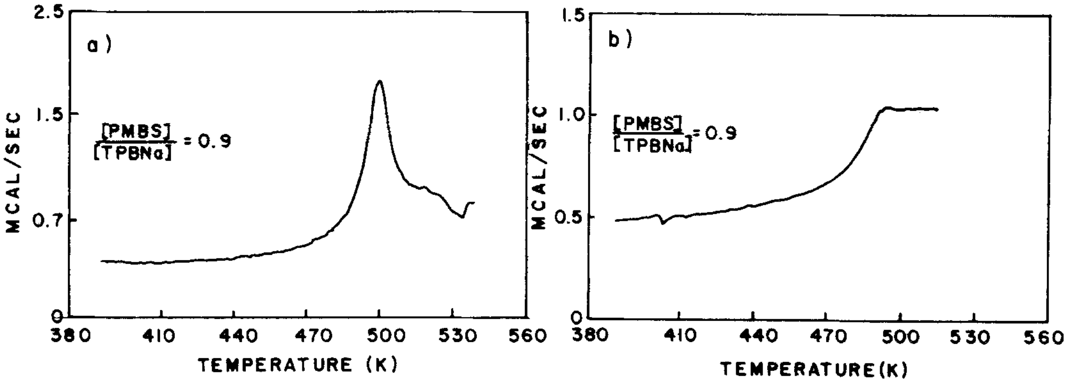


Figure 5. DSC diagrams, showing the presence of a crystalline phase in the first sweep (a). The endothermic peak disappears in the second sweep (b), evidencing the melting of the salt.

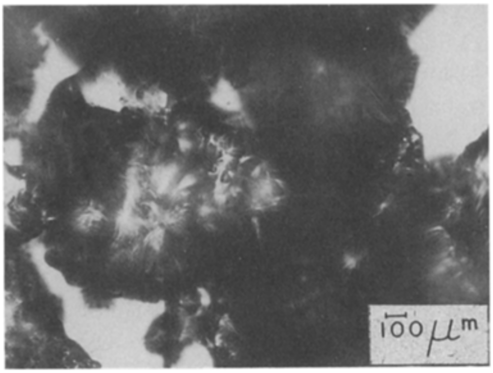


Figure 6. Micrograph of the pure polymer, at T=253°C.

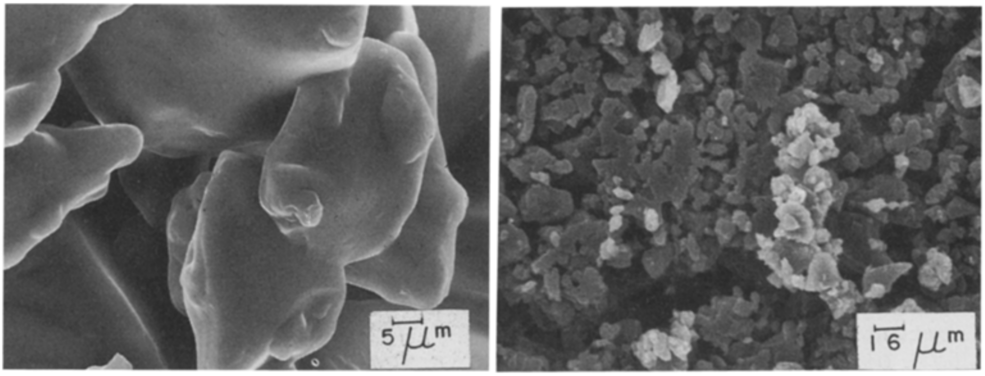


Figure 7. Electron microcopy micrographs showing the morphology of the pure polymer (left) and that of the polymer-salt mix (right), with r=0.8.

Morphology studies on the polymer-salt systems by means of scanning electron microscopy reveal profound differences among polymers with and without salt. In the latter systems, the surface is smooth with evidences of larger agglomerates than in samples with salt (see figure 7). This is probably due to the presence of water in the polymer. The high water binding capability of the zwitterionic groups (water content may be as high as 11%, measured by TGA) is different to that observed in the materials with salt, where water content is 3% in equimolar mixes with TPBNa. Samples with salt show a higher degree of surface roughness, with small size particles embedded in the polymer matrix. A laminar structure is observed, as shown in the second micrograph for the 1:0.8M PMBS-TPBNa sample.

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