Solvent Effects on the Proton Magnetic Relaxation of Poly(ethylene oxide)

Kang-Jen Liu[1] **and J. E. Anderson**

Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121.
Received November 6, 1969

ABSTRACT: The spin–lattice relaxation of poly(ethylene oxide) protons has been studied in a variety of solvents. The experimental relaxation times are found to vary with solvent viscosity, although not as much as those of *p*-dioxane, a monomeric analog of PEO. T_1 studies in CD_3OD–D_2O solutions indicate solvent-induced changes in the conformational structure of PEO as the relative solvent composition is varied.

It is well known that the nmr relaxation of small molecules in solution can be related to the solution viscosity. Generally speaking, the greater the solution viscosity, the shorter the nmr relaxation times (the longer the correlation times) can be expected to be.[2] The relationship between the nmr relaxation of polymer nuclei and solution viscosity has never been critically examined, and there are reasons for suspecting arguments based on the motions of small molecules may not hold. Specifically, it has been previously reported that polymer concentration and molecular weight, two factors that profoundly influence the viscosity of a polymer solution, have no apparent effect on the nmr spin–lattice relaxation of polymer protons over a wide concentration range.[3,4] Furthermore, the following observations have also been reported.

(1) T_1 values of poly(ethylene oxide), PEO, were found to be similar in $CHCl_2CCl_3$ and D_2O, two solvents with significant differences in solvent power and viscosity.[3a]

(2) T_1 values of poly(dimethylsiloxane) were found to be nearly identical in a variety of solvents having widely different solvent power.[3b]

The question then arises whether the local motions of a polymer chain, reflected in nuclear relaxation measurements, are sensitive to the solvent at all. The present study is addressed to this question. We studied the spin–lattice relaxation times, T_1, of PEO in a number of different solvents of varying viscosity and solvent power.

Experimental Section

PEO of molecular weight 4000 was used in this study. This material has been described in a previous article.[3a] Previous work[3a] indicates that the T_1 of the PEO protons is insensitive to molecular weight and polymer concentration, providing the molecular weight is high and the concentration reasonably low. For this reason, we studied PEO-4000 at a fixed composition of 10% by weight in all solutions. Deuterated chloroform, methanol, and water were obtained from Merck Sharpe and Dohme of Canada, and used without any further purification. All the other halogenated solvents were purified according to established procedures.

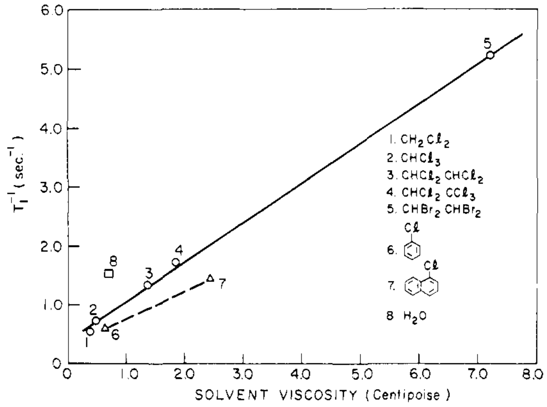

Figure 1. Plot of T_1^{-1} *vs.* solvent viscosity, η, for PEO-4000 in various solvents at 35°.

The sample 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. T_1 measurements were performed at 34.5 ± 0.5° on a modified Varian DA-60 spectrometer, using the "adiabatic passage with sampling" technique.[5] At least 25 measurements of each relaxation time were used. The data appear reproducible within ±5%. Solvent viscosities were obtained with an Ubbelode viscometer by comparing flow times with that of a standard (water).

Results and Discussion

The proton spin–lattice relaxation of PEO in solution has been discussed previously.[3a] The relaxation appears to be mainly governed by segmental rotations of the polymer (rotameric transitions). These rotations may be influenced both by the local viscosity surrounding the individual segments and by the conformational populations of the chain units. Both these factors may be influenced by specific polymer–solvent interactions. In an attempt to minimize conformational differences in going from one solvent to another, and to emphasize viscosity effects, our first experiments studied the T_1 of PEO in a series of halogenated alkanes. It was anticipated that specific polymer–solvent interactions would be similar in each of these solutions. The solvents chosen were CH_2Cl_2, $CHCl_3$, $CHCl_2CHCl_2$, $CHCl_2CCl_3$, and $CHBr_2CHBr_2$. These solvents have viscosities of 0.38, 0.49, 1.36, 1.85, and 7.20 cP, respectively (35°). The results of these experiments are shown in Figure 1,

---

(1) Address correspondence to this author at the Corporate Chemical Research Laboratory, Allied Chemical Corp., Morristown, N. J. 07960.

(2) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 73, 679 (1948).

(3) (a) K. J. Liu and Robert Ullman, *J. Chem. Phys.*, **48**, 158 (1968); (b) K. J. Liu and Robert Ullman, *Macromolecules*, **2**, 525 (1969).

(4) F. A. Bovey and G. V. D. Tiers, *Advan. Polym. Sci.*, 3, 139 (1963).

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

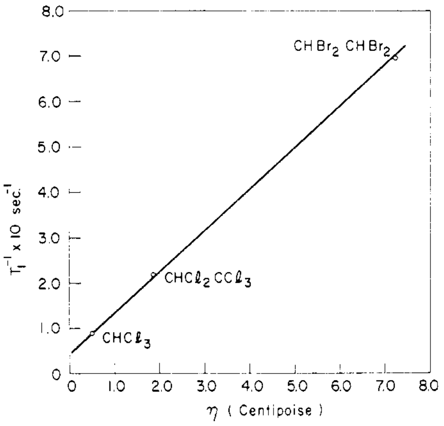

Figure 2. Plots of T_1^{-1} *vs.* solvent viscosity, η, for dioxane at infinite dilution in several selected solvents at 35°.

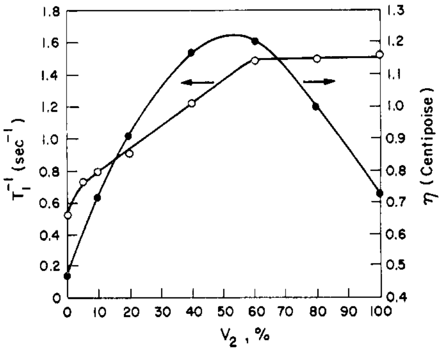

Fig. 3

Figure 3. Plots of solution viscosity and T_1^{-1} of PEO-4000 *vs.* volume composition (V_2 for D_2O) in D_2O–CD_3OD mixtures at 35°.

in a plot of T_1^{-1} *vs.* solvent viscosity, η. The slope of the line drawn through the experimental points is roughly two-thirds that predicted by the BPP–Debye expression.[2] This is not too surprising, for in a polymer there are always nonsolvent units in the immediate neighborhood of each segment—the adjacent segments of the polymer chain! Only a fractional effect of the solvent viscosity should be expected to be transmitted to the polymer on this basis.

For purposes of comparison, the relaxation of *p*-dioxane, a small-molecule analog of PEO, was measured in chloroform, pentachloroethane, and tetrabromoethane. T_1^{-1} values of *p*-dioxane, obtained by extrapolation to 0% dioxane concentration, are plotted against solvent viscosity in Figure 2. The slope of the line through the experimental points is about 90% that predicted by the BPP–Debye expression. This suggests that solvent viscosity may be more important in determining the motions of small molecules than those of a polymer.[6]

When a different class of solvents, such as α-chloronaphthalene and chlorobenzene, were used in preparing PEO solutions, the resulting PEO T_1 values exhibit a significantly different viscosity dependence from that observed in the halogenated alkanes. The viscosity of α-chloronaphthalene is 2.44 cp (35°), yet the T_1 of PEO in this solvent is similar to that in 1,1,2,2-tetrachloroethane, whose viscosity is 1.36 cP. Results obtained in α-chloronaphthalene and chlorobenzene are shown in Figure 1. These T_1 values seem to be less viscosity sensitive than those in the halogenated alkanes. This demonstrates that an experimental relationship between T_1^{-1} and η, established for one family of solvents, is not necessarily followed by solvents of a different type. These differences may result from variations in local viscosity owing to specific polymer–solvent interactions. Alternatively, the different solvents may induce different preferred conformations of the chain units. Our present results cannot distinguish between these alternate explanations.

The influence of solvent-induced conformational changes in PEO may be studied with the aid of independent evidence. The T_1 of PEO in water is peculiarly short, 0.65 sec. The viscosity of water is 0.723 cp (35°). This T_1 result is shown in Figure 1, and it deviates significantly from the T_1^{-1}–η relationship found for the halogenated alkanes. This difference may be attributed to a solvent-induced conformational change. It is known on the basis of ir, nmr,[7] neutron scattering,[8] and theoretical considerations,[9] that water molecules promote a more ordered conformational structure in PEO than that found in other solvents.

Further evidence for conformational changes is provided by the results shown in Figure 3. The solution viscosity of D_2O–CD_3OD mixtures passed through a maximum in the vicinity of the equimolar solution (Figure 3). In contrast, T_1^{-1} of PEO in these solvent mixtures first increases as small amounts of D_2O are added to CD_3OD. T_1^{-1} levels out as the D_2O content is increased and does not decrease, as does the solvent viscosity, when the D_2O concentration is increased beyond 60%. Similar T_1 measurements were made on *p*-dioxane in these solvent mixtures. In the case of this monomeric analog of PEO, the T_1^{-1} values parallel the viscosity results over the entire concentration range. A definite T_1^{-1} maximum is apparent near the equimolar CD_3OD–D_2O solution. These T_1 data strongly suggests a new solvent-induced conformational state of PEO in the water-rich solutions.[10]

In conclusion, we have shown that the magnetic relaxation of a polymer, PEO, does depend on the solvent used. In certain instances, it is predominantly affected by the solvent-induced conformational changes of the polymer units; in other cases, it is governed mainly by the local viscosity of solvent molecules around chain segments. The local viscosity itself seems to be related to, but not necessarily identical with, the solvent viscosity. Presumably, it depends on detailed interactions between the chain units and solvent molecules.

Acknowledgment. We are grateful to Dr. R. Ullman for valuable discussions, and S. Lignowski and W. Gerritz for experimental help.

---

(6) One might worry about the influence of polymer–solvent nuclear dipole interactions on T_1. This intermolecular contribution can be safely neglected for the present purposes: its magnitude is roughly 0.03 sec^{-1} for a proton-rich solvent like C_6H_6 and should decrease for solvents containing fewer protons. Experimental T_1 values of *p*-dioxane in dilute $CDCl_3$ and $CHCl_3$ solutions, and of PEO in H_2O and D_2O, are indistinguishable.

(7) K. J. Liu and J. L. Parsons, *Macromolecules*, **2**, 529 (1969).

(8) P. G. Assarsson, P. S. Leung, and G. J. Safford, *Polym. Preprints*, **10** (2), 1241 (1969).

(9) M. Rösch, *Kolloid-Z.*, **150**, 153 (1957).

(10) It has also been demonstrated that the T_1 of PEO is sensitive to ionic association with the polymer. See K. J. Liu and J. E. Anderson, *Macromolecules*, **2**, 235 (1969).