to the explanation of this apparent discrepancy, which is of secondary significance.

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Nuclear Magnetic Relaxation in Poly(ethylene oxide)–Salt Solutions

Kang-Jen Liu and J. E. Anderson

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan.
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ABSTRACT: This article describes studies of nuclear spin–lattice relaxation in poly(ethylene oxide)–salt solutions. Addition of KI to solutions of PEO in deuterated methanol produces large changes in the relaxation of the polymer protons. These changes can be described quantitatively in terms of free and associated PEO units along the polymer chain. Salting-out effects, as evidenced in the macroscopic solution viscosity, are not reflected in T_1. Aqueous PEO solutions of KI and K_2SO_4 were also studied. Under these conditions, neither salt has an effect on spin relaxation.

Previous reports from this laboratory[1,2] have concerned nuclear relaxation in solutions of poly(ethylene oxide), PEO. It has been found that many factors influencing the macroscopic transport properties of PEO solutions have little effect on nuclear relaxation. For example, both polymer concentration and molecular weight, two factors that profoundly influence solution viscosity have no observable effect on T_1, the nmr spin–lattice relaxation time. This result is readily understandable, since T_1 is sensitive to localized molecular motions, and is insensitive to the grosser motions of the polymer chain. At the same time, this result points up the important distinction between macroscopic and molecular transport properties in polymers. We pursue this distinction in the present article.

The macroscopic solution behavior of PEO is known to be sensitive to the presence of neutral salts.[3–5] However, it is not known how neutral salts affect the local motions of polymer segments. We have performed T_1 measurements on PEO in certain selected salt solutions in order to examine this question.

Experimental Section

Two PEO samples, having molecular weights of 6000 and 300,000, were studied. These materials, designated PEO-6000 and PEO-300,000, have been described in an earlier article.[2] Deuterated methanol and water were obtained from Merck Sharpe and Dohme of Canada. Potassium iodide and potassium sulfate were obtained from Baker and Adamson and were used without further purification.

The solutions were prepared in standard nmr tubes. Each solution was subjected to four freeze–pump–thaw cycles to remove dissolved oxygen, and sealed under vacuum.

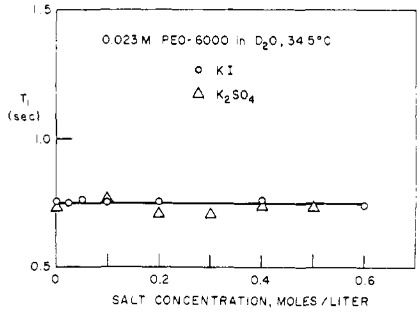

Figure 1. T_1 measurements on 0.023 *M* PEO solutions in D_2O. The effect of added KI and K_2SO_4 is illustrated.

T_1 measurements were performed at 34.5 ± 0.5° on a modified Varian DA-60 spectrometer, using the "adiabatic passage with sampling" technique.[6] The relaxation data were time-averaged in a Varian C1024 computer. At least 25 measurements of each relaxation time were used. The data appear reproducible within ±5%.

Viscosity was measured with a three-bulb Ubbelode dilution viscometer at 34.5 ± 0.02°. The solvent flow time was such that kinetic energy corrections were negligible.

Results and Discussion

Our experiments contrasted the proton relaxation of PEO in KI–CD_3OD solutions with that observed in KI–D_2O. Results for PEO-6000 are plotted in Figures 1 and 2. When KI is added to CD_3OD solutions of PEO, it has a pronounced effect on T_1. Experimental T_1 values change from 1.9 sec with no added salt to 0.50 sec in 0.6 *M* KI solution. In contrast, KI has no apparent effect on the relaxation of PEO in D_2O. We observed almost identical behavior for KI solutions of PEO-300,000.

It has been shown[4,5] that a definite association complex is formed between K^+ and PEO in methanol.

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(1) K-J. Liu, International Symposium on Macromolecular Chemistry, Tokyo, Japan, 1966; reprints, 7, 48 (1966).

(2) K-J. Liu and R. Ullman, *J. Chem. Phys.*, **48**, 1158 (1968).

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(4) R. D. Lundberg, F. E. Bailey, and R. W. Collard, *J. Polym. Sci., Part A-1*, **4**, 1563 (1966).

(5) K-J. Liu, *Macromolecules*, **1**, 308 (1968).

(6) J. E. Anderson, J. Steele, and A. Warnick, *Rev. Sci. Instr.*, **38**, 1139 (1967).

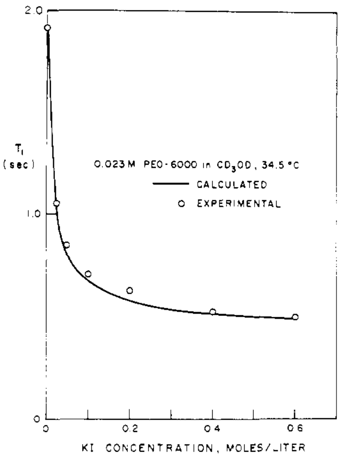

Figure 2. T_1 measurements on 0.023 *M* PEO solutions in CD_3OD. The concentration of KI was varied. Curve is calculated by the method described in the text.

This complex has not been detected in KI–PEO–water solutions. One can reasonably seek to explain the observed differences in relaxation behavior in terms of this complex. We pursue this hypothesis in subsequent paragraphs. Alternatively, the effect of KI on the two solvents must be considered.[7] One could speculate that the added salt drastically changes the solution viscosity of methanol, through ion–solvent interactions, without interacting with PEO. Under these circumstances, a larger effective solvent viscosity would presumably impede polymer mobility, and lower the T_1 values. Experimentally, we found the solution viscosity of 0.6 *M* KI in methanol to be 30% greater than the viscosity of methanol. The solution viscosity of KI-methanol solutions varied linearly with added KI over this concentration range. The small variation of η and its linear KI dependence argue strongly against any pronounced ion–solvent effects on the polymer T_1 values, when these factors are contrasted with the large, nonlinear concentration dependence of T_1. For completeness, we also examined the viscosity of KI–water solutions. The viscosity of a 0.6 *M* KI–water solution is 4% lower than the viscosity of water.

We now examine the effect of complex formation on PEO relaxation. It is reasonable that coordination of K^+ with a PEO chain segment would reduce the mobility of that segment relative to the mobility of the uncoordinated units. Accordingly, the effective relaxation time of the coordinated (or bound) species, $(T_1)_b$, should be shorter than the relaxation time of the free units, $(T_1)_f$.[8] The T_1 data can be treated in terms of an exchange process between free and bound states. Chemical exchange enters because the mean lifetime of a particular "bound" state is short compared to T_1.[9]

$$(T_1)_{\text{calcd}}^{-1} = (1 - \alpha)(T_1)_f^{-1} + \alpha(T_1)_b^{-1} \qquad (1)$$

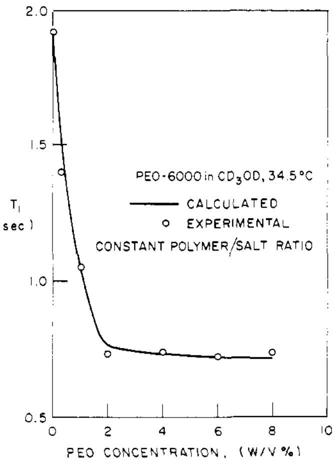

Figure 3. T_1 measurements on PEO solutions in CD_3OD. The KI molarity was one-ninth that of PEO in all solutions. Curve is calculated by the method described in the text.

The quantity α in eq 1 is the fraction of bound PEO units. This quantity can be calculated from the known formation constants.[5] The experimental $(T_1)_f$ was 1.92 sec. $(T_1)_b$ was chosen to be 0.089 sec. These quantities, together with values of α, generate the curve shown in Figure 2. Agreement between experiment and the calculated curve is excellent. This analysis implies that the mobility of individual PEO segments is strongly restricted through association with K^+. It is perhaps restricted as much as $(T_1)_f/(T_1)_b = 21$ times.

Figure 3 illustrates further T_1 measurements on PEO-6000 in CD_3OD solution. In these experiments, the polymer concentration was varied while the polymer/salt ratio remained constant. The curve in Figure 3 was calculated from eq 1, using the same values of α, $(T_1)_f$, and $(T_1)_b$. Once again the agreement is satisfactory. These curves show that the dependence of T_1 upon KI concentration in CD_3OD can be simply explained in terms of complex formation between the salt and the polymer. This interpretation is also consistent with the insensitivity of these experiments to the MW of PEO.

It is known that addition of neutral salts to polymer solutions reduces the over-all dimensions of the polymer chains (the "salting out" effect). The reduction in chain dimensions is reflected in the polymer viscosity. In contrast, nuclear relaxation is primarily concerned with the relative motions of neighboring nuclei. It deals with distances the order of ångströms, rather than thousands of ångströms. We used T_1 measurements to study salting out effects at this local level. We confined our attention to aqueous PEO solutions of K_2SO_4, since this salt is known to have a large salting-out effect on PEO. Salting out undoubtedly occurs in $KI-CD_3OD$ as well. We felt its effect on T_1 would be masked by the K^+–polymer coordination complex described earlier.

The results of this study are presented in Figures 1 and 4. The data indicate that added K_2SO_4 has no effect on PEO relaxation in D_2O. In contrast, this salt has a profound effect on the polymer viscosity. Particularly striking results were found in the system containing PEO-300,000. As shown in Figure 4, the re-

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(7) We are indebted to our referee for raising this point.

(8) This point may not be entirely obvious. On the basis of earlier measurements, reported in ref 2, our present T_1 measurements are known to be in the region of "extreme motional narrowing." Under these conditions, T_1 is inversely proportional to molecular mobility.

(9) J. R. Zimmerman and W. E. Britten, *J. Phys. Chem.*, **61**, 1328 (1957).

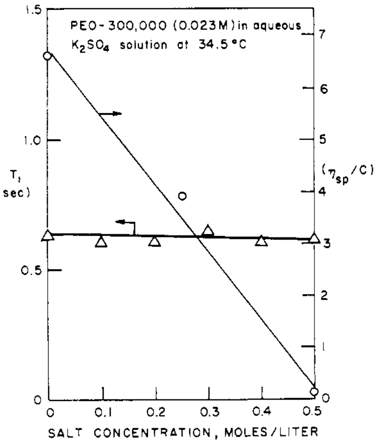

Figure 4. T_1 and reduced viscosity data for D_2O solutions of PEO-300,000.

duced viscosity of the polymer decreases more than 50 times passing from aqueous solution to 0.5 *M* K_2SO_4, where the polymer is on the verge of phase separation. No appreciable change in T_1 was observed over the same concentration range. These results indicate that the local segmental motion of the polymer chain is not affected by the presence of unbound ions.

We are now in possession of the following information: (1) the previously detected complex between K^+ and PEO in CD_3OD has a pronounced effect on T_1; (2) a looser polymer–salt interaction, such as that responsible for "salting out" in K_2SO_4–PEO–D_2O solutions, has no apparent effect on T_1; (3) the salting out interaction has a pronounced effect on solution viscosity. Complex formation may also affect polymer viscosity, but it is difficult to separate its influence from the salting-out process.

Of the above, only the relationship between salting out, T_1, and polymer viscosity merits further comment, or speculation—for it is, of course, extremely speculative to infer anything of a general nature from such meager knowledge. It may be somewhat difficult to understand how salting out can have such a pronounced effect on viscosity, and yet have no observable influence on T_1. The answer, we feel, is that η and T_1 are basically sensitive to different things, although both measure transport properties of polymers. It is well established[1,2] that nuclear relaxation of PEO in solution is mainly controlled by segmental rotameric transitions. For example, T_1 is influenced by the rates at which local *trans–trans–trans*, *trans–gauche–trans*, and other sequences interconvert. By altering these rates, through the introduction of a complexing agent like K^+, one produces changes in T_1. On the other hand, the viscosity of a polymer solution is governed primarily by polymer dimensions. Polymer dimensions can be theoretically expressed in terms of the numbers of *trans–gauche–trans*, *trans–trans–trans* sequences, etc.; and the way these sequences are arranged relative to one another along the macromolecular chain. Polymer dimensions do not reflect sequence interconversion rates directly although to be sure the equilibrium probability of each sequence is determined by the relative rates of transfer into, and out of, that local configuration. The present results suggest that addition of neutral salts to polymer solutions causes slight variations in the probabilities in these local sequences, or in their order along the chain. These changes need not be large to reduce the macroscopic chain dimensions, and lower the polymer viscosity. We can only speculate that any concurrent variations in the rates of rotameric transitions are too small to be detected in our T_1 measurements.

220-MHz Proton Magnetic Resonance Spectra of Polymers. I. Poly(methyl methacrylate)

Raymond C. Ferguson

Contribution No. 1530 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.
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ABSTRACT: High resolution 220-MHz pmr spectra of a number of poly(methyl methacrylates) having grossly different tacticities have been measured on chlorobenzene solutions at 120°. The resonances associated with different tetrad and pentad configurational sequences have been resolved and identified. Broadening of the tetrad methylene and pentad α-methyl resonances, attributed to hexad and septad sequence effects, limits the reliability of tetrad and pentad distribution estimates. Nevertheless, more complete characterizations of stereoregularity and tests of statistical models for stereoregular polymerization are facilitated.

Since the discovery of configurational sequence (tactic placement) effects on the 40-MHz pmr spectra of poly(methyl methacrylates) by Bovey and Tiers,[1] nmr spectroscopy has been applied extensively to the characterization of PMMA and other vinyl polymers.[2] The increased resolution and sensitivity of nmr spectrometers operating at higher frequencies improved the ability to measure triad placements in PMMA, but the unexpectedly complex fine structure in the methylene region led to some difficulty in interpretation and analysis of dyad effects. This difficulty was correctly attributed by some workers to tetrad effects. Partial resolution of the tetrad methylene resonances[3,4] and de-

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(1). F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).

(2) F. A. Bovey, *Accounts Chem. Res.*, **1**, 175 (1968).