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NMR Study of Poly(ethylene oxide) Complexes with $LiCF_3SO_3$

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ABSTRACT: Proton NMR has been used to reveal the effect of adding $LiCF_3SO_3$ on both the structure and dynamics of poly(ethylene oxide) melts. A range of molecular weights from unentangled to entangled chains was examined at different salt concentrations. The transverse relaxation was interpreted using recent theoretical models due to Brereton. Short chains were shown to undergo Rouse dynamics with salt merely altering the local monomer friction coefficient and not influencing the structure of the melt. From the higher molecular weight chains it was possible to measure the entanglement density, which was shown to be independent of salt concentration. The main conclusion of this paper is that the salt only affects the viscosity experienced by the chain without forming cross-links.

Introduction

Solid polymer electrolytes, by nature of their mechanical properties and relatively high ionic conductivity, are now of interest as both a fundamental and an applied science. In 1978 Armand highlighted the importance of poly(ethylene oxide) (PEO) as material for a novel class of ionic conductor.[1] PEO-based complexes were thus the first solvent-free polymer electrolytes to be investigated, and from then on have received a wealth of attention.[2] The most important application arising from this research is high-energy-density batteries.

A polymer electrolyte consists of a salt dissolved in a polymer matrix which acts as an ionizing solvent. The resulting ions enable the polymer to conduct electricity in the same way as a conventional liquid electrolyte. It is believed that the resulting conductivity in these polyether−salt complexes is dependent on the segmental mobility of the polymer molecules.[3] High chain mobility is required for fast ion diffusion, but adding salt significantly increases the viscosity experienced by the polymer, allegedly forming transient cross-links across the ether oxygens of neighboring chains.[4]

The effect of salt on both the structure and dynamics of the melt is not clear. In this study proton nuclear magnetic resonance (NMR) will be used to investigate the influence of salt on both chain motion and network structure. The possibility of the formation of transient cross-links will be addressed. To these aims a range of molecular weights for the PEO chains has been used which span the entanglement weight. These were investigated at 125 °C in a range of salt ($LiCF_3SO_3$) concentrations, from unsalted up to a concentration of one lithium per eight ethoxy monomers.

At low molecular weights the transverse relaxation of nuclear magnetization is a single exponential. From the molecular weight dependence of this decay we show that the Rouse model is applicable. The molecular weight of a Rouse subunit and the spectrum of relaxation times governing the chain can then be determined.

At higher molecular weights entanglements restrict the motion of the polymer and Rouse dynamics no longer correctly describe the motion of the chain. In NMR this is reflected in a more complex signal. As opposed to previous simplistic parameterization, the relaxation is fitted to a theoretical decay function.[5] This incorporates a general hierarchy of chain dynamics which can be used to accommodate the Rouse model at small space and time scales and a variety of other models, e.g. reptation, at larger space and time scales. This procedure yields the entanglement density and various correlation times corresponding to the differing types of motion undergone by the chain. The role of salt in the melt, its influences on chain motion and network structure, can then be revealed.

Experimental Section

NMR measurements were made on a Chemagnetics CMX-200 spectrometer, operating at 200 MHz for protons. The transverse relaxation was studied by the Levitt−Freeman[6] modification of the Carr−Purcell echo train:

$$\left(\frac{\pi}{2}\right)_x - \mathrm{T} - \left[\left(\frac{\pi}{2}\right)_x \pi_y \left(\frac{\pi}{2}\right)_x - 2\mathrm{T}\right]_n$$

This is a self-compensating sequence which ensures that every second echo is correct, providing that diffusional processes are not significant. Full quadrature phase cycling was employed. The $(\pi/2)$ pulse width was 2 μs, and the dephasing time T typically 2 ms. A single-point acquisition mode was used, such that the top of every second echo was captured. A total of 300 points were acquired in the free induction decay (FID), and each FID is the result of 64 accumulations, with a 20 s recycle delay. Some measurements were carried out on a Bruker SXP spectrometer at 100 MHz using the identical pulse sequence, the results from both spectrometers being the same, within experimental error.

The preparation of the polymer electrolyte followed that outlined by Cruickshank.[7] The samples were then put through a number of freeze−melt cycles while attached to a vacuum line (10^{-4} Torr). This was to remove any oxygen absorbed within the electrolyte which would affect the NMR free induction decay due to its paramagnetic effect.

No Entanglements—The Rouse Regime

The transverse relaxation of nuclear magnetization is sensitive to the segmental motion of the polymer chain. Dipolar interactions of the proton pairs, which are attached to the polymer backbone, cause the dephasing of the transverse nuclear magnetic components. The resultant line shape of the relaxation function, $G(t)$, is then determined by the correlation times of the various chain segments.

Cohen-Addad showed that by averaging over several, N_a, monomers a scale invariant model of the polymer chain could be developed.[8] Short chains, which are less than the critical entanglement molecular weight, M_c,

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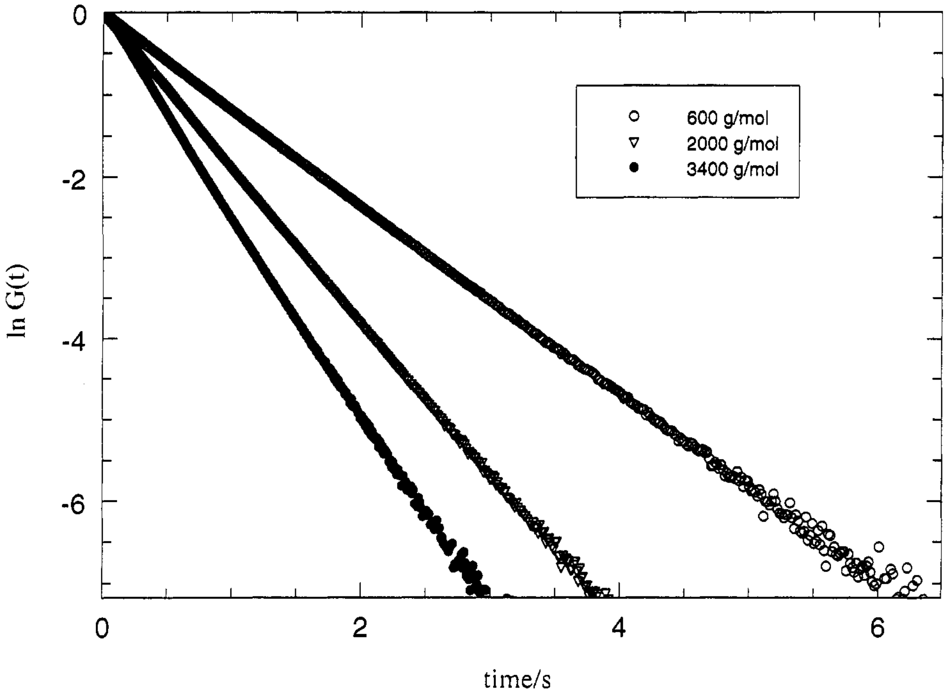

Figure 1. Transverse relaxations from low molecular weight PEO at 125 °C and 20:1 salt concentration (number of ethoxy monomers to a lithium).

undergo Rouse dynamics.[9,10] In this model the bond–bond correlation function is written as a sum over relaxation times, τ_p, for each normal mode p, with[11]

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

where N is the number of Rouse units required to represent the chain and τ is the fundamental Rouse relaxation time, which is directly related to the local friction coefficient ν by[12]

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

where T is the temperature, b is the average length of the Rouse submolecule, and k is the Boltzmann constant. The relaxation function generated by this model is[11]

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

where

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

and Δ is the dipolar interaction strength given by

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

with d being the proton–proton distance within the proton pair and γ the gyromagnetic ratio for a proton. The value for d in PEO was taken as 1.76×10^{-10} m.

The $G(t)$ for a series of molecular weights less than the critical entanglement weight were measured, and some of the results are displayed in Figure 1. It can be seen that the decays are exponential.

For a polymer of molecular weight M_n, composed of Rouse units of molecular weight $N_a m$ (m is the monomer molecular weight), the number N of Rouse units is given by $M_n/N_a m$). Hence the $\ln(N)$, in (4), can be 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} against $\ln M_n$ will enable both $\Delta^2\tau$ and N_a to be determined. From (5) Δ can be found by using the value of N_a and hence τ is obtained from $\Delta^2\tau$. In Figure 2 the results of the unentangled data, $M_n < M_c$, are plotted in the above form. The results of this analysis are displayed in Table 1.

The straight line relationships of Figure 2 show that the chains can be described by Rouse dynamics, even at the highest salt concentration. The molecular weight of the Rouse subunit is constant over the entire salt range and the value of $N_a \sim 1.5$ corresponds to 4–5 main chain bonds. This is sufficient to consider the subunit as approximately Gaussian. The number of monomers needed to connect together to obtain Gaussian statistics should be independent of salt, which should only alter the dynamic properties of the chain. These results support the validity of the Rouse model.

If the results of Table 1 are plotted as a function of salt, then a log linear relationship is found; see Figure 3. The Rouse relaxation time τ is proportional to viscosity η,[12] which for amorphous polyelectrolytes can be described by the Vogel–Tammann–Fulcher (VTF) equation.

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \tag{7a}$$

A similar equation[3] describes the temperature dependence of the ionic conductivity σ.

$$\sigma = \sigma_0 T^{-1/2} \exp\left(\frac{B}{T - T_0}\right) \tag{7b}$$

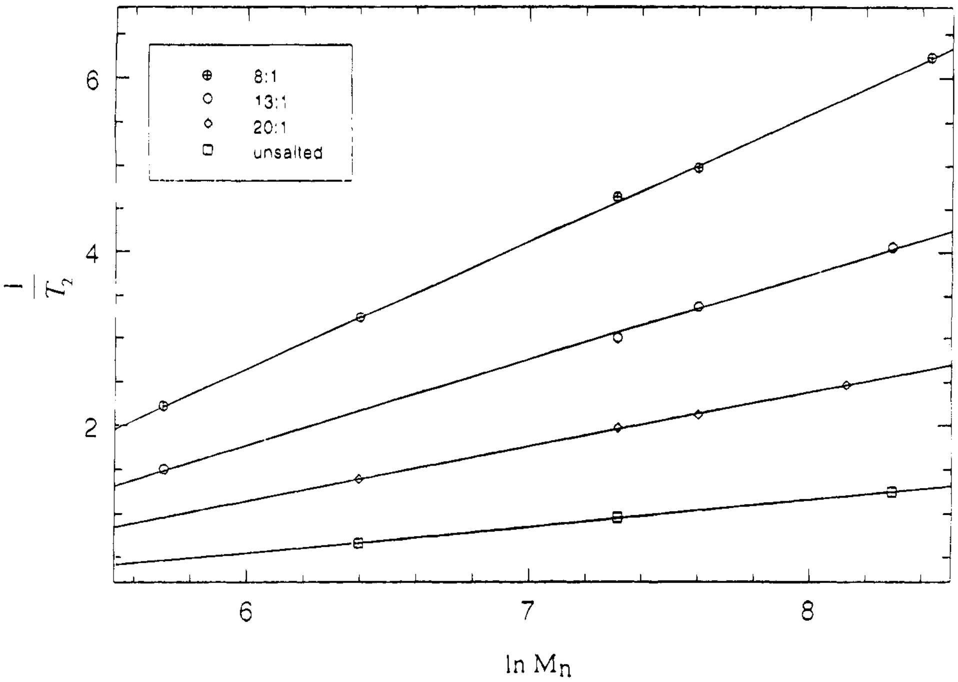

Figure 2. Fitting of the Rouse model to the measured T_2 for various salt concentrations written as the number of ethoxy monomers to a lithium.

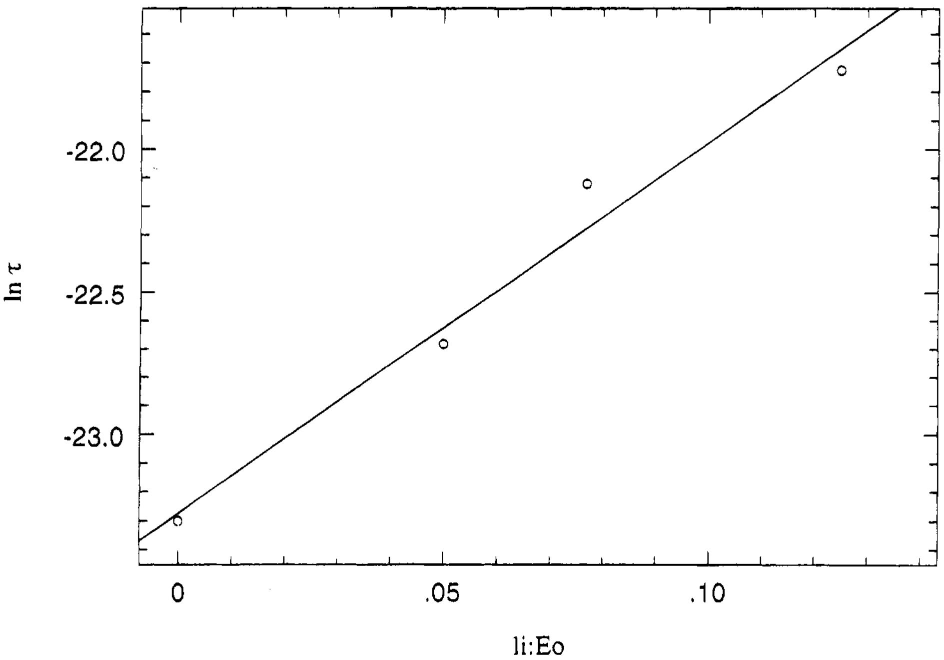

Figure 3. Salt dependence of the Rouse relaxation times/local monomer friction coefficient. Li:Eo is the number of lithiums to an ethoxy monomer.

Table 1. Rouse Chain Parameters

Eo:Li	N_a[a]	$10^{10}\tau$/s
8	1.51	3.67
13	1.51	2.47
20	1.44	1.41
unsalted	1.51	0.76

[a] N_a of 1.5 corresponds to a dipolar interaction strength Δ of 46 100 s^{-1}.

Extensive studies recently undertaken on these materials[7,13-15] have found that both the conductivity and viscosity can be adequately described by (7a,b). The parameter T_0 is the "ideal" glass transition temperature at which the configurational entropy vanishes. It is not necessarily simply related to the measured glass transition T_g. In these studies T_0 was found to be independent of the salt concentration and the parameter B varied linearly with the salt concentration. If we can describe the temperature dependence of τ, the other NMR determined correlation times, by a similar relationship, it follows that at a given temperature the concentration dependence of τ will be of the form

$$\tau \propto \exp(\beta c) \tag{8}$$

where β is a constant and c the salt concentration, defined as the number of lithiums per ethoxy monomer. Figure 3 thus supports the view that the ideal glass transition temperature is not influenced by the presence of salt, which in turn points to the nonformation of cross-links.[7]

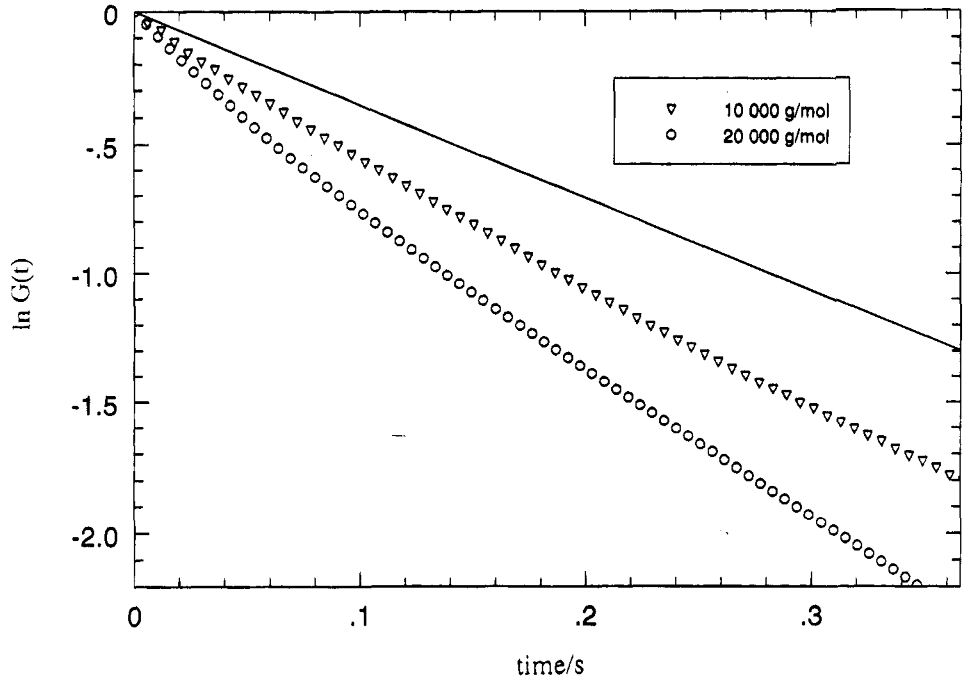

Figure 4. Transverse relaxations from higher molecular weight PEO at 125 °C and 20:1 salt concentration (number of ethoxy monomers to a lithium). The solid line represents the theoretical signal from a Rouse chain of 20 000 molecular weight.

Entanglements—The Reptation Regime

At molecular weights above M_c the polymer is entangled. The steady state viscosity dramatically increases as $M_n^{3.4}$ instead of M_n. The NMR signals become nonexponential with the decay being more rapid than that expected from the Rouse model; see Figure 4. This reflects the more restricted motion of the chain due to the constraints imposed by its neighbors.

A model based on ideas originally put forward for entangled polymer motion by de Gennes and Edwards[12,16] has been developed. The chain is described in terms of entanglement vectors $\{\mathbf{R}_i\}$ spanning subgroups of N_e Rouse units; see Figure 5. The $\{\mathbf{R}_i\}$ vectors could in general be undergoing relaxation mechanisms distinctly different from that of the Rouse units. For the purpose of modeling the $\{\mathbf{R}_i\}$ vectors will be given one correlation time $\tau_\mathbf{R}$. As indicated by previous measurements the chain ends will relax differently from the central polymer segments.[17] The chain is taken as having two free ends, each of an entanglement length and given its own correlation time τ_{end}.

The Rouse relaxation is very fast ($\Delta\tau \sim 10^{-5} \ll 1$) which leads to a rescaling onto the slower motion of the entangled sections.[5] This renders the nature of the Rouse-like motion unnecessary in the same way that the atomic details became irrelevant when using the representative Rouse chain. The original dipolar interaction strength corresponding to a Rouse segment, Δ, is rescaled to become Δ^* with[5]

$$\Delta^* = \frac{\Delta}{N_e} \tag{9}$$

For chains of few entanglement lengths the motion of the central segments will not be highly restricted. In the conditions $\Delta^*\tau_\mathbf{R} \leq 0.2$ the relaxation function generated from the constrained section, $G_\mathbf{R}(t)$, is given by the familiar single relaxation result[18]

$$G_\mathbf{R}(t) = \exp\left(\frac{-3\Delta^{*2}\tau_\mathbf{R}t}{2}\right) \tag{10}$$

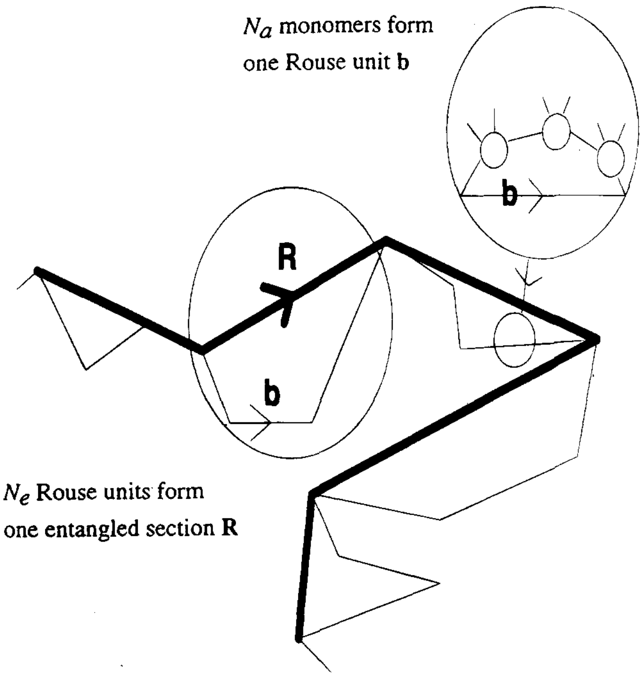

Figure 5. Hierarchical model for the NMR properties of entangled chains shown to incorporate two scales of dynamics. N_a monomers containing the spin pairs are connected to form one Rouse unit. N_e Rouse units form an entanglement vector **R**.

A similar expression for the signal generated from the chain end, $G_{\text{end}}(t)$, can be written, which due to the expected more mobile nature will also be valid for the above conditions. The resultant relaxation function is then given by

$$G(t) = \frac{2M_e}{M_n}\exp\left(\frac{-3\Delta^{*2}\tau_{\text{end}}}{2}t\right) + \left(\frac{M_n - 2M_e}{M_n}\right)\exp\left(\frac{-3\Delta^{*2}\tau_\mathrm{R}}{2}t\right) \tag{11}$$

where

$$M_e = mN_aN_e \qquad (12)$$

This above analysis explains the reason for the nonexponential nature of higher molecular weight decays. There are two types of chain motion, central reptating segments and outer more Rouse-like motion.[17] For very large chains with many entanglement lengths where the reptating segments become highly constrained, the above analysis will break down. It would still be possible to interpret their relaxation using a more detailed description applying theories already developed,[5] but for the data to be examined it is not necessary.

The above procedure was used to investigate the 20 000 molecular weight chains in differing salt environments. This chain should not be too highly entangled, only being several M_c in length. By fitting (11) to the data, it is possible to determine the molecular weight between entanglements, M_e, and the two correlation times τ_R and τ_{end}.

From Figure 6, M_e is approximately constant at 6800 with salt concentration, showing that the salt does not cause any further topological constraints to the chain motion. This value (6800) of the entanglement molecular weight, determined as a parameter in the NMR analysis based on eq 11, is larger than the value of 2500 found by rheological methods. At present we do not have any convincing explanation of this discrepancy. A constant M_e of 6800 is taken and the data are refitted; see Table 2 and Figure 7. The relaxation times are then plotted with the fundamental Rouse times as a function of salt; see Figure 8.

From the measured M_e the rescaled interaction strength Δ^* can be evaluated as 445, which confirms the previous approximation $\Delta^*\tau_R \leq 0.2$ for all salt concentrations.

Discussion

The dynamic properties of the chain are given by the local monomer friction coefficient. In the NMR experiment this is revealed by the determination of a Rouse relaxation time. The effect of salt on this relaxation time was found to be consistent with the viscosity data at the same temperature and described by (8).

Table 2. Parameters of the Hierarchical Model for the 20 000 Molecular Weight Chain

Eo:Li	$10^5\tau_R$/s	$10^5\tau_{end}$/s
8	16.3	4.40
10	14.9	3.83
13	10.1	3.12
20	5.54	1.76
30	5.31	1.48
unsalted	2.29	0.652

The static properties of the chain, the polymer flexibility, determine the number of monomers required to constitute a Rouse submolecule. This is the minimum number of monomers needed to achieve Gaussian statistics and is related to the persistence length. The experimental value of 1.5 monomers per Rouse submolecule, which agrees well with computer modeling of PEO done at Leeds University, reveals the high flexibility of the chain. The invariance of this property under the addition of salt is indicative of the role of salt in the melt; salt merely alters the dynamical properties of the chain without influencing the structural properties.

Even at the highest salt concentration Rouse dynamics still correctly models the chain motion. If cross-links form, this would influence the chain dynamics by adding extra constraints to the motion of the chain. This would be revealed in the transverse relaxation by a more rigid-like rapid decay. The molecular weight dependence of the T_2's in (4) would be violated. Then the straight line relationships of Figure 2 would not hold for the higher salt concentrations.

At higher molecular weights $M_n > M_c$ the relaxation function is more complex and can no longer be described by a single exponential. This reflects further anisotropies in the motion of the polymer chains, which we assign to the effects of entanglements. If we measure the time T_2^* for the NMR signal to decay by e^{-1} then these results together with the previous results shown in Figure 2 are shown in Figure 9. Rouse dynamics, which predicts a linear relation between T_2^{-1} and $\ln M_n$, then fails to correctly model the motion of the chain for

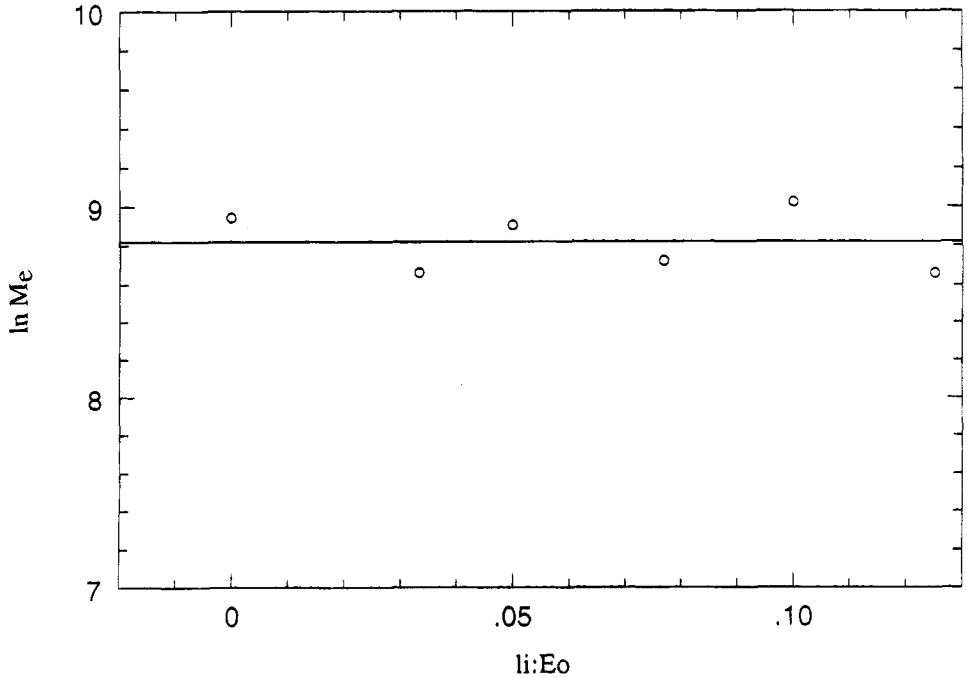

Figure 6. Entanglement density, M_e, as a function of salt concentration. Li:Eo is the number of lithiums to an ethoxy monomer.

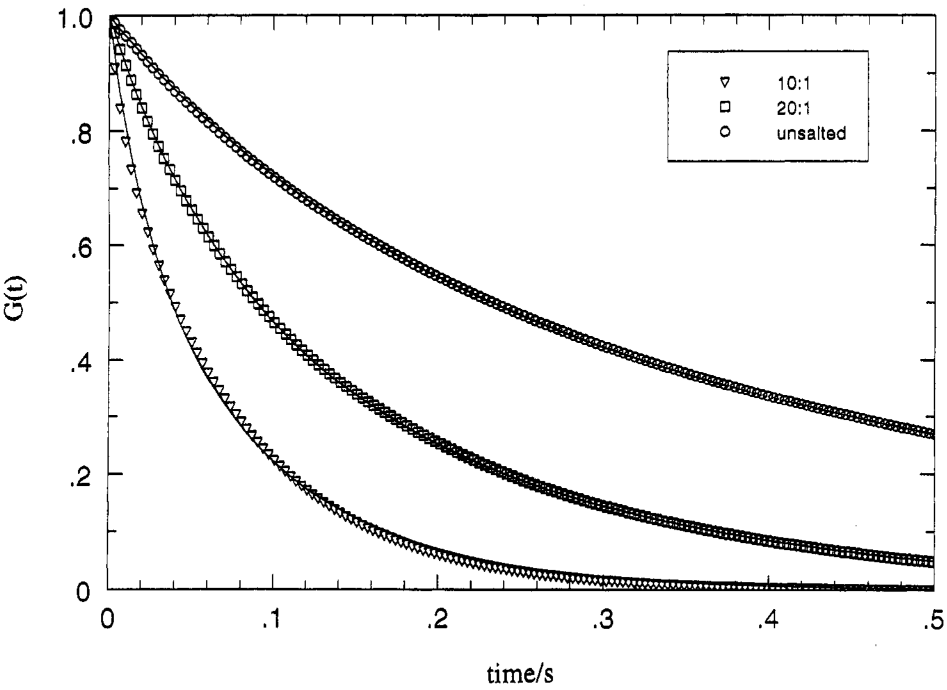

Figure 7. Model fit to the experimental 20 000 molecular weight data for various salt concentrations written as the number of ethoxy monomers to a lithium.

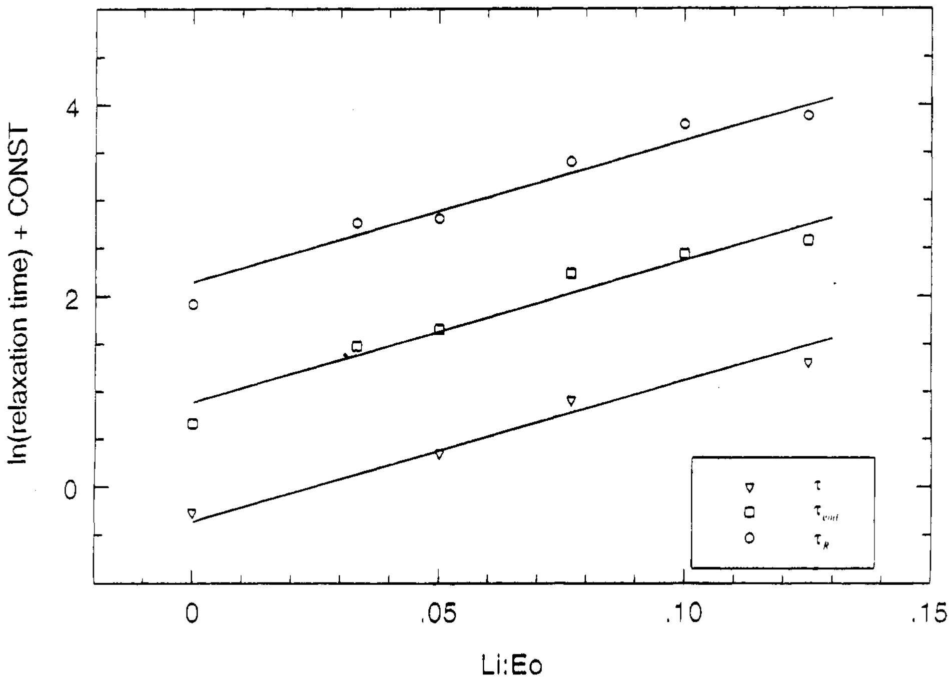

Figure 8. Influence of salt on the various modes of relaxation. Li:Eo is the number of lithiums to an ethoxy monomer.

$M_n > M_c$. As shown in Figure 4 the decay is more rapid than that predicted. The region over which this deviation occurs is plotted against salt concentration and reveals the invariance of M_c; see Figure 10. This is further evidence that the salt is not adding any extra topological constraints to the chain and merely alters the viscosity experienced by the polymer segments.

To model the 20 000 molecular weight chains, a more complex analysis is required. A new chain structure at larger space and slower time scales given by **R** vectors shown in Figure 5 can be introduced. This represents a simple attempt to describe the effect of entanglements on the NMR properties of the polymer chains along the lines of the tube model of de Gennes and Edwards.[12,16] It is also taken into account that the chain motion at the ends of the polymer are distinct from that of the more central segments. As shown by Kimmich, the chain ends undergo more Rouse-like dynamics.[17] This gave rise to the requirement of the two correlation times, τ_R, for the central, and τ_{end}, for the outer segments, and a final relaxation function given by (11).

This modeling approach enabled the entanglement density to be measured. The molecular weight between entanglements, M_e, depends on the melt structure. Through this parameter it is possible to examine the influence of salt on the melt configuration. Formation of cross-links between chains or even within a chain would alter the network structure. The NMR would perceive this as an increase in the entanglement density, and a corresponding decrease of the molecular weight between entanglements. Over the whole range of salt concentrations this was not found, with the

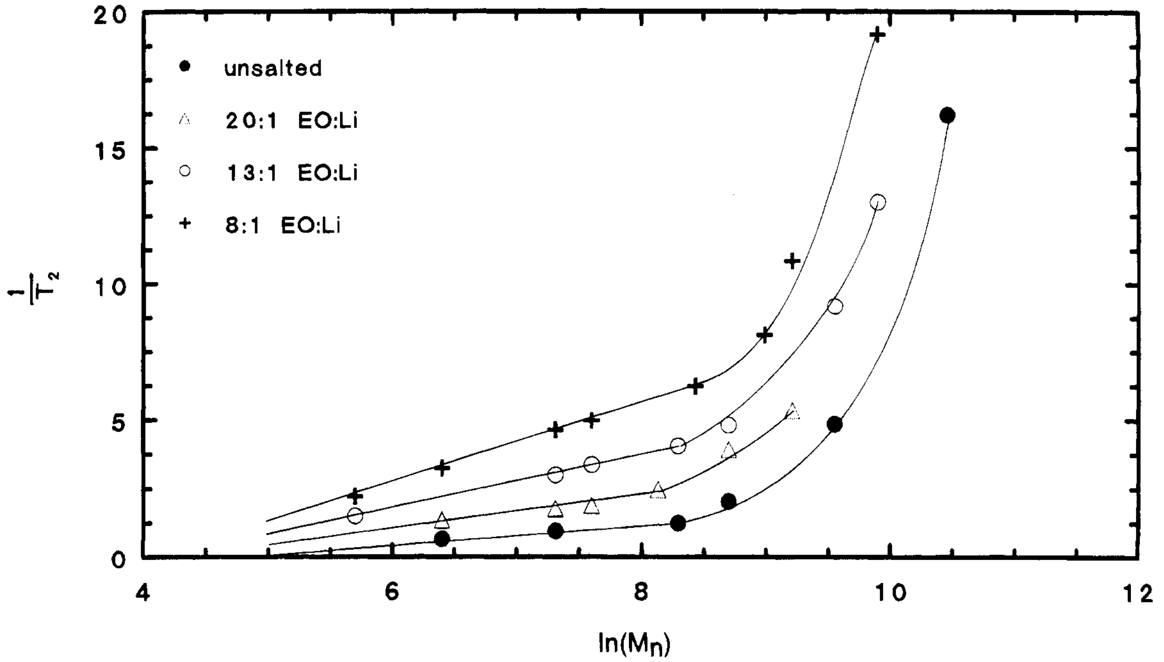

Figure 9. Transverse relaxation times as a function of the molecular weight for various salt concentrations.

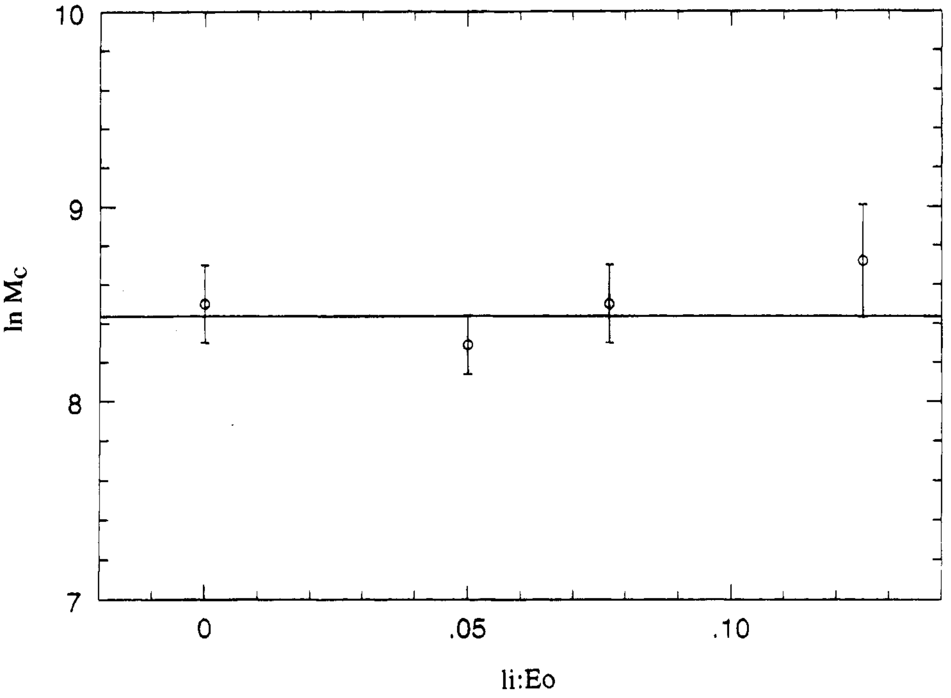

Figure 10. The critical entanglement molecular weight, M_c, as a function of salt concentration. Li:Eo is the number of lithiums to an ethoxy monomer.

entanglement density remaining constant. Again in the entangled regime the role of salt is to vary the dynamic properties of the polymer without influencing the structure of the melt.

The correlation times τ_R, for the central, and τ_{end}, for the outer segments, reveal the dynamic properties of the network. Before discussion of the influence of salt on these various modes of relaxation, it is worth mentioning that the value of τ_{end}, and thus the consequent decay generated by these outer segments, is very similar to that of Rouse chains with lengths close to M_e. This confirms the proposal of Kimmich[17] that the chain ends are indeed displaying Rouse-like behavior. The decay is slightly more rapid than that of a free chain, and this reflects the constraint of being connected to the polymer. (The decay rate of the NMR signal is directly related to the average of the dipolar interaction between the proton and increases with the severity of the constraint.) Secondly, it confirms the measurement of the entanglement density, and the application of the hierarchical model.

The correlation times of the inner and outer segments were then determined. These parameters enable the investigation of the role of salt on the dynamic properties of the chain. The salt was found to have an equivalent effect on the chains various modes of relaxation; see Figure 8. Rouse, reptating, and free ends all obey the same relationship (8). This suggests that all the dynamics stem from the local chain motion. It affirms the overall chain conformation as revealed by the magnitude of the Rouse unit remaining constant. It is of particular interest that in the entangled regime this is also true, which reveals that the introduction of salt does not lead to the formation of cross-links. Therefore in both the entangled and Rouse regimes the role of salt is clear, simply increasing the segmental viscosity without altering the melt structure.

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