Miscible Polymer Blends with Large Dynamical Asymmetry: A New Class of Solid-State Electrolytes?

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Received July 27, 2007; Revised Manuscript Received December 17, 2007

ABSTRACT: We have employed broadband dielectric spectroscopy to investigate the ionic conductivity of poly(vinyl methyl ether)/polystyrene blend (PVME/PS) doped with lithium perchlorate, i.e., an archetype miscible polymer blend with large dynamical asymmetry. We have found that the temperature dependence of the ionic conductivity mimics that of the PVME segmental relaxation in PS. This results in a crossover from super-Arrhenius to Arrhenius behavior, which can be attributed to the restricted motion of confined PVME chains in PS, in analogy with polymer nanocomposites. This crossover produces, for some blends with high PS concentration that are therefore structurally solid, ionic conductivities of the same order as those of liquid PVME. This means that the miscible polymer blends are appealing candidates for making solid-state electrolytes.

1. Introduction

Investigation in the field of solid-state ionics has been recently the subject of intense research. Strong interest in this field has been driven by the appealing idea of obtaining materials with the mechanical properties of a solid and the ionic conductivity of a liquid. Nanocomposites made of silicates or other types of ceramic materials, conferring mechanical stability, and a polymer with high mobility are good candidates for this purpose.[1−8] The most interesting feature of these systems is that the intercalation of the polymer into the silicate implies the confinement of the polymer at length scales of the order of nanometers. This results in the appearance of a relatively fast relaxation with a (quasi) Arrhenius-like temperature dependence, which has been attributed to the restricted motion of the confined polymer chains in the silicate matrix.[9−11] To obtain an effective confinement at the length scale of the dynamics associated to the glass transition (the structural dynamics), the intercalation of the polymer is required, since a confinement length scale of the order of nanometers is obtained in this case. A length scale between 1 and 3 nm has been found to control the structural dynamics for both polymers[12,13] and low molecular weight glass formers.[14] This means that restricted motion can only occur if intercalation of one or two polymer chains (confinement length of the order of 1 nm) is achieved and, therefore, exfoliation, i.e., dispersion of the silicate in a continuous polymer matrix, should be avoided. In the latter case, no confinement at the length scale of nanometers is achieved. On the other hand, compatibility between the polymer and the silicate has to be guaranteed. In other words, the polymer must be able to penetrate between silicate layers. This implies that the intercalation of the polymer into the silicate without exfoliation is the result of a subtle balance between enthalpic and entropic forces, the former being dependent on the interaction between the polymer and the silicate and the latter being always energetically unfavorable, as intercalated polymer chains always assume a more ordered configuration with respect to the bulk polymer.[3] To overcome negative entropic forces through more favorable interactions between the polymer and the silicate, modification of the silicate surface is often carried out through the introduction of alkyl ammonium salts.[3] From a technological point of view, the issue of the intercalation of the polymer into the silicate implies a number of drawbacks which can be challenging.

In an attempt to introduce a new class of solid-state electrolytes, in this work, we have investigated the ionic conductivity of a miscible polymer blend, i.e., poly(vinyl methyl ether)/polystyrene blend (PVME/PS). This blend represents a model system since its dynamical[15−17] as well as structural properties[18] have been widely investigated in recent years. It presents a very large dynamical asymmetry, i.e., a large difference in glass transition temperature (T_g) between the two polymers: 249 K for PVME and 373 K for PS. Recent dielectric spectroscopy results on the dynamics of dilute PVME in PS highlight the presence of a low activation energy motion with Arrhenius-like behavior.[16] This relaxation, in analogy with polymer/nanocomposites systems, has been attributed to the restricted motion of PVME chains[16] due to the presence of frozen PS as a consequence of the selective freezing occurring in miscible polymer blends.[19] In particular, a crossover from a super-Arrhenius behavior, i.e., an increase of the apparent activation energy with decreasing temperature at high temperature, normally observed in fragile glass-forming systems, to a milder Arrhenius temperature dependence is observed for PVME dynamics in PS.[16,17] This crossover is normally observed along the T_g range of the blend, namely, where the rigid component gets frozen. The T_g range of the blend is defined as the temperature range in which the specific heat jumps from the value of the glassy state to that of the liquid.

Starting from these premises, we have used broadband dielectric spectroscopy to study the ionic conductivity properties of PVME/PS blends as well as those of the pure polymers. We have mostly focused on blends highly concentrated in PS, namely, those blends for which the effect of confinement on PVME is most prominent. Blends with 10, 20, 30, and 50 wt

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10.1021/ma071679v CCC: $40.75

% of PVME have been investigated. In addition, 1 wt % of lithium perchlorate ($LiClO_4$) has been added to all blends to improve the ionic conductivity and perform a straightforward comparison among their conductivities. Our results suggest that for blends with PVME less than 30 wt % a clear crossover from super-Arrhenius to Arrhenius temperature dependence of the ionic conductivity occurs, mimicking the behavior of PVME dynamics in PS.[16] This finding strongly supports the idea that charge transport essentially takes place along mobile paths within confined PVME chains. The main striking consequence of the crossover to a low-temperature Arrhenius behavior implies that the ionic conductivity of some structurally glassy PVME/PS blends is higher than that of pure liquid PVME. In addition, comparing structurally analogous systems, we demonstrate that miscible PVME/PS blends display ionic conductivities orders of magnitude larger than those of the pure polymers.

2. Experimental Method

Poly(vinyl methyl ether), polystyrene, and lithium perchlorate were purchased from Sigma-Aldrich. The molecular weight of the two polymers were $M_n = 7300$ g/mol ($M_w/M_n = 3$) and $M_n = 140\,000$ g/mol ($M_w/M_n = 1.64$), respectively. Lithium perchlorate had a purity of 99.99%. Poly(methyl vinyl ether)/polystyrene/lithium perchlorate mixtures were prepared dissolving the three components in a common solvent, namely, tetrahydrofuran. The solvent was subsequently removed via freeze drying at −80 °C and then in a vacuum oven above the T_g of the blend (to remove any traces left). Achievement of constant weight was used as the criterion for full removal of the solvent.

Dielectric measurements were carried out on all mixtures using a high precision dielectric analyzer (ALPHA, Novocontrol GmbH) and a Novocontrol Quatro cryosystem for temperature control with a precision of ±0.1 K. Measurements were performed over a wide frequency (10^{-2}−10^{6} Hz and in some cases down to 10^{-3} Hz) and temperature range in isothermal steps starting for the highest temperature. Mainly, the dielectric permittivity was analyzed to extract the direct current (dc) conductivities, i.e., the low-frequency limit (static) value of the conductivity. The analysis was based on the fitting of the complex dielectric permittivity in the frequency domain through a sum of Havriliak−Negami (HN) functions[20] plus a conductivity term:

$$\epsilon^*(\omega) = -i\frac{\sigma_{dc}}{\epsilon_0\omega} + \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau_{HN})^{\alpha_{HN}}]^{\gamma_{HN}}} \qquad (1)$$

where σ_{dc} is the dc conductivity, ϵ_0 the permittivity of vacuum, ϵ_∞ is the high-frequency limit value of the dielectric constant, $\Delta\epsilon$ is the dielectric strength of the relaxation process, and α_{HN} and γ_{HN} are the shape parameters of the HN function describing, respectively, the symmetric and asymmetric broadening of the complex dielectric permittivity. The dielectric analyzer has a resolution for the loss part of the permittivity higher than $\epsilon'' = 10^{-3}$. This, at frequency of the order of 0.1 Hz, corresponds to a resolution higher than $\sigma = 10^{-17}$ S/cm for the ionic conductivity.

Calorimetric measurements were carried out by means of a differential scanning calorimeter (DSC-Q1000) from TA-Instruments. Measurements were performed in a standard mode at a scanning rate of 20 K min^{-1}. These DSC measurements were performed on samples directly cut from the films investigated through dielectric relaxation spectroscopy.

3. Results and Discussion

In Figure 1, specific heat vs temperature plots are displayed for all investigated PVME/PS/$LiClO_4$ systems. A single specific heat jump, though broad, indicates the miscibility at the molecular level of the mixtures.[16] In addition, the curves are within the experimental error identical to those of PVME/PS blends reported in ref 16. This implies, at least for what concerns the calorimetric response of the mixtures, the structural equivalence between pure PVME/PS blends and those containing 1 wt % of $LiClO_4$. Table 1 summarizes the T_g of all investigated systems as a function of PVME wt %.

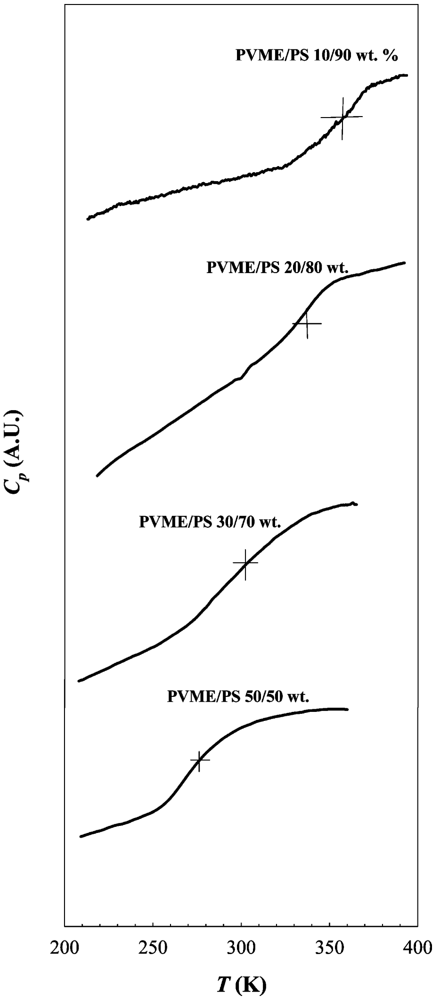

Figure 1. Specific heat vs temperature plots for all PVME/PS/$LiClO_4$ systems.

Table 1. Composition Dependence of the T_g for PVME/PS/$LiClO_4$ Systems

PVME (%)	0	10	20	30	50	100
T_g (K)	373	355	340	312	275	249

In Figure 2, the loss (a) and real (b) parts of the dielectric relative permittivity are displayed for a system with 10 wt % PVME at a temperature of 353 K as an example. The fit of the loss part of the permittivity would suffice to obtain the dc conductivity, as this term only appears in the loss part of the complex permittivity as a power law and mostly detectable at relatively low frequency. However, we notice that, although the conductivity term is dominant in the low-frequency side of the permittivity loss spectrum, a slow relaxation can be detected in the real part of the permittivity, manifesting with a dispersion of this function at relatively low frequencies. The presence of a relatively low-frequency relaxation is characteristic of heterogeneous systems and is attributed to interfacial polarization caused by charges blocked at some internal boundaries.[21] To take into account this relaxation, we have performed the simultaneous fitting of the loss and real parts of the permittivity. This procedure allows for a univocal subtraction of any relaxational contribution from the dc conductivity term in the loss part of the permittivity. As observed in Figure 2, the

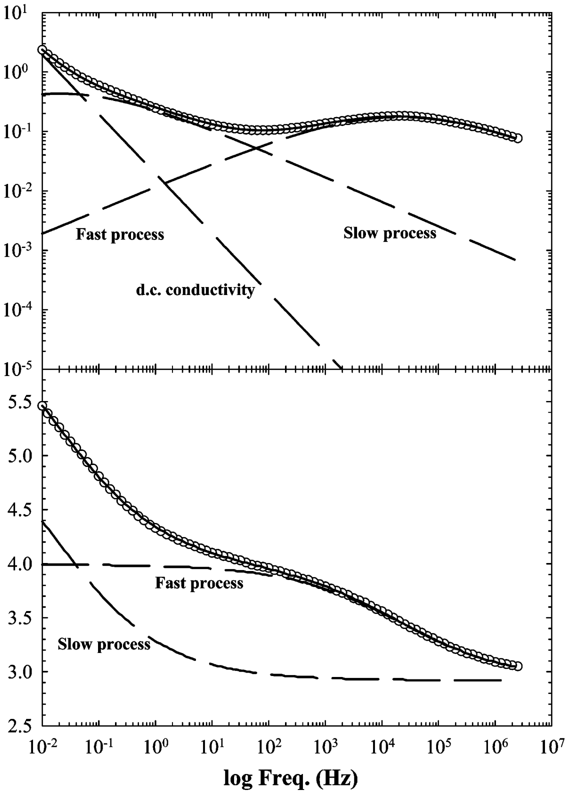

Figure 2. Dielectric permittivity vs frequency for PVME/PS (10/90 wt %) with 1 wt % of $LiClO_4$ at 353 K: (a) loss and (b) real part. The solid lines are datafit to eq 1, whereas the dashed lines are the various contributions to the overall fit.

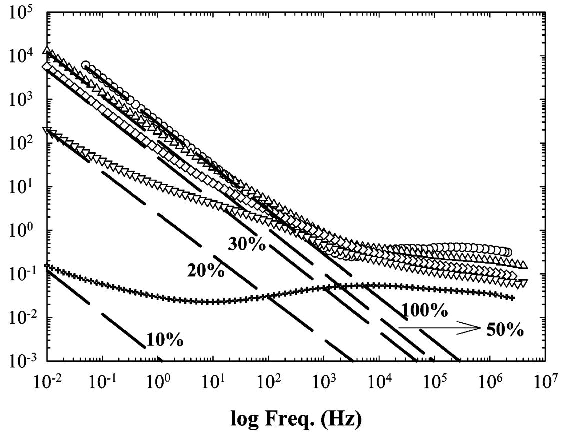

Figure 3. Loss part of the dielectric permittivity vs frequency for PVME/PS/$LiClO_4$ systems at 313 K with the following PVME weight percentages: 10% (crosses); 20% (down triangles); 30% (diamonds); 50% (up triangles); 100% (circles). Solid lines are experimental data fit to eq 1. Dashed lines are the dc conductivity contributions to the fits.

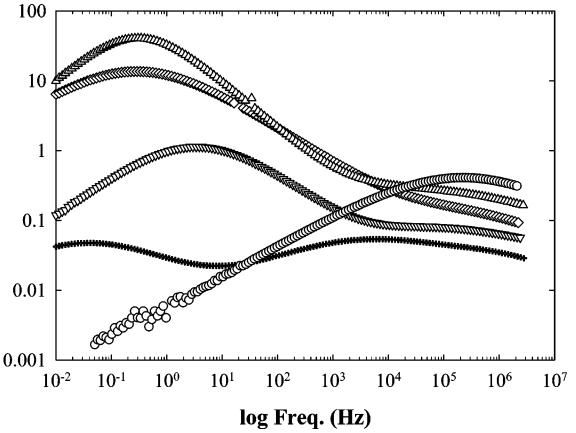

Figure 4. Loss part of the dielectric permittivity vs frequency for PVME/PS/$LiClO_4$ systems at 313 K after subtracting the dc conductivity and the slowest contribution to the relaxation pattern (frequency < 10^{-2} Hz) with the following PVME weight percentages: 10% (crosses); 20% (down triangles); 30% (diamonds); 50% (up triangles); 100% (circles).

agreement between experimental data and the fit by eq 1 is excellent.

In Figure 3, the experimental data of the permittivity loss vs frequency for blends at all concentrations as well as those of pure PVME are displayed at 313 K. The dashed lines are the contributions from the dc conductivity to the fits. From the inspection of the low-frequency part of the plot, it is possible to conclude that, as expected, the ionic conductivity decreases with increasing PS content, with this decrease being more marked for the blend with 10 wt % PVME. However, it is noteworthy that even the blend with only 10 wt % PVME still presents a measurable ionic conductivity. This result is quite remarkable considering that pure PS ionic conductivity (not shown Figure 3) is practically absent at 313 K, with the polymer being deep in the glassy state at this temperature.

In Figure 4, the experimental data after removing the dc conductivity are shown at 313 K for all investigated systems. The slow relaxation always present for all investigated systems (except for the system with 10 wt % PVME) with characteristic frequency lower than 10^{-2} Hz has also been subtracted. From inspection of Figure 4, it is possible to distinguish a relatively low-frequency relaxation peak (between 10^{-2} and 1000 Hz depending on the system) that, as discussed, likely arises from the heterogeneous nature of PVME/PS/$LiClO_4$ systems, which is absent in the PVME/$LiClO_4$ system. Apart from this peak, a relaxation peak at about 10^5-10^6 Hz is present in all spectra. This can be attributed to the motion of the PVME moieties, with the relaxation time of this process being comparable to that reported by Lorthioir et al.[16] for undoped PVME/PS blends. In addition, the strength of this process increases with PVME concentration, thus confirming the close relation between this process and the PVME motion. It is worth noticing that the relaxation data reported by Lorthioir et al.[16] for the blend with 50 wt % PVME match with those reported in Figure 5 only for temperatures higher than about 290 K. This is due to the fact that the present relaxation data of PVME/PS (50/50 wt %) blend correspond to the resolved high frequency shoulder of the whole response of the blend.[16] On the other hand, the relatively slow process is not visible in our experiments, which is probably obscured by the high conductivity present in PVME/PS/$LiClO_4$ systems.

In Figure 4, apart from the aforementioned relatively fast relaxational process, the system with 10 wt % PVME also presents a relaxation peak at about 1000 Hz. We tentatively attribute this process to the motion of lithium cations that can in principle be present in other PVME/PS/$LiClO_4$ systems. For systems with a PVME content higher than 10 wt %, this would not be unveiled in the relaxation spectrum, which is likely due to the presence of stronger relaxational processes.

To look at the ionic conductivity properties of PVME/PS blends in detail and compare them with those of the pure polymers, we report the temperature dependence of the ionic conductivity for PVME/PS/$LiClO_4$, PVME/$LiClO_4$, and PS/$LiClO_4$ systems in Figure 5 (lower panel). The upper panel of Figure 5 displays the relaxation time related to the PVME motion in all PVME/PS/$LiClO_4$ systems and that related to PVME/$LiClO_4$ and PS/$LiClO_4$ systems. For the pure polymers

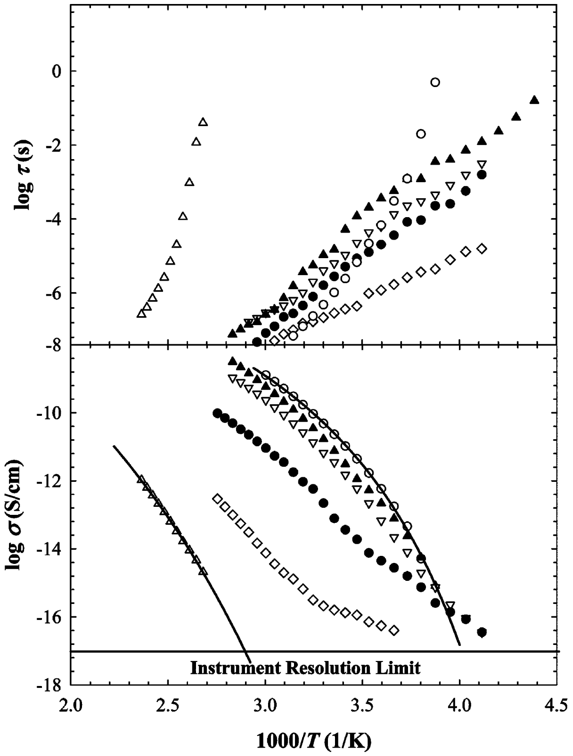

Figure 5. Log plots of the relaxation time (upper panel) and the ionic conductivity (lower panel) vs inverse temperature for PVME/PS/$LiClO_4$ systems with the following PVME weight percentages: 10% (empty diamonds); 20% (filled circles); 30% (empty down triangles); 50% (filled up triangles). The plots are also shown for PS (empty up triangles) and PVME (empty circles). The solid lines are the fits to the VFT equation of PS and PVME experimental data.

with $LiClO_4$, a clear super-Arrhenius behavior, i.e., an increase of the apparent activation energy with decreasing temperature, can be observed mimicking the temperature dependence of the structural relaxation time. The ionic conductivity of PVME/$LiClO_4$ is in good agreement with that reported by Zhang and Runt.[22]

With regard to the ionic conductivity of PVME/PS/$LiClO_4$ systems, the following observations can be made: (i) despite the high concentration of PS, the ionic conductivity is closer to that of PVME/$LiClO_4$ system except for the blend with 10 wt % PVME; and (ii) systems with less than 30 wt % PVME present a crossover from non-Arrhenius to Arrhenius temperature dependence. The first issue can be simply explained assuming that the ionic transport preferentially occurs along the most rapid paths, which are mainly associated with the relatively more mobile polymer of the blend (PVME). This result in not unexpected, since PVME segmental dynamics in PS, to which ionic conductivity is correlated, does not decouple too much from that of pure PVME.[12,15,16] The idea that the ionic transport takes place along the PVME percolating mobile channels qualitatively agrees with the decoupling between self- and pair-correlation function occurring in binary blends of bead−spring polymer chains.[23] The fact that the ionic conductivity, in the case of the system with 10 wt % PVME, is strongly depressed compared to systems richer in PVME also agrees with the loss of the aforementioned decoupling in bead−spring polymer blends at a low concentration of the more mobile polymer.[23] For blends with low PVME content, the impossibility of having a complete percolation of the PVME moieties is probably responsible for the sudden drop of the ionic conductivity. The main consequence of this is a partial decoupling between the PVME related dynamics and the ionic conductivity that in this case starts to be strongly affected by the presence of PS matrix. It is noteworthy that while for systems with larger concentrations of PVME the temperature where the ionic conductivity of the blend matches with that of the pure PVME is close to the one for which the same matching occurs for the relaxation time this does not occur for the system with 10 wt % PVME.

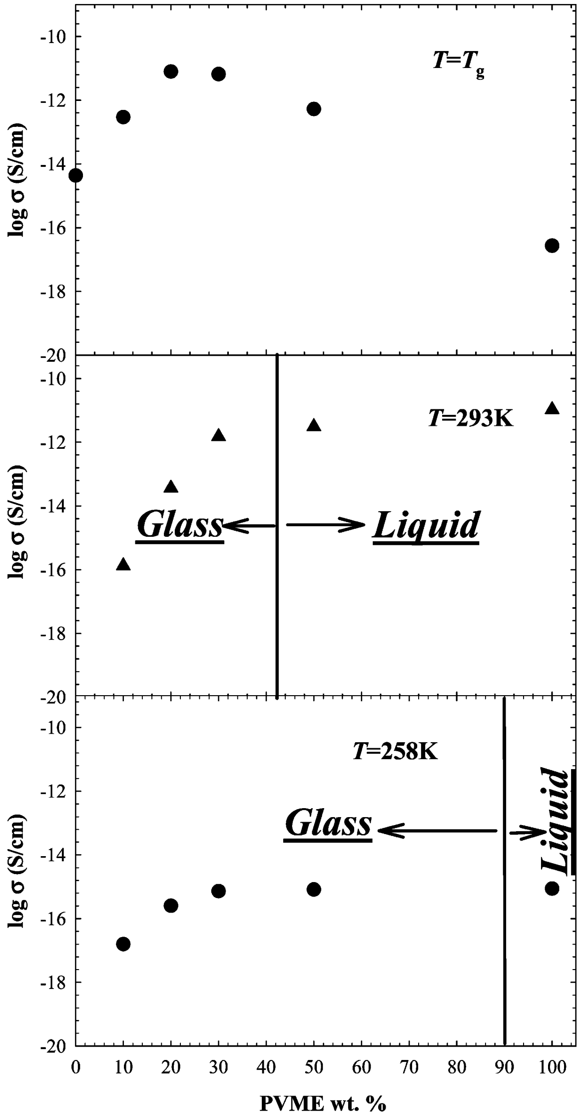

Figure 6. Composition dependence of the ionic conductivity at two fixed temperatures, 258 K (lower panel) and 293 K (middle panel), and at the T_g values of the PVME/PS/$LiClO_4$ systems.

The most intriguing result, however, is the crossover from non-Arrhenius to Arrhenius temperature dependence, which, alike the structural relaxation time, can be attributed to the confinement of PVME chains by the rigid PS, hindering the growth of PVME characteristic length scale.[10−13,16] We speculate that this crossover mainly implies that at relatively low temperatures the ionic conductivity mainly couples to the Arrhenius process displayed in the upper panel of Figure 5. On the other hand, at relatively higher temperatures, the ionic conductivity would mainly couple to the cooperative motion in a system still (partly) in equilibrium giving rise to the aforementioned super-Arrhenius temperature behavior. It is worth noticing that the crossover from non-Arrhenius to Arrhenius temperature dependence implies at relatively low temperature, in blends with 20 and 30 wt % of PVME, the ionic conductivity matches with that of pure PVME with the same amount of $LiClO_4$. This means that systems which are prevalently composed of PS, and therefore are structurally solid, present ionic conductivities equal or even larger than those of liquid PVME. To better highlight this point, in the lower and middle panels of Figure 6, the composition dependence of the ionic conductivity at two fixed temperatures (258 and 293 K) is displayed. From Table 1, where T_g values as a function of PVME concentration are reported, it is possible to determine the concentration that marks the transition between glassy and liquid state at each of the two fixed temperatures. From the observation of the two panels it is clear that, compared to pure PVME, the ionic conductivity is only slightly decreased for blends with PVME concentration as low as 20 wt %, namely, for polymer blends mainly composed of glassy PS. It is noteworthy that the PS/LiClO4 system presents negligible ionic conductivity at both of the two displayed temperatures.

As a further indication of the improved ionic conductivity properties of PVME/PS blends, it is interesting to compare the isostructural values of this property. This is done in Figure 6 (upper panel) using the T_g as a criterion for isostructural systems. As can be observed, the ionic conductivity at the T_g of PVME/PS blends with 1 wt % of $LiClO_4$ is orders of magnitude larger than that of the pure polymers with the same amount of $LiClO_4$, with a maximum between 20 and 30 wt % of PVME.

4. Summary

We have shown that miscible polymer blends with large dynamical asymmetry can present ionic conductivities in the glassy state comparable to those of liquid PVME. This result has been discussed in relation to the coupling between ionic conductivity and structural relaxation time. This implies a crossover from super-Arrhenius to Arrhenius-like temperature dependence, where the latter behavior has been attributed to the restricted motion of PVME in rigid PS. This result is comparable to those previously found for polymer nanocomposites.[10,11] However, we emphasize here that, whereas polymer nanocomposites present serious technological drawbacks due to the necessity of obtaining intercalated nanocomposites rather than exfoliated or immiscible, in the case of polymer blends thermodynamic miscibility is the only requirement apart from the large dynamical asymmetry.

It is worth remarking that, though PVME/PS system does not display technologically relevant ionic conductivities (above $10^{-4}-10^{-3}$ S/cm), our results may provide further impetus to study other miscible polymer blends as well as polymer-plasticizer systems with large dynamical asymmetry. Analogous to PVME/PS blends, the dynamics of poly(ethylene oxide) in poly(methyl methacrylate)[24,25] and that of poly(vinylidene fluoride) in poly(methyl methacrylate)[26] are characterized by the presence of a fast Arrhenius-like dynamics attributed to the restricted motion of the low T_g component. These systems are therefore good candidates to explore the ionic conductivity properties and their possible application in the field of solid-state ionics.

Acknowledgment. The authors acknowledge the University of the Basque Country and Basque Country Government (Ref. IT-436-07, Depto. Educación, Universidades e Investigación) and Spanish Minister of Education (MAT 2004-01617) for their support. The support of the European Community within the SoftComp program is also acknowledged.

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MA071679V