Proton NMR Study of Rouse Dynamics and Ideal Glass Transition Temperature of Poly(ethylene oxide) $LiCF_3SO_3$ Complexes

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ABSTRACT: A range of low-molecular-weight linear poly(ethylene oxide) chains with $LiCF_3SO_3$ have been examined via the transverse proton NMR relaxation. From the measured relaxation functions it is shown that the chains obey Rouse dynamics. This analysis gives the molecular weight of a Rouse statistical subunit and the fundamental Rouse relaxation time. It was found that varying the temperature and salt concentration had no effect on the size of a Rouse statistical segment and therefore none on the conformation of the chains. The temperature dependence of the fundamental Rouse relaxation time was found to be well modeled by the Vogel−Tamman−Fulcher equation. The NMR-measured correlation times were then successfully used to predict the glass transition temperature as measured by DSC. The main conclusion of this paper is that under the addition of salt the ideal glass transition temperature T_0 is found to remain constant or indeed to slightly decrease.

Introduction

A polymer electrolyte consists of a salt dissolved into a coordinating macromolecule that acts as an ionizing solvent. On the local level fast atomic relaxational processes enable ions to conduct electricity in the same way as a conventional liquid electrolyte, whilst on the larger scale entanglements provide mechanical properties that are similar to those of a solid. Amongst the applications now under development for these novel electrolytes are electrochromic displays and rechargeable high-energy-density lithium batteries.[1]

Experimental studies on solid polymer electrolytes have focused mainly on the conductivity behavior because this is a very important property in view of their potential applications. Since the original publications of Armand,[2,3] the Vogel−Tamman−Fulcher (VTF) equation[4−6] has often been employed to describe the temperature dependence of the conductivity. At a temperature T_0, termed the ideal glass transition temperature, polymer configurational entropy vanishes and the material becomes nonconducting. It is therefore crucial to understand the influence of both salt species and concentration on this parameter, and correspondingly many studies in the literature have been devoted to this aim.[7−9]

Following the discovery by Wright[10] and the pioneering work of Armand, the poly(ethylene oxide) (PEO)/lithium salt complexes have become the most studied solid polymer electrolytes. In this system the ether oxygen atoms on the polymer backbone coordinate the lithium cations, leading to the solubilization of the salt. This interaction may be expected to alter both the local structure and dynamics of the polymer matrix.[11] An understanding of the role of the salt in the electrolyte would give a framework within which to interpret other experimental data, such as those from conductivity studies, but despite extensive work on this system the influence of the salt on the PEO chains still remains unclear.

In this paper proton NMR spin−spin relaxation has been used to investigate the effect of salt on both the conformation and relaxation dynamics of the chains in the archetypal polymer electrolyte PEO/$LiCF_3SO_3$. Unlike conductivity studies, which are concerned with the mobility of charged species, NMR gives direct access to the correlation times relating to the chain dynamics. Ionic conduction is believed to be closely dependent on the motion of the polymer, but complications such as ion pairing can occur, reducing the number of available charge carriers and therefore the conductivity. The relaxation times measured by NMR thus provide a more direct test of the VTF formalism to model the temperature dependence of the chain motion. From the NMR-measured correlation times the ideal glass transition temperature can be accurately determined and the effect of salt concentration on this parameter revealed.

In an earlier study,[12] carried out at the University of Leeds, we examined the polymer molecular weight dependence of the proton transverse NMR relaxation for the PEO/$LiCF_3SO_3$ system. In that work both the entanglement density and the critical entanglement molecular weight were found to be independent of salt concentration, from which it was concluded that the salt was not forming cross-links in the polymer electrolyte. This work extends that study now, by considering the temperature dependence of the proton NMR spin−spin relaxation.

A selection of low-molecular-weight PEO chains all below the critical entanglement molecular weight was examined over a range of temperatures using proton transverse NMR relaxation. From the molecular weight dependence of the NMR decays it is shown that the chains undergo Rouse dynamics. The molecular weight of a Rouse statistical segment and the fundamental Rouse relaxation time can then be determined. The analysis thus enables the effect of the salt on both the conformation and the dynamics of the PEO chains to be measured.

Experimental Section

A MARAN bench-top pulse NMR analyzer, manufactured by Resonance Instruments Ltd, U.K., operating at 20 MHz for protons, was used to acquire data. The transverse relaxation was measured by the Carr−Purcell−Meiboom−Gill

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sequence:[13,14]

$$90_x - \tau - (180y - 2\tau)_n$$

This is a self-compensating sequence that ensures every second echo is correct. The 90_x pulse width was typically 3.5 μs, $\tau \sim 1$ ms, and $n \sim 1000$. Each free induction decay is the result of 32 scans with a 15 s recycle delay. Some measurements have been carried out on a Chemagnetics CMX 200 and a Bruker SXP 100 spectrometer using the Levitt–Freeman[15] modification of the above Carr–Purcell–Meiboom–Gill echo train. The results from all the spectrometers were the same within experimental error.

The polymer electrolytes were prepared following the method outlined by Cruickshank.[8] Each sample underwent a series of freeze–melt cycles whilst attached to a vacuum line (10^{-4} Torr). This removed any oxygen absorbed within the sample that would have otherwise affected the free induction decay, owing to its paramagnetic effect.

Results and Analysis

The dephasing of the transverse nuclear magnetic components is caused by the dipolar interactions of the proton pairs along the polymer backbone. Cohen-Addad first showed that, by averaging the NMR properties over several, N_a, monomers, a scale invariant model of the chain could be constructed.[16] The NMR decay function $G(t)$ is then determined by the spectrum of relaxation times governing this representative chain.

Small linear chains below the critical entanglement molecular weight in the melt obey Rouse dynamics.[17] In this model the bond–bond relaxation function is written as a sum over correlation times, τ_p, for each mode p, where[18]

$$\tau_p = \frac{\tau}{\sin^2(\pi p/2N)} \tag{1}$$

with N the number of Rouse units comprising the chain and τ the fundamental Rouse relaxation time, which can be related to the local friction coefficient ν by,[18]

$$\tau = \frac{b^2}{12kT}\nu \tag{2}$$

where k is the Boltzmann constant and b is the size of a Rouse statistical segment.

From the above Rouse description of chain dynamics the theoretical transverse decay function can be derived.[19] In this calculation the full spectrum of relaxation times are taken into account, giving

$$G(t) = \exp\left(\frac{-t}{T_2}\right) \tag{3}$$

with

$$\frac{1}{T_2} = \frac{6\Delta^2\tau \ln(N)}{\pi} \tag{4}$$

where Δ is the dipolar interaction strength specified by

$$\Delta = \frac{\gamma^2\hbar\mu_0}{8\pi N_a d^3} \tag{5}$$

with d the proton–proton distance within a proton pair, μ_0 the permeability of a vacuum, γ the gyromagnetic ratio for a proton ($=26.75 \times 10^7$ T^{-1} s^{-1}),[20] and N_a the number of monomers required to form a Rouse unit. The value of d for PEO was taken as 1.76×10^{-10} m. The ln N term in eq 4 arises from the sum over the Rouse modes of the chain.

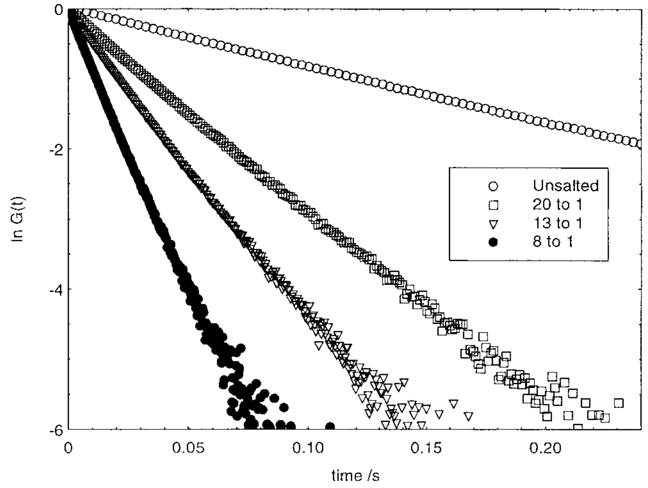

Figure 1. Transverse NMR decay functions from 300 g mol^{-1} PEO chains at 298 K for four different salt concentrations (written as the number of ethoxy monomers to a lithium ion).

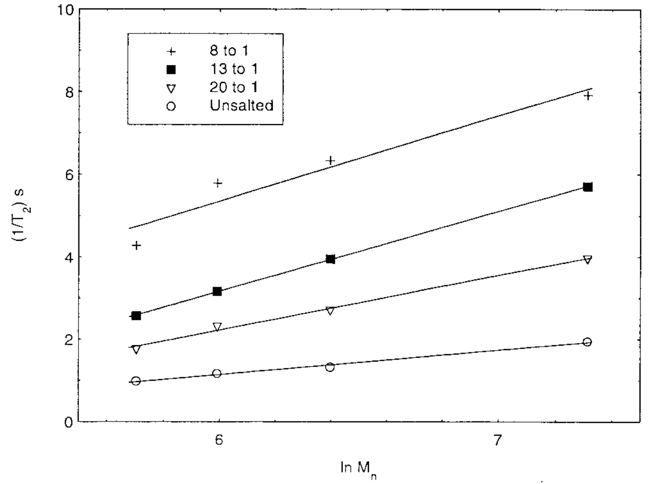

Figure 2. Relaxation rate $1/T_2$ as a function of the PEO molecular weight at 378 K for four different salt concentrations (displayed as the number of ethoxy monomers to a lithium ion). The solid lines are fits to the Rouse model predictions.

For a polymer with monomer weight m and molecular weight M_n the number of Rouse units required to represent the chain is $M_n/N_a m$. In eq 4 the term ln(N) can be more usefully written as

$$\frac{1}{T_2} = \frac{6\Delta^2\tau(\ln M_n - \ln N_a m)}{\pi} \tag{6}$$

A plot of T_2^{-1} versus ln(M_n) enables the Rouse parameters τ and N_a to be obtained. The slope of such a graph gives $\Delta^2\tau$ with the ratio of the intercept to the slope determining N_a. Equation 5 then specifies Δ, and hence τ can be found from the product $\Delta^2\tau$.

In Figure 1 a selection of experimental transverse decay functions is displayed. The signals are clearly all exponential, as predicted by eq 3. This is true even for the highest salt concentration. Figure 2 displays the relaxation rate $1/T_2$ as a function of molecular weight for a selection of salt concentrations at 378 K. The anticipated linear dependence (eq 6) of T_2^{-1} on ln(M_n)

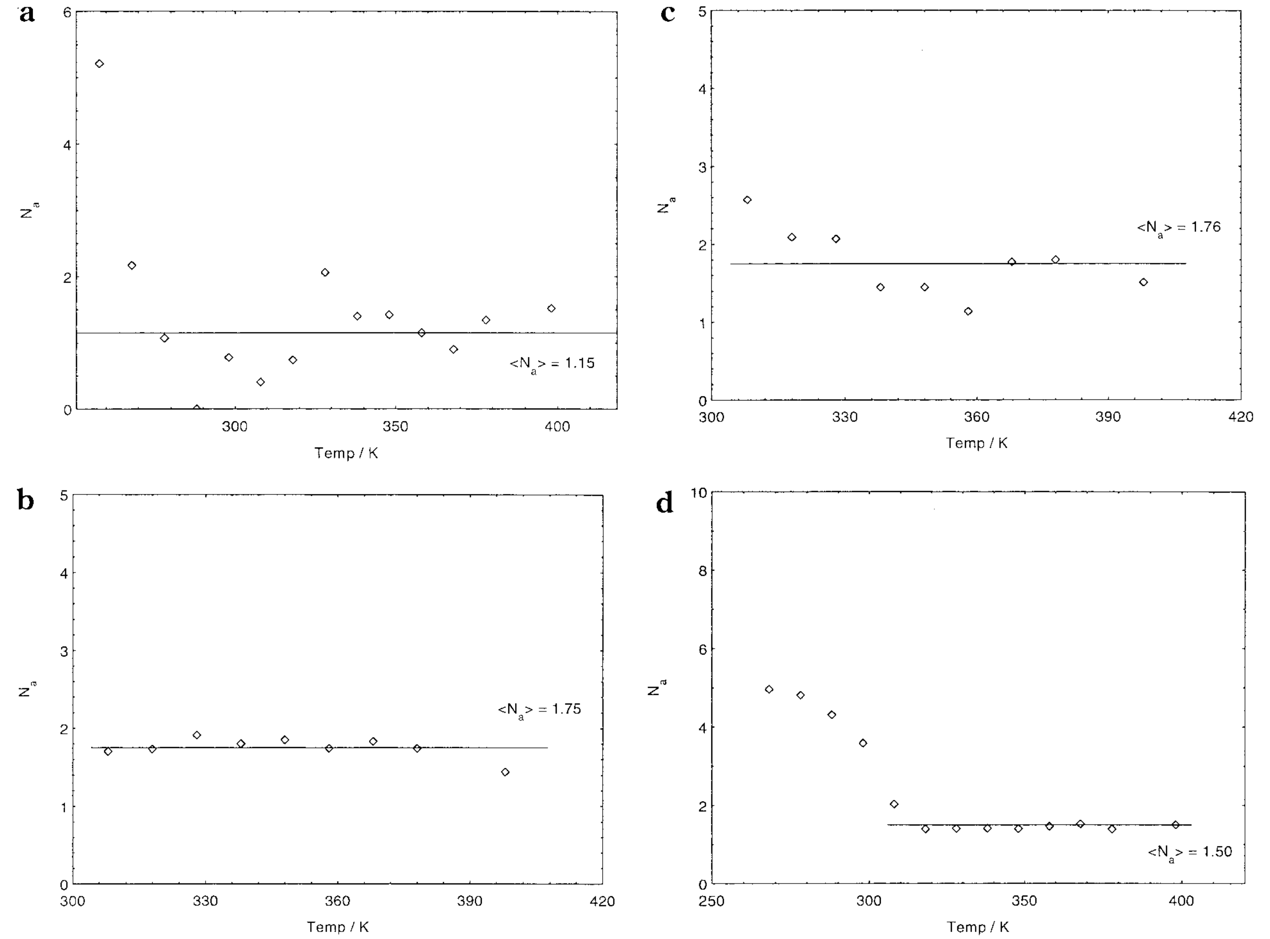

Figure 3. Number of monomers per Rouse unit as a function of temperature for the (a) unsalted PEO sample and (b) 20 to 1, (c) 13 to 1, and (d) 8 to 1 salt concentrations (number of ethoxy monomers to a lithium ion).

is found. This reveals that the motion of the chains is consistent with that of Rouse dynamics.

At all the measured salt concentrations eq 6 is found to describe accurately the molecular weight dependence of the characteristic decay rate T_2 (Figure 2). If the salt was altering the melt structure by the introduction of cross-links, then the dynamics of the spin pairs between cross-link points would deviate from the simple Rouse description. The spectrum of correlation times governing the dynamics of the monomers between junction points would no longer be that specified by Rouse theory. The spin pairs would have a residual dipolar coupling produced by the cross-link points that would alter the shape of the relaxation function, giving the known “frozen bond” result.[21] The decay rates predicted from the Rouse model would also be numerically incorrect. This would be revealed by a deviation of T_2^{-1} from its expected dependence on $\ln(M_n)$. The NMR results therefore indicate that inter- or intrachain cross-linking does not occur, consistent with previous work.[8,12,22] Indeed recent computer simulations support the conclusion that the cation does not act as an effective cross-linker.[23]

It is important to note that even the lowest molecular weight used, 300 g mol^{-1}, lies on the anticipated linear dependence (eq 6); recall Figure 2. Despite the chain being comprised of only six monomers, it is still large enough to obey Rouse dynamics. Also these lowest molecular weight samples have the highest concentration of free ends. If this higher presence of end groups was altering the role of the salt in the sample, then it would have been observed in Figure 2 as a departure from the predictions of eq 6.

From the relationship between the decay time T_2 and the chain molecular weight M_n, the number of monomers required to form a Rouse unit can be determined. This procedure is applied to all the different salt and temperature measurements. As the temperature is reduced below 348 K, the higher molecular weight monomers begin to crystallize. A departure from the linear dependence of eq 6 is then found. These samples at these lower temperatures are therefore not used in the analysis, as they are no longer correctly modeled by Rouse dynamics.

The number of monomers per Rouse unit at various salt concentrations is displayed as a function of temperature in Figure 3. A value for N_a of 1.5 corresponds to four or five main chain bonds. Only one or two monomers are needed to connect together to generate Gaussian end-to-end statistics, with this revealing the high flexibility of the chain. This measure of the persistence length N_a is found to be independent of temperature right down to the point that the chains themselves crystallize.

The values of N_a as a function of temperature are also supportive of the isolated spin pair assumption made in the theoretical analysis[19] of the transverse relaxation function. The number of monomers per Rouse unit is extremely small, ~1.5. This indicates that there is rapid C−C bond rotation, providing decoupling between the methylenes along the polymer backbone. In earlier work[24] this assumption was found to be valid on poly-

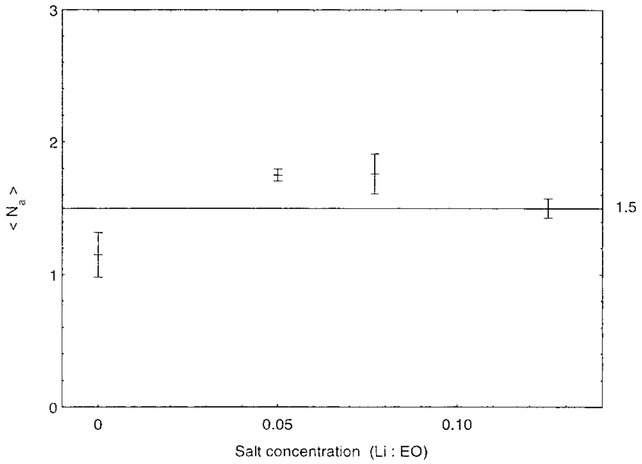

Figure 4. Average number of monomers per Rouse unit as a function of salt concentration, written as the number of lithium ions per ethoxy monomer.

(ethylene), where the backbone flexibility is far less than that of poly(ethylene oxide). This parameter N_a is also very sensitive to the transverse decay rates, so if, as the temperature was lowered, coupling between methylene pairs was introduced, it would be expected to alter its value. This is not evident until the chains begin to crystallize, whereupon its value rapidly increases; note Figure 3a.

For each salt concentration studied an average value of N_a over the temperature range where the samples have not crystallized can be determined from Figure 3. This parameter $\langle N_a \rangle$ with error bars showing the standard deviation in the mean value is plotted in Figure 4 and found to be independent of the salt concentration. The addition of salt thus does not affect the melt structure. If for example the average end-to-end distance was altered by the presence of salt, this would change the characteristic ratio of the polymer. In terms of a representative chain this would be reflected in a variation in the size of a statistical segment or, as in this analysis, a dependence of N_a on salt concentration. Again the salt is found to not alter the structure of the melt.

Extensive studies[7,8,25] undertaken on this system have found that both the conductivity and viscosity can be well described by the VTF equation. The fundamental Rouse relaxation time is proportional to viscosity;[18] hence, a similar equation is expected to govern the correlation time τ, that is,

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{7}$$

where τ_0 is a constant, B is a pseudoactivation energy, and T_0 is the ideal glass transition temperature. At T_0 the correlation times governing the chain motion diverge and configurational entropy vanishes.

An interesting way of fitting the VTF formalism to the experimental correlation times is to consider the term $(-\tau/\dot{\tau})^{1/2}$, where $\dot{\tau}$ is $d\tau/dT$. From eq 7 it follows that

$$\sqrt{\frac{-\tau}{\dot{\tau}}} = \frac{1}{\sqrt{B}}(T - T_0) \tag{8}$$

This reduces the VTF expression to one with a simple linear dependence on temperature. A plot of $(-\tau/\dot{\tau})^{1/2}$ versus temperature will generate a straight line if the data are obeying the VTF equation. The slope of this graph will give the pseudoactivation energy term B, and the intercept on the temperature axis the ideal glass transition temperature T_0.

To fully investigate the VTF dependence of τ, it is necessary to have measurements over a wide temperature range with some values close to T_0. Polymers that crystallize do so well above their ideal glass transition temperature. Once crystal regions have formed in the sample, the assumption that Rouse dynamics govern the motion of the chains is incorrect. This puts a limit on the lowest temperature below which the analysis is not applicable. The smallest chains used in this study, 300 g mol^{-1}, have the lowest crystallization temperature, $T_m \sim 240$ K.[8] Therefore the following analyses will focus on the NMR signals from the 300 g mol^{-1} samples, as this allows measurements nearest to T_0.

Information about polymer dynamics can be obtained from the NMR decay curves using eq 6. The characteristic decay time T_2 is dependent on several terms: the molecular weight of the polymer M_n, the fundamental Rouse relaxation time τ, and the size of a statistical segment N_a. The above work has shown that both salt and temperature have little effect on the structural term N_a; recall Figures 3 and 4. Any differences in the relaxation function, brought about by variations in temperature or salt concentration, can be fully attributed to changes in the relaxation time τ. Thus for a constant molecular weight we can write

$$\frac{1}{T_2} \propto \tau \tag{9}$$

The constant of proportionality in eq 9 can be found from substituting eq 5 into eq 6, taking $N_a = 1.5$, $M_n = 300$, and the monomer molecular weight m = 44, giving $1/T_2 = (6.16 \times 10^9)\tau$. This procedure translates the T_2 times into correlation times τ that are of the order of 10^{-10} s.

To analyze the behavior of the correlation times using eq 8, the term $\dot{\tau}$ needs to be evaluated numerically. This is the rate of change of τ with respect to temperature. Three successive temperature measurements of τ are fitted to a quadratic, the parameters of which then specify the slope $\dot{\tau}$ for the middle temperature τ measurement. In Figure 5 is plotted the expression $(-\tau/\dot{\tau})^{1/2}$ against temperature for the various salt concentrations. The anticipated linear dependence (eq 8) of this term on temperature is found, revealing that the Rouse times are governed by a VTF relationship.

From the slopes and intercepts of Figure 5 the ideal glass transition temperature T_0 and the pseudo-activation-energy B can be evaluated for each salt concentration; recall eq 8. As in other work[7] the parameter B is found to have a linear dependence on salt concentration; see Figure 6. The second plot in Figure 6 is the parameter B found from a different analysis and will be discussed later. In Figure 7 T_0 and the glass transition temperature T_g, which has been measured in a previous study,[8] are plotted as a function of salt concentration. Although the glass transition temperature is seen to increase with the addition of salt, the ideal glass transition temperature itself slightly decreases. This adds weight to the idea, previously concluded by Cruickshank et al.,[7] that these two parameters are not necessarily simply related. It therefore challenges the accepted notion that $T_g - T_0$ is a constant. These results also support the argument that

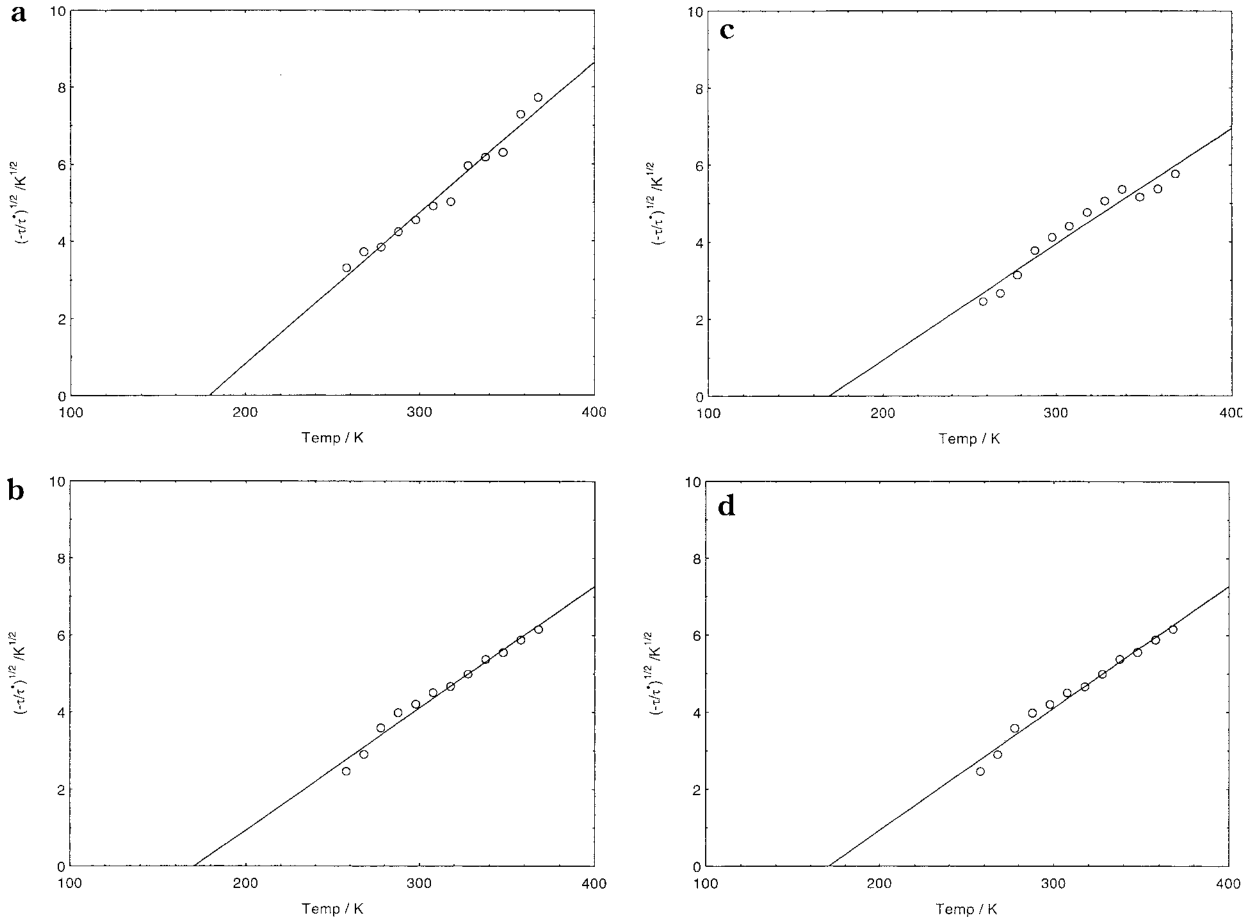

Figure 5. Term $(-\tau/\dot{\tau})^{1/2}$ as a function of temperature for the (a) unsalted PEO sample and (b) 20 to 1, (c) 13 to 1, and (d) 8 to 1 salt concentrations (number of ethoxy monomers to a lithium ion).

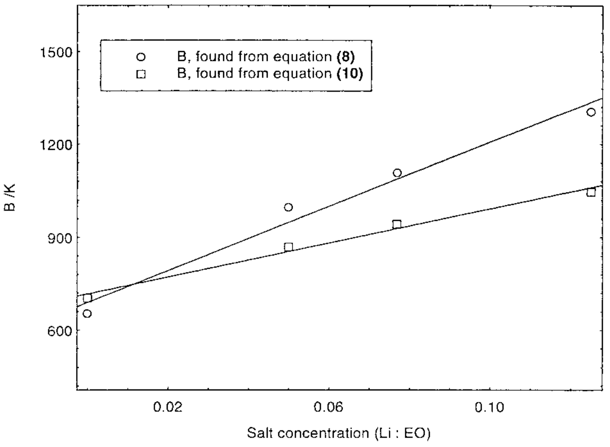

Figure 6. Pseudo-activation-energy term *B* found from the analysis of the correlation times using eq 8 displayed with those found from eq 10. Li:EO is the number of lithium ions to an ethoxy monomer.

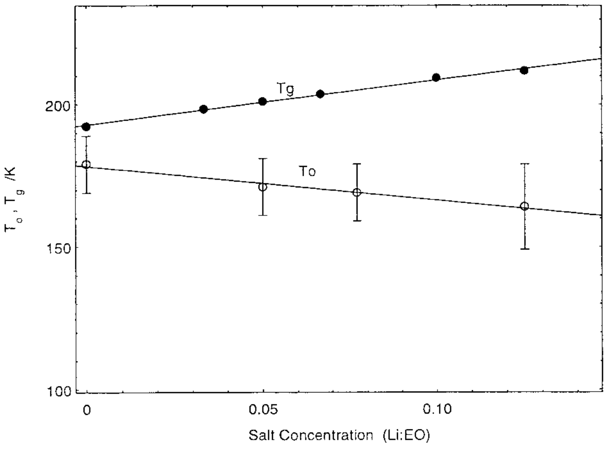

Figure 7. Glass transition temperature and the ideal glass transition temperature as a function of salt concentration. Li:EO is the number of lithium ions to an ethoxy monomer. The T_g data are taken from ref 8; T_0 data are from the present work.

salt is not cross-linking the chains, for if this were the case, T_0 would be expected to increase with salt concentration, consistent with the cross-links reducing the number of available conformations.[8]

Conductivity studies[7,8] have suggested that the ideal glass transition temperature for this system is a constant independent of salt concentration. Although a decrease in T_0 with the addition of salt seems to be the trend found in this work (recall Figure 7), a constant value of 170 K could be permitted within the measured uncertainties. It is interesting to see how well therefore the VTF formula with a constant T_0 fits the data over the entire temperature range and salt concentrations. Equation 7 can be rewritten as

$$\ln(\tau) = \ln(\tau_0) + \frac{B}{T - T_0} \qquad (10)$$

where $\ln(\tau_0)$ is a constant independent of both temperature and salt. This is the more usual way to examine data that follows a VTF dependence. All the measured

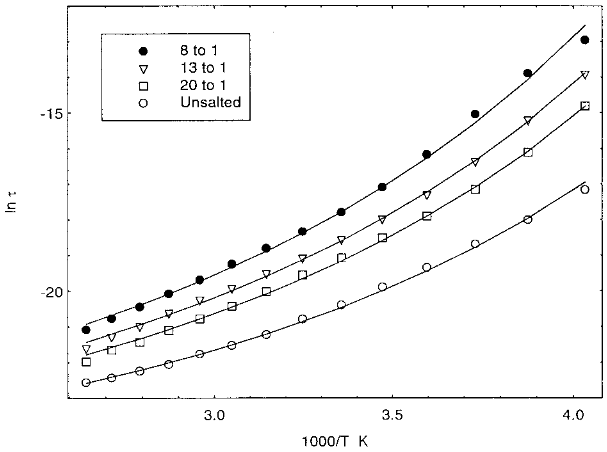

Figure 8. Fundamental Rouse relaxation time as a function of temperature for the various salt concentrations written as the number of ethoxy monomers to a lithium ion. Solid lines are simultaneous fits to all data sets using eq 10, with T_0 fixed at 170 K and a constant global τ_0 as a fitting parameter.

correlation times from the 300 g mol^{-1} sample will now be fitted simultaneously using eq 10. The ideal glass transition temperature will be set at 170 K, and the constant term ln(τ_0) will be the same for each salt concentration with only the *B* parameter being allowed to depend on the concentration.

In Figure 8 ln(τ) for the various salt concentrations is displayed as a function of reciprocal temperature with the corresponding fits to eq 10. Over the complete salt and temperature range the VTF fits are excellent. This is especially remarkable, since only the *B* parameter was free to depend on salt concentration. In Figure 6 is shown how *B*, from this analysis, varies as a function of the number of lithium ions to an ethoxy monomer. Again it is found to have a linear dependence on the salt concentration. The actual numeric values found from this analysis are in good agreement with those of the previous method that employed eq 8. Finally the value of the term ln(τ_0) was found to be −25.96; this gives τ_0 to be 5.3×10^{-12} s.

It is interesting to consider the relationship between the DSC-measured glass transition temperature T_g and the parameter *B*. Both these terms were found to have a linear dependence on the salt concentration; recall Figures 6 and 7. An earlier study related these two terms through the VTF expression.[7] In this interpretation the dynamics of the glass transition are assumed to be governed by the VTF formula (eq 7). At a temperature T_g the correlation time τ reaches some value τ_g (∼100 s for DSC), where now molecular relaxation times become too long to allow the establishment of equilibrium on an experimental time scale. In terms of the experiment the polymer sample now behaves as a solid. From eq 7 we can write

$$\tau_g = \tau_0 \exp\left[\frac{B}{T_g - T_0}\right] \tag{11}$$

This can be rearranged to give

$$T_g = T_0 + \frac{B}{\ln(\tau_g/\tau_0)} \tag{12}$$

where since both τ_g and τ_0 are constants, this can be written as

$$T_g = T_0 + k'B \tag{13}$$

with

$$k' = \left[\ln\left(\frac{\tau_g}{\tau_0}\right)\right]^{-1} \tag{14}$$

The relationship in eq 13 then explains why the glass transition temperature is able to rise with salt concentration whilst T_0 remains constant. Adding salt to the polymer system increases the microviscosity by reducing local segmental mobility, reflected as an increase in *B*. The salt thus increases the time taken for the chains to jump between available configurations but does not reduce the total number of available states. Since the correlation times are now longer due to the addition of salt, a higher temperature is needed to satisfy the experimental condition $\tau = \tau_g$, producing a rise in the measured T_g. Therefore the glass transition temperature would be expected to increase with salt concentration even if T_0 were constant.

It is possible to estimate the value of k' using the previously found value for τ_0 (∼10^{-12} s) and taking $\tau_g \sim 10^2$ s. This value of 10^2 s for τ_g is merely the time scale of a DSC experiment. Any polymer dynamics with correlation times longer than this value will not be able to relax within the experimental run. Inserting τ_g and τ_0 into eq 14 gives an expected value for k' of 0.031. It is interesting to note that since $B \sim 1000$ K and thus the product $k'B \sim 30$, eq 13 becomes close to the accepted rule of thumb $T_0 \approx T_g - 50$.

Both the dependences of the glass transition temperature (Figure 7) and the parameter *B* (Figure 6) on salt concentration are known. It is therefore possible to plot T_g against *B*, see Figure 9. As expected a linear dependence of T_g on *B* is found. The solid line represents a fit to eq 13, taking $T_0 = 170$ K and allowing k' to vary. A value for k' of 0.037 is found, with this being remarkably near to the above-anticipated value of 0.031. This close agreement confirms the validity of the above argument (eq 13) and reinforces the view that the ideal glass transition temperature is independent of salt concentration.

Conclusions

In this paper proton transverse NMR relaxation has been employed to study poly(ethylene oxide) complexes with $LiCF_3SO_3$. The molecular weight dependence of the T_2 decay times revealed that the chains obey Rouse dynamics; recall Figure 2 and eq 6. At the highest salt concentration measured in this study, one lithium ion to eight ethoxy monomers, the predictions of the Rouse model still held. Adding salt is found merely to increase the slope of a T_2^{-1} versus ln M_n plot, indicating a rise in the Rouse relaxation time τ. This study thus shows that the salt is only altering the microviscosity of the melt without disturbing its structure.

The number of monomers required to form a statistical segment N_a was determined to be ≈1.5. This small value, indicating the high flexibility of the PEO chain, has in an earlier study been confirmed by computer modeling.[12] This measure N_a of the persistence length was found to be independent of both salt and temperature down to the point that the samples crystallized; recall Figure 3. The constancy of N_a and the ln M_n dependence of T_2 indicates the validity of the Rouse model to describe the chain motion. Changes in the

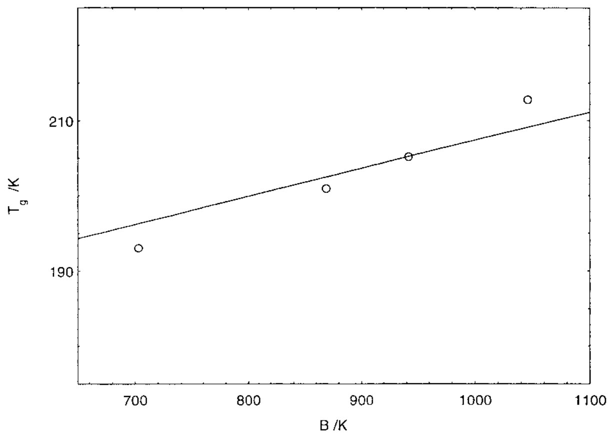

Figure 9. Glass transition temperature as a function of *B* (from Figures 6 and 7). The solid line represents the prediction of eq 12.

environment of the polymer melt only altered the relaxation times governing the dynamics of the chain, through the parameter τ, without disturbing the size of a statistical segment. Again the salt is found to influence the dynamics of the chain but not its structure.

The temperature and salt dependences of the fundamental Rouse relaxation times τ were determined from the experimental transverse decays. An alternative way of fitting this range of correlation times to the VTF expression was presented; see eq 8. A graph of $(-\tau/\dot{\tau})^{1/2}$ versus temperature produced a straight line for each salt concentration (Figure 5), revealing how well the data followed the VTF equation. As in previous studies[7] the parameter *B* was found to increase linearly with salt concentration; see Figure 6. More interestingly the ideal glass transition temperature was found to decrease slightly with increasing salt. In Figure 7 the glass transition temperature T_g is compared to T_0, revealing that the difference between these two parameters, $T_g - T_0$, is far from constant.

Extensive work[7,8,25] on these PEO materials has found that both the viscosity and conductivity can be adequately described by the VTF formula (eq 7). In these studies the ideal glass transition temperature was found to be independent of the salt concentration. The present work has shown a slight reduction in T_0 upon the addition of salt, but a constant value of 170 K is readily acceptable within the measured uncertainties. As a thorough test of the VTF formalism to correctly model the behavior of the chain dynamics, the NMR-measured correlation times for all the salt concentrations and the entire temperature range were fitted simultaneously taking a constant T_0. It was found that the VTF expression (eq 10) fitted all the data remarkably well (see Figure 8), giving added weight to the idea of a constant ideal glass transition temperature.

A novel explanation for the increase in the glass transition temperature upon the addition of salt has been proposed. This makes use of the idea that T_g is dependent on the time scale of the experiment used to measure it. Once the correlation times governing the chain reorientation become greater than that of the experimental run, then the polymer system would appear as a glassy solid. Manipulation of the VTF formalism reveals how T_g is related to the ideal glass transition temperature; recall (eq 13). Adding salt increased the microviscosity, which is indicated by an increase in *B* that drives the difference between T_g and T_0. Furthermore, by considering the time scale of a DSC run, denoted τ_g, it was possible to predict the dependence of T_g on the parameter *B* (see Figure 9). This interpretation has therefore linked up two very different experimental techniques, with the NMR-measured correlation times being used to correctly predict the DSC-measured glass transition temperatures. The success of this interpretation is highly supportive of the use of the VTF formalism and the constancy of T_0.

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