Properties of styrene ionomers containing zwitterion-type salts

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Summary

The properties of poly(styrene-*co*-styrenesulfonic acid) (PSSA) ionomers mixed with NaOH and *p*-aminobenzoic acid (ABA) were investigated dynamic mechanically. It was found that when NaOH was added to the PSSA+ABA solution to neutralize two acid groups, the properties of the blends were similar to those of Na-sulfonated polystyrene ionomer. In these blend systems, the Na-aminobenzoate probably acted as filler. In the blend of the PSSA polymer and Na-aminobenzoate, it was suggested that the so-called core-shell type multiplets form. However, when Na-sulfonated polystyrene was mixed with the ABA, the ABA molecules acted as a polar plasticizer. It was also found that in the blend system of PSSA+ABA partly neutralized with NaOH, the property fell somewhere between those of the two latter blend systems.

Introduction

Over the last 3 decades, extensive studies have been performed aiming to improve our understanding of the properties of ionomers (1-6). These polymers have unique properties owing to ionic interactions. It is generally accepted that ionic groups aggregate to form multiplets (7) which are surrounded by regions of restricted mobility of polymer chains (8). At very low ion contents, it is only multiplets that are present. At this time, only a matrix glass transition (Tg) is observed. As the ion concentration increases, the regions of reduction in mobility start to overlap to form large contiguous regions of restricted mobility. These regions are now called clusters (8), the dimensions of which exceed ca. 100 Å. In this state, the ionomer shows a second Tg associated with the glass transition of the cluster phase.

Extensive studies have revealed that a number of parameters are of importance in the formation of multiplets and clusters in ionomers. Among them are the ion concentration, types, sizes, and positions of ionic groups, etc. (6). However, only a few studies have investigated the properties of ionomers having ammonium ions as counterions for anionic groups of the ionomers. Weiss et al. compared the properties of sulfonated polystyrene (PSSA) ionomers with a wide range of ammonium counterions (9). They found that the matrix T_g values of the PSSAZn and PSSA+ammonium ionomers as

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a function of ion content showed a similar trend while the T_gs of PSSA ionomers containing alkyl amines exhibited a different trend. It was found that the samples containing amines with shorter chain lengths showed "universal" behavior in that a T_g is a function of the chain length; however, for longer alkyl chain lengths, the degree of substitution affected the behavior of the materials, especially the trends in the drop of a T_g.

Smith and Eisenberg found that the matrix T_g of a PSSA ionomer increased considerably upon the addition of amines consisting of a large rigid ring system (10). For example, it was found that the matrix T_g of the unneutralized PSSA ionomer (8.1 mol% of ions) was ca. 122 °C, while that of the ionomer neutralized with 1-adamantanamine was ca. 137 °C. The matrix T_gs of PSSA ionomers neutralized with various bifunctional and multifunctional amines were also studied by Fan and Bazuin (11). It was found that the basicity of the amines did not change the matrix T_g.

In the present study, the properties of a PSSA ionomer blended with NaOH and *p*-aminobenzoic acid were investigated. The *p*-aminobenzoic acid has an amine group, which is a base, and a carboxylic acid group. Thus, these blends have two types of an acid group ($-SO_3H$ and $-COOH$) and one base group ($-NH_2$). This work is thought to explore primarily the effects of the order of mixing on the morphology and dynamic mechanical properties of ionomers containing aminobenzoate.

Experimental

Sample preparation

Polystyrene (MW = ca. 300,000) was synthesized by bulk free-radical polymerization using benzoyl peroxide as the initiator. The method developed by Makowski et al. (12) for homogeneous sulfonation was used to produce the poly(styrene-*co*-styrenesulfonic acid) (PSSA) samples containing approximately 6.3 mol% of functionalized repeat units. To determine the ion concentration, a sample was dissolved in a benzene/methanol (90/10, v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic sodium hydroxide to the phenolphthalein end point.

In order to study the effects of the order of mixing, the PSSA acid copolymer, *p*-aminobenzoic acid (ABA), and NaOH were added in different orders. In all of the blends, the mole ratio of the ABA molecules to a sulfonate group of PSSA polymers was 1:1. In the case of the PSSA+ABA blend, an ethanolic *p*-aminobenzoic acid (ABA) solution was added to a PSSA acid polymer in benzene/methanol (9/1 v/v) mixture. For the PSSA+ABANa and the PSSA+ABANa2 samples, 100% and 200% Na-neutralized ABA molecules, respectively, in ethanol were added to a PSSA solution. A PSSA polymer and ABA molecules were mixed and then methanolic NaOH was added subsequently to the solution to make an 1:1 or 2:1 ratio of Na^+/sulfonic acid groups of PSSA, respectively, and the samples were denoted as the (PSSA+ABA)Na and the (PSSA+ABA)Na2. In the case of the PSSANa+ABA sample, a sodium neutralized sulfonated polystyrene ionomer was mixed with an ABA solution. All of the solutions mentioned above were stirred for 25 min, freeze-dried and then dried under vacuum at 80 °C for at least 24 h.

For the DMTA measurements, the samples were compression-molded at ca. 230 °C; a pressure of ca. 20 MPa was applied for 5 min, then slowly released, and the mold was allowed to cool to below the matrix T_g. The molded samples, with approximate dimensions of 2.5 x 6.0 x 30.0 mm, were annealed for 24 h in vacuum at 80 °C.

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical measurements were performed using a Polymer Laboratories Mark II dynamic mechanical thermal analyzer (DMTA) in the dual cantilever bending mode, at frequencies of 0.3, 1, 3, 10 and 30 Hz and a heating rate of 1 °C/min. For each sample, the storage moduli ($E´$), loss moduli (E"), and loss tangents (tan δ) were obtained as a function of temperature, over the range of 80—320 °C.

Results and discussion

Figure 1 shows the storage modulus and loss tangent values as a function of temperature of four samples, i.e. PSSA+ABA, PSSA+ABANa2, (PSSA+ABA)Na2, and sodium sulfonated polystyrene (PSSANa) samples. For the PSSA+ABA sample, it is seen that the modulus drops drastically at ca. 140 °C. In addition, two loss tangent peaks are seen at ca. 140 and 160 °C; one peak at low temperatures is associated with the matrix glass transition, and the other at high temperatures is due to the cluster T_g. For the PSSA+ABANa2, (PSSA+ABA)Na2, and PSSANa samples, the moduli change with temperature from a glassy modulus, through a matrix glass transition, through an "ionic" modulus, through a cluster glass transition, and to a rubbery modulus. The difference in the modulus curves appears only above the matrix T_g; ionic moduli of the two blend systems are higher than that of the ionomer, i.e. PSSANa. Two well-separated loss tangent peaks are also seen. The matrix and cluster loss tangent curves of the last three samples are similar to each other. The glass transition temperatures are listed in Table 1. The activation energies for the matrix and cluster transitions were calculated from an Arrhenius plot of log frequency against inverse temperature of the peak maxima; the activation energy (E_a) values are also listed in Table 1.
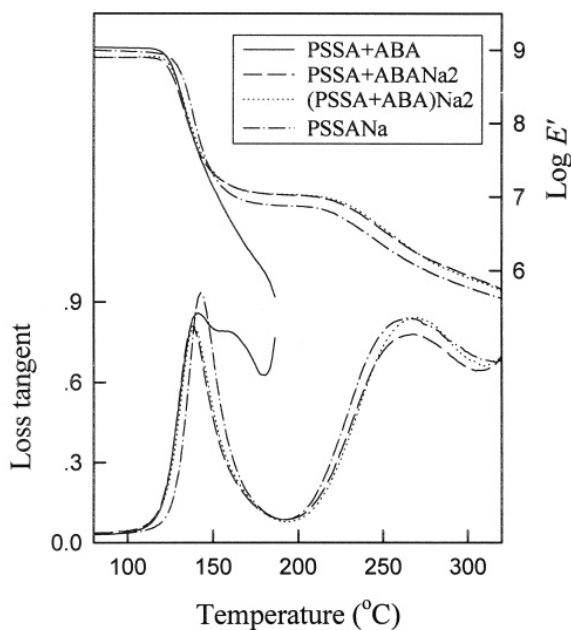

Figure 1. Storage moduli and loss tangents measured as a function of temperature at 1 Hz for PSSA+ABA, PSSA+ABANa2, (PSSA+ABA)Na2, and PSSANa samples.

Table 1. Glass transition temperatures and activation energies for the glass transitions

sample	matrix T_g (°C)	E_a (matrix T_g) (kJ/mol)	cluster T_g (°C)	E_a (cluster T_g) (kJ/mol)
PSSA+ABA	141	581	160	350
PSSA+ABANa2	139	519	267	178
(PSSA+ABA)Na2	139	503	270	199
PSSANa	143	512	264	181
PSSA+ABANa	130	545	166	191
(PSSA+ABA)Na	132	502	174	201
PSSANa+ABA	134	506	186	211

The relatively low cluster T_g in the PSSA+ABA system can be understood if the size of a cation in a multiplet is considered. When the PSSA polymer was mixed with the ABA molecules, the protons of the sulfonic acid group transferred to basic amine groups, which resulted in the formation of -SO_3^- and +H_3N- ion pairs (Scheme 1-a). In this

(a)   (b)   Scheme 1
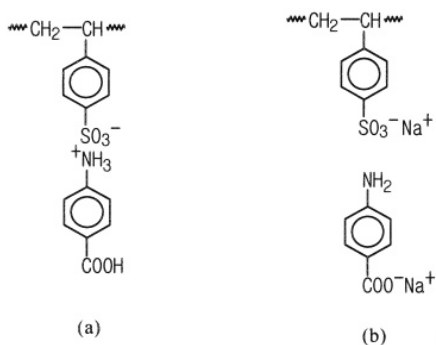
case, the size of the cation is so large that the ionic interactions between ionic groups in the multiplet cannot be strong enough to hold down the ionic groups at high temperatures (13). Thus the ion-hopping (14) occurs at lower temperatures in the PSSA+ABA system than it does in the PSSANa system which has a smaller cation, i.e. Na^+. Similar results were observed by Smith and Eisenberg (10).

In the cases of the PSSANa, PSSA+ABANa2 and (PSSA+ABA)Na2 systems, the similarity in the shapes of modulus and loss tangent curves implies that the morphologies of the three systems are similar. One can understand this finding by looking at Scheme 1-b. In the PSSA+ABANa2 and the (PSSA+ABA)Na2 blends, the amount of a neutralizing agent, NaOH, was enough to neutralize completely two acid groups, i.e. -COOH and -SO_3H groups. It leads us to conclude that the order of mixing does not affect the morphology and properties of these two materials. In this case, the Na-sulfonate ionic groups are believed to form multiplets, and sodium *p*-aminobenzoate organic salts may simply act as filler (15) both in the multiplets and in the region of hydrocarbon polymer chains (in the form of isolated organic salts in the latter). Therefore, the morphology of these two blend systems is believed to be similar to that of the pure ionomer, PSSANa. Only an increase in the ionic modulus by the presence of filler is expected (15), which was indeed what is observed here (see Figure 1). The activation energy values for the

matrix and cluster transitions of all three blends are similar to each other at ca. 510 and 190 kJ/mol, respectively. These values show good agreement with the values obtained by Hird and Eisenberg (14), and Kim et al. (17,18). This result also implies that the morphological structures of the multiplets in the three blends resemble that of the PSSANa ionomers. At this point, it should be noted that the activation energies of the PSSA+ABA sample are higher than those of the PSSANa ionomer, which means that the morphology of the PSSA+ABA sample is probably different from that of the ionomer. It should, however, also be recalled that the glass transition temperatures are related to the strength of ionic interactions in the multiplets, whereas they show no direct relation to the activation energies (15).

In Figure 2, the storage modulus and loss tangent curves of PSSA+ABANa, (PSSA+ABA)Na, and PSSANa+ABA samples are shown. The modulus decreases rapidly at ca. 130 °C, and passed the temperature, decreases further in a mild manner. Two loss tangent peaks are also observed. While the positions of the matrix loss tangent peaks are different slightly, those of the cluster loss tangent peaks are different significantly. The glass transition temperatures of the PSSA+ABANa are the lowest, and those of the PSSANa+ABA are the highest (see Table 1). This result is reasonable considering of the difference in the morphology of these blends; when the PSSA polymer was mixed with the sodium p-aminobenzoate molecules, the proton transfer took place from the sulfonic acid of the PSSA to the amine group of the ABA molecules (see Scheme 2-a).
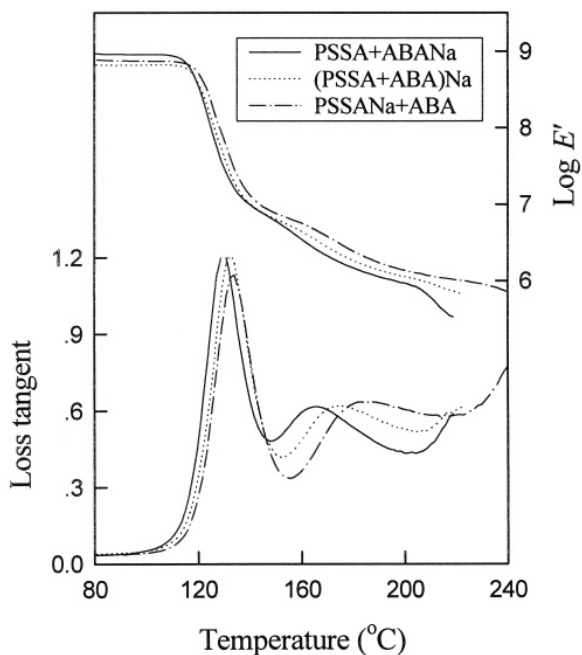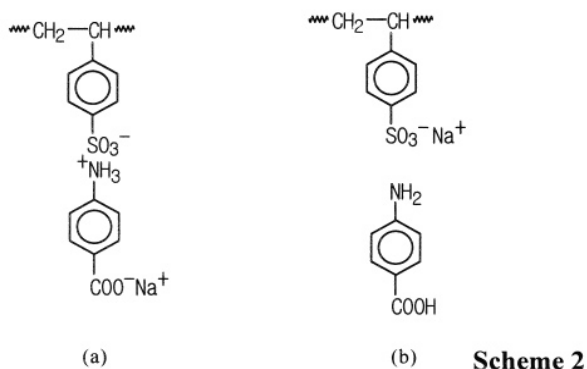

Figure 2. Storage moduli and loss tangents measured as a function of temperature at 1 Hz for PSSA+ABANa, (PSSA+ABA)Na, and PSSANa+ABA samples.

(a)   (b)   **Scheme 2**

Thus the ionic aggregate consists of two kinds of ion pair, i.e. —SO_3^- ^+H_3N— and —COO^- ^+Na ion pairs. This aggregate may look like more or less a core-shell type multiplet; —COO^- ^+Na ion pairs reside at the core and —SO_3^- ^+H_3N— ion pairs in the outer shell. At this point, it should be noted that the ionic interactions are weaker between —SO_3^- and —NH_3^+ ion pairs than between —COO^- and Na^+ ion pairs owing to the larger size of NH_3^+ ion than Na^+ ion. Thus, when the temperature increases, the —SO_3^- ^+H_3N— ion pairs start dissociating (i.e. hopping) at relatively lower temperatures (14).

  When the ABA solution is added to the PSSANa ionomer solution, the ABA molecules probably act as a polar plasticizer (see Scheme 2-b) (6,16). Thus the polar ABA resides in the multiplets, leading to the decrease in a cluster T_g. In the case of the (PSSA+ABA)Na system, a NaOH solution is added to a polymer solution containing carboxylic acid and sulfonic acid groups. The hydroxide anions can generate acid-base reactions more or less evenly with the acidic protons of both the carboxylic acid and the sulfonic acid groups. Thus, chemical structures of ionic species of the resulting blends are speculated to be, to some extent, similar to those of both the PSSA+ABANa (Scheme 2-a) and the PSSANa+ABA (Scheme 2-b). As a result, the property of the (PSSA+ABA)Na blend falls between those of two other blends.

  From Table 1, it is seen clearly that the order of the cluster T_g of these three blends is the PSSANa+ABA (186°C) > the (PSSA+ABA)Na (174°C) > the PSSA+ABANa (166°C). It is also seen that the activation energies of these three ionomer blends are independent of the sample preparation method at ca. 200 and 210 kJ/mol for the matrix and cluster T_gs. In the PSSA+ABA (see Scheme 1-a) and the PSSA+ABANa (see Scheme 2-a) systems, one might well expect that the cluster T_gs and their activation energies should be similar if only ion-hopping had occurred at the cluster T_g. However, it was observed that the two cluster T_gs were not much different whereas the activation energies were quite different. This is probably due to the fact that the activation energy of the glass transition of the cluster phase reflects not only ion-hopping, but also a contribution from the chain mobility (15). Because of the differences in the multiplet size and ionic groups in the multiplet, the chain motions in the two systems are expected to be different. Thus, the difference in the activation energy in the two systems is not surprising.

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