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Chain Mobility Restrictions in Random Ionomers Studied by Electron Spin Resonance Spectroscopy

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ABSTRACT: Electron spin resonance (ESR) spectroscopy has been used to obtain information on chain mobility in spin-doped poly[styrene-*co*-(sodium methacrylate)] random ionomers. The results show that spin probe molecules randomly dispersed in ionomers respond to the matrix glass transition. However, when the probe molecules are anchored to the ionic multiplets, their mobility is reduced, indicating that the polymer segments adjacent to the ionic multiplets are constrained, and their mobility is restricted. Significant motions of the probe molecules start only when the kinetics of the ion-hopping process becomes relevant. Plasticization of the ionomers with polystyrene oligomers allowed for the simultaneous observation of two different mobility regimes, assigned to the matrix and cluster phases. These findings support the suggestion, which is a major component of the EHM model for the morphology of random ionomers, that regions of restricted mobility exist around the ionic multiplets.

Introduction

Restricted Chain Mobility in Ionomers. Considerable research effort has been devoted during the last 30 years to the understanding of the morphology, rheology, and mechanical properties of polymers containing ionic groups.[1] Such materials are called random ionomers when the ionic groups are distributed randomly along the polymer chain, and their bulk properties are governed by ionic interactions in discrete regions of the material; the ion content is usually below 20 mol %.[2] The mechanical properties of ionomers are strongly dependent on the ion content. For amorphous ionomers, for instance poly[styrene-*co*-(sodium methacrylate)], it is observed that above a particular ion content, a second peak appears in the tan δ vs temperature spectrum at a higher temperature than that of the glass transition of the corresponding nonionic polymers. This peak grows at the expense of the main glass transition peak and shifts to higher temperatures as the ion content increases.[3] The mechanism of the second glass transition is thought to involve not only the usual polymer relaxations but also ion-hopping, which consists of the removal of an ion pair from a multiplet and its reinsertion into another. This process is crucial because it allows for the unlocking of the polymer chains from the multiplets while they essentially retain their integrity.[3c,4] When ionomers are plasticized, they exhibit different behavior depending on the nature of the plasticizer. Both tan δ peaks shift to lower temperatures in the case of nonpolar plasticizers such as diethylbenzene or dioctyl phthalate, while only the high-temperature peak is appreciably affected when polar plasticizers are used, for instance glycerol.[5] Many other experiments have shown that polymer properties such as viscosity,[6] crystallinity,[7] or thermal expansion[8] are affected significantly by the incorporation of ionic groups. In addition, small-angle X-ray scattering (SAXS) measurements have been of great importance in understanding the morphology of random ionomers. The striking feature of the SAXS spectra is the appearance of a peak upon neutralization of the acid groups of ionomers.[9] This peak has been called the "ionic" peak, and its characteristics have been studied as a function of ion content, water content, temperature, and nature of the counterion, as well as other parameters.[10,11]

The most important question arising from these experimental results concerns the kind of ionomer morphology that gives rise to the above-mentioned complex behavior. It is a common feature of most models of ionomer morphology to suggest that the ionic groups in ionomers interact to form ion pairs or higher order aggregates for reasons that are related to both the electrostatics and the satisfaction of the coordination spheres of the ions. These structures are called multiplets.[12] In one approach developed by Cooper and co-workers,[11,13] the "ionic" peak was ascribed to intermultiplet scattering. In a different approach proposed by MacKnight and co-workers,[14] it was suggested that an ionic core (multiplet) is surrounded by a shell of polymer which does not contain any ions. This, in turn, is covered by a layer of polymer containing some ionic groups. In this model, called the "core−shell" model, the characteristic distance giving rise to the "ionic" peak is the one between the two ion rich regions—the ionic core and the outer shell. Although the models discussed above provide plausible interpretations for the SAXS spectra of ionomers, they do not account for their complex mechanical properties. Recently, a model attempting to unify both sets of results was presented by Eisenberg, Hird and Moore (EHM model).[15] In this model it was postulated that the polymer segments surrounding the multiplets are characterized by lower mobility when compared with more distant segments. At low ion contents, these regions of restricted mobility are small and isolated; hence, they do not exhibit a separate glass transition (T_g). As the ion concentration increases, these regions begin to overlap. When their size exceeds *ca.* 10 nm, a distinct glass transition becomes observable, at which point they are called clusters. The second tan δ peak is thus due to the glass transition of these overlapping restricted mobility regions, which exceed the minimum size required for independent phase behavior. The SAXS "ionic" peak is ascribed by the model to intermultiplet scattering.

Although the EHM model is in agreement with a very wide range of experimental observations, data supporting the existence of restricted mobility regions in random ionomers are still only fragmentary. Risen and

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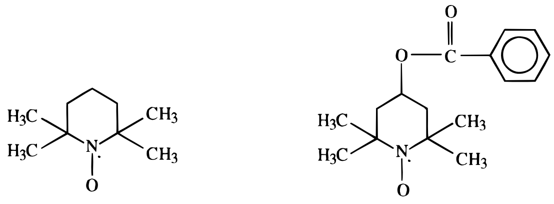
co-workers[16] measured by differential scanning calorimetry (DSC) the T_g and the heat capacity change, ΔC_p, for a series of sulfonated polystyrene ionomers, neutralized with +1, +2 and +3 ions of the alkali, alkaline earth, and lanthanide groups. It was observed that the T_g and ΔC_p varied only with the degree of sulfonation but not with the cation charge. The effect of the degree of sulfonation on the ΔC_p was taken to indicate that at high ion contents, some styrene units adjacent to sulfonated sites were constrained from participating in the glass transition. Other studies have focused on telechelic ionomers and block ionomers, which are considered to be model materials for random ionomers. Specifically, regions of restricted mobility were shown to exist in telechelic ionomers by dielectric measurements in the solid state[17] and nuclear magnetic resonance (NMR) (relaxation time) measurements both in solution[18] and the solid state.[19] Multiplets are formed in these materials, but the ion content is too low for a second glass transition to appear in mechanical measurements. NMR measurements of block ionomer reverse micelles in solution revealed that the mobility of styrene units near the ionic core is reduced relative to that of styrene units away from the micelle core.[18]

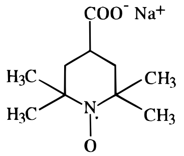
The above discussion suggests that while experimental evidence exists to support the concept of restricted mobility in model ionomer systems, the question of proof of the EHM model postulates still remains for random ionomers in bulk. Specifically, two important questions arise. The first deals with the existence of restricted mobility regions in random ionomers, while the second concerns the identification of the second glass transition as arising from these regions. Simply put, do restricted mobility regions exist, and is the effect severe enough to cause the appearance of a separate glass transition?

Recently, the second question has been answered affirmatively when the mechanical properties of polymers filled with very fine silica particles were examined.[20] It was discovered that the regions of restricted mobility in these systems give rise to a second glass transition phenomenon at higher temperatures than the T_g of the unfilled polymers. The question that remains to be answered in order to prove the validity of the EHM model is whether the regions of restricted mobility exist in random ionomers. Here we attempt to answer this question by measuring the chain dynamics of a representative ionomer as a function of temperature and ion content by electron spin resonance (ESR) spectroscopy.

Polymers and ESR Spectroscopy. ESR spectroscopy has been used in certain cases to characterize ionomers neutralized with transition metal ions, *e.g.*, Mn^{2+}, Cu^{2+}, and VO^{2+}.[21] Therefore, most of these studies provided useful insight into the state of the cations and water in ionomers but little, if any, information on chain dynamics. Experiments that enable one to obtain such information usually involve the incorporation of nitroxide free radicals (spin probes) into the solid polymer and following their dynamics by ESR as a function of temperature. This method has been used as early as 1969 to obtain the T_g of common polymers such as polyethylene or polystyrene,[22] as well as block copolymers[23] and polymer blends.[24] The spin probes used are those of the TEMPO family. They exhibit a well-understood three-line ESR spectrum. When the spin probe molecule is incorporated into a polymer, its spectrum reflects the mobility of the polymer chains. Below the polymer T_g, the spectrum is broad (outer peak separation $W \approx 65$ G), characteristic of the probe molecule being immobilized or tumbling very slowly. As the temperature increases, the spectrum becomes progressively sharper, and when the temperature exceeds T_g, the spectrum is one of a freely rotating spin probe molecule (outer peak separation $W \approx 35$ G). The temperature at which the outer peak separation is 50 G is denoted as T_{50G} and has been correlated to the T_g of the polymer.[25] In this type of experiment (spin doping), the spin probe is situated in the free volume voids in the polymer and, therefore, is expected to diffuse to unoccupied voids, provided that they exceed a critical size. Consequently, the results can be interpreted in terms of free volume, as was discussed by Kusumoto *et al.*[26] and Cameron and co-workers.[27] It was shown that the difference between T_{50G} and T_g depends on the ratio of the molecular volume of the probe molecule to the volume of the polymer segment rearranging at T_g, thus explaining the variation of the T_{50G} value with the structure and size of the spin probe.



TEMPO   4-hydroxy-TEMPO benzoate (hTb)



Sodium TEMPO carboxylate (NaTc)

Figure 1. Nitroxyl free radicals used for doping the random ionomers.

In this work, the ESR spectra of polystyrene ionomers doped with ionic and nonionic spin probes have been measured as a function of temperature, in order to identify regions of different chain mobilities. In addition, similar measurements have been performed on polystyrene ionomers containing diethylbenzene and polystyrene oligomers as plasticizers in order to evaluate their effect on the chain mobility.

Experimental Section

The styrene-*co*-(sodium methacrylate) ionomers used in this study, containing 1.4, 4.2, 7.7, and 16.2 mol % methacrylate units, were prepared by bulk free radical copolymerization of styrene and methyl methacrylate with benzoyl peroxide followed by hydrolysis of the ester groups and neutralization of the resulting acid groups with a methanolic sodium hydroxide solution. Their weight-average molecular weight was measured to be *ca.* 10^5 by size exclusion chromatography (SEC).

The nitroxyl free radicals TEMPO, 4-hydroxy-TEMPO benzoate (hTb), and sodium TEMPO carboxylate (NaTc) were the spin probe molecules used. They were obtained from Aldrich Chemical Co., and their structures are shown in Figure 1. Stock solutions were made by dissolving 100 mg in 100 mL of tetrahydrofuran (THF). The doped ionomer samples were prepared by dissolving 0.1 g of the ionomer in 5 mL of toluene/methanol (90/10, v/v) and adding 1 mL of the spin probe solution. After letting the solutions stir for 1 h, they were poured in Teflon containers which were placed in an oven at 90 °C. After 12 h, they were placed in a vacuum oven and heated at 170 °C for 24 h. In the case of samples doped with sodium TEMPO carboxylate, the stock solution contained the

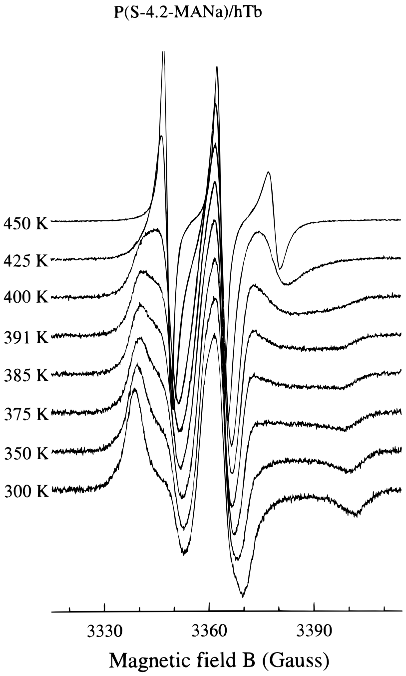


Figure 2. ESR spectra of poly[styrene-*co*-(sodium methacrylate)] ionomer (4.2 mol % ions), doped with hTb, measured at different temperatures. The spectra have been normalized in height and shifted vertically for clarity.

acid form of the probe molecule, which was added to the polymer solution. Then the proper amount of a methanolic sodium hydroxide solution was added to neutralize the carboxylic acid groups. The preparation of ionomer samples plasticized with diethylbenzene (DEB) or polystyrene (PS) oligomers of average molecular weight 450 was carried out in a similar way. The proper amount of the plasticizer to achieve a 17 wt % content was added to the polymer solution. After drying the samples at 90 °C under ambient conditions, they were heated at 50 °C for 24 h in a vacuum oven.

The ESR spectra of the spin-doped polymers were measured with a Brucker ESP300 spectrometer, operating in the X-band (*ca.* 9.45 GHz). The temperature of the sample was controlled within 1 K from the desired set point.

Results

In Figure 2 the ESR spectra of a styrene-*co*-(sodium methacrylate) ionomer (4.2 mol % ions), doped with hTb, measured at different temperatures, are presented. Each spectrum consists of three lines which become progressively sharper as the temperature increases. The extreme separation of the two outer peaks, W, is *ca.* 65 G at low temperatures, indicating a slowly tumbling probe, and it decreases to *ca.* 35 G at higher temperatures, characteristic of a fast moving probe. The temperature at which $W = 50$ G is called T_{50G} and has been found to correlate well with the usual T_g of the polymer. In Figure 3 the extreme separation W is plotted as a function of temperature for homopolystyrene (0.0 mol %) and styrene ionomers containing 4.2, 7.7, and 16.2 mol % carboxylate groups, doped with hTb. It is observed that T_{50G} increases with the ion content. In Table 1 the values of T_{50G} are reported along with the values of the matrix (T_{g1}) and cluster (T_{g2}) glass transition temperatures determined by dynamic mechanical thermal analysis (DMTA) at 1 Hz. The T_{50G} values are in reasonable agreement with the values of the matrix (first) T_{g1}.

Similar measurements were carried out on samples doped with TEMPO, in order to examine the effect of probe size on T_{50G}. The values of T_{50G} are also reported in Table 1 and are smaller than the corresponding T_{50G} values for for hTb probe. It is found that there is no significant variation of T_{50G}, as the ion content increases.

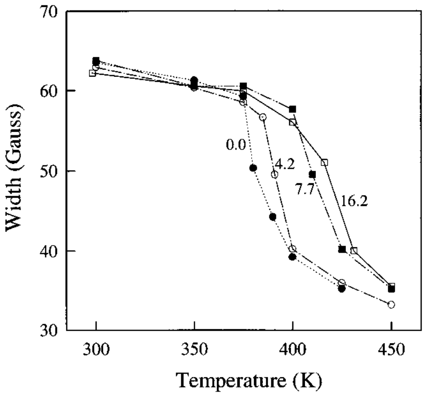


Figure 3. Extreme outer peak separation (W) versus temperature for the ionomers doped with hTb, with the following ion contents: (●) 0.0, (○) 4.2, (■) 7.7, and (□) 16.2 mol %. The lines serve as a guide to the eye.

Table 1. Values of T_{50G} for the Poly[styrene-*co*-(sodium methacrylate)] Ionomers Doped with Different Spin Probe Molecules, Obtained by ESR Spectroscopy, and Corresponding Glass Transition and Ion-Hoping Temperatures, Obtained by DMTA Measurements at 1 Hz

ion content	ESR results, T_{50G} (K)			DMTA results (1 Hz)		
(mol %)	hTb	TEMPO	NaTc	T_{g1} (K)	T_i (K)	T_{g2} (K)
0.0	380	270		391		
1.4			422	396	437	462
4.2	390	267	444	403	450	474
7.7	410	271	477	417	465	489
16.2	418		*a*	413	515	551

[a] Could not be measured.

In order to probe the mobility adjacent to the ionic multiplets, the ionomers (1.4, 4.2, 7.7, and 16.2 mol %) were doped with NaTc, which is expected to be attached on the multiplets. In Figure 4 the ESR spectra of the 4.2 mol % ionomer, measured at different temperatures, are presented. The spectra are similar to the corresponding spectra of the other spin probes, but higher temperatures are required in order to observe a narrow spectrum. Also, it should be noted that in the case of the 4.2 mol % ionomer, above 450 K the high-field peak appears to be split into a sharp and a wide component. As the temperature increases further, these components become more evident. No corresponding splitting was observed at the low-field side of the spectra. The values of T_{50G} for NaTc, obtained from the variation of W with temperature, are also reported in Table 1, along with the temperatures of ion-hopping (T_i), measured by DMTA at 1 Hz. It is observed that the values of T_{50G} fall between the two glass transitions, and they are in agreement with the ion-hopping temperatures.

Plasticization Experiments. The ionomer containing 4.2 mol % ionic groups was used in the plasticization experiments because it has been shown that the volume fraction of the reduced mobility regions is *ca.* 50%.[3c] The ESR spectra of this ionomer containing hTb and 17 wt % DEB are shown in Figure 5. The T_{50G} is 355 K, and is 35 K lower than that of the unplasticized material. It is also evident that the spectra at temperatures near T_{50G} have two minima in the high-field region, while for the unplasticized material a single broad feature is observed at corresponding temperatures. This fact may

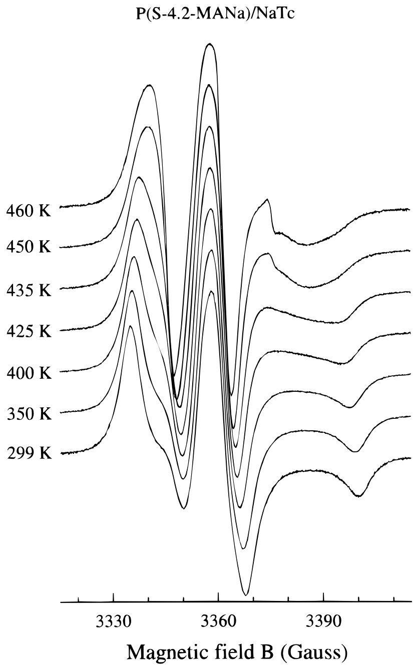


Figure 4. ESR spectra of poly[styrene-*co*-(sodium methacrylate)] ionomer (4.2 mol %), doped with NaTc, measured at different temperatures. The spectra have been normalized in height and shifted vertically for clarity.

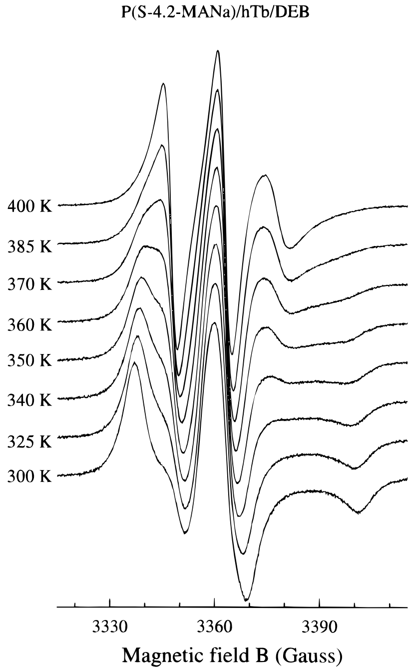


Figure 5. ESR spectra of poly[styrene-*co*-(sodium methacrylate)] ionomer (4.2 mol % ions), containing 17 wt % DEB and doped with hTb, measured at different temperatures. The spectra have been normalized in height and shifted vertically for clarity.

reflect the location of probe molecules in two slightly different environments.

Similar spectra for the same ionomer plasticized with PS oligomers are shown in Figure 6. At temperatures above 335 K, two minima are observed at the high-field side as was the case for DEB. At the same time the size of the shoulder located at the side of the low-field peak increases with temperature, but it does not merge completely with the main peak, and two peaks can be clearly distinguished at temperatures between 340 and 365 K. The two sets of signals reflect the motions of rapidly tumbling (small outer peak separation) and slowly tumbling (large outer peak separation) probe molecules.

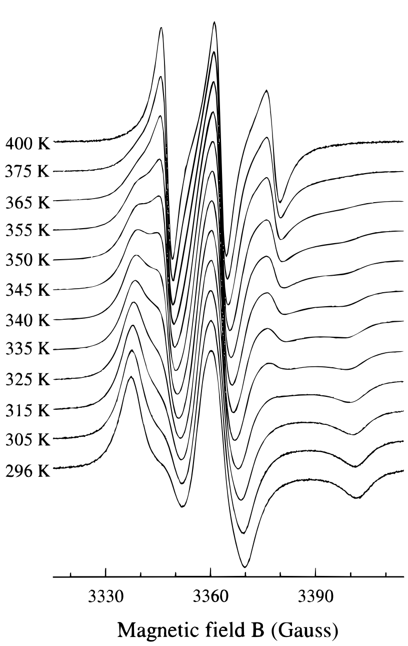


Figure 6. ESR spectra of poly[styrene-*co*-(sodium methacrylate)] ionomer (4.2 mol % ions), containing 17 wt % PS oligomers and doped with hTb, measured at different temperatures. The spectra have been normalized in height and shifted vertically for clarity.

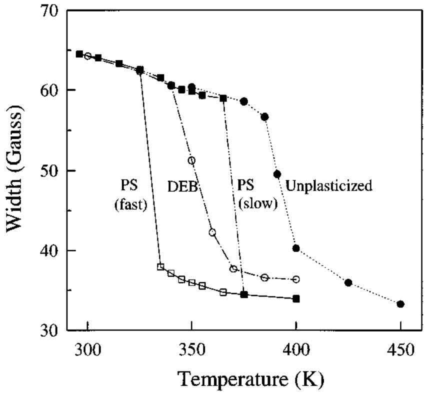


Figure 7. Extreme outer peak separation versus temperature for the poly[styrene-*co*-(sodium methacrylate)] ionomer (4.2 mol % ions) doped with hTb and (●) unplasticized, or plasticized with (○) DEB, (■) PS oligomers (slow signal), and (□) PS oligomers (fast signal). The lines serve as a guide to the eye.

When the 4.2 mol % ionomer is doped with NaTc and plasticized with DEB, the T_{50G} is 414 K, 30 K lower than that of the unplasticized sample. Moreover, there is no sharp feature accompanying the usual broad features.

In Figure 7, the extreme outer peak separation W is plotted versus temperature, in the case of the unplasticized poly[styrene-*co*-(sodium methacrylate)] ionomer (4.2 mol % ions) doped with hTb and of the same ionomer plasticized with DEB and PS oligomers (fast and slow signals). The comparison of the four curves reveals that the effect of the DEB plasticizer can be regarded as an average of the effect of PS oligomers on the matrix and cluster phases of the ionomer. Indeed, for the DEB-containing sample, $T_{50G} = 355$ K, while the average of the T_{50G} of the fast and slow signals of the ionomer containing PS oligomers is 349 K. In Table 2, the values of T_{50G} are reported for the plasticized

Table 2. Values of T_{50G} for the Poly[styrene-*co*-(sodium methacrylate)] Ionomer (4.2 mol % ions) Doped with hTb or NaTc and Either Unplastized or Plasticized with 17 wt % DEB or PS Oligomers[a]

sample	T_{50G} (K)	ΔT_{50G} (K)[b]	ΔT_{g1} (K)[b]	ΔT_{g2} (K)[b]
hTb/unplasticized	390			
hTb/DEB	355	35	~60[c]	~60[c]
hTb/PS oligomers (fast)	330	60	~30[d]	~20[d]
hTb/PS oligomers (slow)	368	22		
NaTc/unplasticized	444			
NaTc/DEB	414	30		

[a] Differences in the values of T_{50G} and glass transition temperatures, measured by DMTA, between plasticized and unplasticized materials. [b] $\Delta T_{50G} = T_{50G}$(unplasticized) $-T_{50G}$(plasticized). $\Delta T_{g1} = T_{g1}$(unplasticized) $- T_{g1}$(plasticized), matrix glass transition. $\Delta T_{g2} = T_{g2}$(unplasticized) $- T_{g2}$(plasticized), cluster glass transition. [c] Data taken from ref 5a, for the poly[styrene-*co*-(sodium methacrylate)] ionomer containing 5.1 mol % ionic groups. [d] Data taken from ref 28 for the poly[styrene-*co*-(sodium methacrylate)] ionomer containing 4.8 mol % ionic groups.

materials, along with the differences in the values of T_{50G} between the unplasticized and plasticized samples. The corresponding data measured by mechanical analysis at 1 Hz are also reported in Table 2.

Discussion

From the results presented above, it is of interest to extract information on the mobility of the ionomer segments which are adjacent to the ionic multiplets constituting the cluster phase and of the segments away from the multiplets forming the matrix phase. The type of experiment performed is an indirect method to achieve this objective, since the mobility of the polymer chains is not probed *per se*; rather, the mobility of the probe molecule is evaluated. The motions of the probe are significantly affected by the free volume and the mobility of the polymer chains.[24,25] However, the motions of the probe are complicated, since they involve not only rotations but also diffusion. Such complications undoubtedly cause incomplete motional narrowing of the spectra, which is not related to the polymer motions.

It should also be mentioned that since, at least in the case of hTb, there is only *ca.* 1 probe molecule/1000 styrene units, the influence of the probe on the polymer relaxation is expected to be very small on a macroscopic scale. Thus, there is no significant plasticization effect due to the presence of the probe molecules. The problems related to guest−host effects in ESR have been the topic of several investigations and are discussed in refs 26 and 27; the interested reader is referred to the original literature. They are not believed to affect the conclusions of the present study (described below).

With the above caution in mind, an interpretation of the experimental findings can be attempted. When hTb is used as the probe molecule, the measured T_{50G} correlates well with the first glass transition of the polymer. The fact that the T_{50G} values are close to the values of the first T_g of these ionomers (T_{g1}) is a fortunate coincidence, related to the size of the particular probe as compared to the size of the moving polymer segments. This is supported by the fact that when the smaller probe TEMPO is used, T_{50G} is low and does not vary significantly with the ion content. Since TEMPO is capable of moving fast and isotropically at 320 K, 60 K lower than the actual glass transition of polystyrene, its motions are not influenced by the ionomer glass transition. The larger hTb, though, requires larger voids than TEMPO to achieve fast isotropic motions, and these are attained only at temperatures around T_g. Moreover, it is probable that the hTb molecules residing initially at the cluster phase, at temperatures above the matrix T_g, diffuse to the matrix phase, which has larger free volume. The result is that hTb is not sensitive to the cluster glass transition.

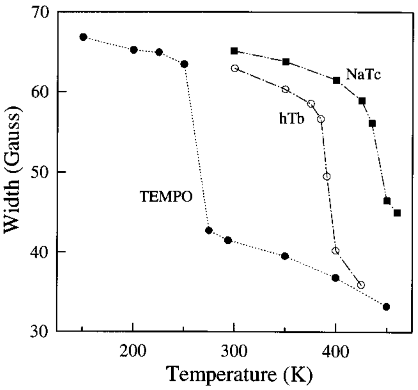


Figure 8. Extreme outer peak separation versus temperature for the poly[styrene-*co*-(sodium methacrylate)] ionomer (4.2 mol % ions) doped with (●) TEMPO, (○) hTb, and (■) NaTc. The lines serve as a guide to the eye.

When NaTc is used as the probe molecule, the situation is rather different. On the basis of experiments of ionomer plasticization with amphiphilic molecules, such as sodium dodecylbenzenesulfonate, it is expected that NaTc will be attached to the ionic multiplets.[28] At 4.2 mol % ion content, there are also some isolated ion pairs, and some of the probe molecules are expected to associate with these. If the behavior of TEMPO, hTb, and NaTc is compared, as illustrated for the 4.2 mol % ionomer in Figure 8, where W is plotted versus temperature, it is observed that T_{50G} for NaTc is 177 K higher than that of the similarly-sized TEMPO and 54 K higher than that of the significantly larger hTb. These differences become even larger in the case of ionomers with higher ion contents (7.7 and 16.2 mol %). Actually, it was not possible to measure the T_{50G} of the 16.2 mol % ionomer because it was higher than the decomposition temperature of the probe. These differences reflect the dramatic reduction in mobility for the species attached to the multiplets, in complete support of the EHM ionomer model. Because of its special location, the probe does not respond at all to the first glass transition of the ionomer. It is found that it responds to the ion-hopping process, which is thought to precede the second glass transition because it unlocks the polymer chains from the multiplets, allowing them to undergo the second glass transition. The sharp feature observed in the spectra of the ionomer containing 4.2 mol % ionic groups above 440 K can be tentatively assigned to probe molecules participating in ion pairs. Therefore, their motions are less constrained than those of the probe molecules attached to multiplets.

Plasticization. The findings of the measurements on the plasticized ionomers are in agreement with mechanical measurements performed previously.[5] It is observed here that DEB lowers the T_{50G} of both the ionomer doped with hTb and with NaTc by nearly the same amount (*ca.* 30 K), as expected by the fact that DEB has been found to plasticize equally well both the matrix and the cluster regions.[5(a)]

The plasticization with PS oligomers yields slightly different results when hTb is used as the probe molecule. This plasticizer has been found to plasticize the matrix more effectively than the cluster phase.[29] Thus,

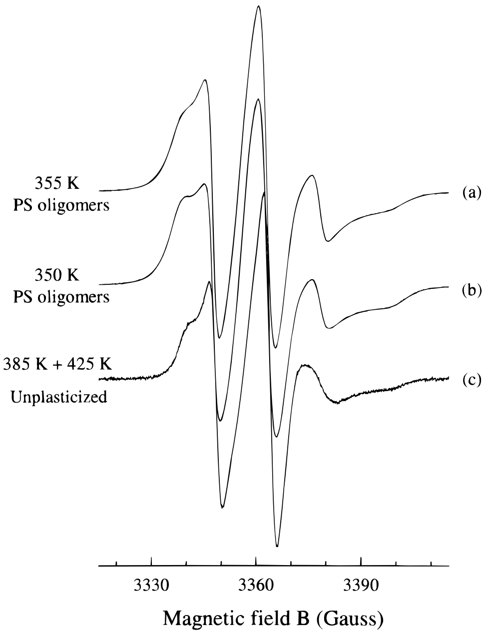


Figure 9. ESR spectra of the poly[styrene-*co*-(sodium methacrylate)] ionomer (4.2 mol % ions) doped with hTb and plasticized with PS oligomers, measured at (a) 355 K and (b) 350 K. (c) Constructed spectrum by adding the ESR spectra measured at 385 K and 425 K, of the same ionomer but unplasticized. The spectra have been normalized in height and shifted vertically for clarity.

it is expected to increase preferentially the mobility of the matrix. Indeed, the two distinct signals of different width, *W*, can be interpreted as originating from probe molecules residing in the matrix phase (fast signal) and the cluster phase (slow signal). This result is in agreement with the postulate of the EHM model in that regions of different mobility exist in random ionomers.

In the cases of vulcanized rubbers[26] and polystyrene/poly(vinyl methyl ether) blends,[24] the presence of a fast and a slow signal in the ESR spectra was interpreted as indicative of the existence of several different microenvironments, in which the free radicals were located. A similar interpretation is probably valid here also. It is thought that the different environments in the case of plasticized ionomers arise from the different chain mobilities in the matrix and cluster phases and also from the presence of the plasticizer, PS oligomers. If the effect of the plasticizer on the motions of the probe is only indirect by increasing the mobility of polymer chains in the matrix phase, it should be possible to construct the spectra of the plasticized ionomer by adding two spectra of the same material without plasticizer, one below and another above T_{50G}. In Figure 9, the constructed spectrum is shown along with the spectra of the 4.2 mol % ionomer plasticized with PS oligomers, at 350 and 355 K. The constructed spectrum is the sum of the spectra at 385 and 425 K of the same ionomer without plasticizer. These spectra were selected because their extreme outer peak widths are close to the corresponding values of the two features observed in the spectra of the plasticized ionomers in the range of 350−355 K. Since it has been calculated from mechanical measurements that the volume fractions of the matrix and cluster phases are roughly equal,[3c] the weight factor for each spectrum in the sum was 1.

The comparison of the three spectra in Figure 9 reveals that the constructed spectrum is of the same general shape as the spectra of the plasticized ionomer. The relative intensities of the low- and high-field features of the spectrum at 355 K are closely represented by the constructed spectrum. On the other hand, the peak at low field of the constructed spectrum is narrower than the peak of the other spectra. Also the high-field sharp feature is wider in the case of the constructed spectrum, indicating that in reality the motions of the probe molecules responsible for the fast feature are faster. Hence, it may be concluded that the plasticizer affects the motions of the spin-probe molecules not only indirectly by enlarging the differences of chain mobility between the matrix and cluster phases but also directly by introducing new and faster relaxation components in the already existing probe environments.

In order to gain some further understanding of the effect of the plasticizer on the ESR results, it is useful to compare these results with corresponding data from mechanical measurements, which are reported in Table 2. In the case of the sample plasticized with PS oligomers, the value of ΔT_{50G} for the slow component is 22 K, in agreement with the value of ΔT_{g2} (difference of the cluster T_g between the unplasticized and plasticized ionomers) measured by DMTA to be *ca*. 20 K. This reinforces the assignment of the slow signal of the ESR spectrum to the probe molecules located in the reduced mobility (cluster) phase. The value of ΔT_{50G} for the fast signal is 60 K, two times as large as the corresponding value of ΔT_{g1} (difference of the matrix T_g between the unplasticized and plasticized ionomers) measured by DMTA to be *ca*. 30 K. This difference reflects the complicated effect of PS oligomers on the environment of the spin probe molecules. They affect the motions of these molecules by both increasing the mobility of the polymer chains of the matrix phase and participating in the surroundings of the probe molecules and affecting their motion directly.

Conclusion

The ESR measurements of spin-doped ionomers have shown that the chain mobility near the ionic multiplets is significantly reduced and that ion-hopping takes place at temperatures between the two glass transitions of the ionomer. Similar measurements on plasticized ionomers showed that DEB is an efficient plasticizer for both the matrix and cluster phases. Plasticization with PS oligomers leads to the indirect simultaneous observation of the two mobility regimes by preferentially affecting the matrix phase. The above results support the notion presented in the EHM model that polymer segments adjacent to multiplets experience mobility restrictions. Together with our recent work on filled systems, which showed that polymer regions of reduced mobility exhibit their own glass transition, and the relevant DSC and NMR experiments, the present results constitute a solid proof of the mobility arguments of the EHM model of the morphology of random ionomers.

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