Nuclear Magnetic Resonance Studies of Polymer Solutions. V. Cooperative Effects in the Ion–Dipole Interaction between Potassium Iodide and Poly(ethylene oxide)

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ABSTRACT: The interaction of potassium iodide with poly(ethylene oxide), PEO, was studied in methanol by a high-resolution nmr technique as a function of chain length. Oligomers from monomer to heptamer were studied in addition to high polymers of different average molecular weight. Experimental results indicate that the interaction of potassium iodide with low oligomers ($n \leq 6$) is very weak, and becomes strong as $n \geq 7$. The polymeric-type interaction sets in at $n = 7$, suggesting that a cooperative effect of this interaction appears only when $n \geq 7$. The results also indicate that the positively charged potassium ion is actually the species which directly interacts with the polymer. Once the polymer associates with potassium ions in methanol, it behaves as a polyelectrolyte. The apparent association constant of the potassium iodide to PEO, obtained from the data of chemical shifts, decreases as one increases either the salt to polymer ratio at constant polymer concentration or the polymer concentration at constant salt to polymer ratio. No association between PEO and potassium iodide was observed in aqueous solutions.

The interaction of a macromolecule with small molecules and ions is a very interesting subject to polymer chemists. It is a general prerequisite for solution catalysis by either a synthetic polymer or a biological enzyme, because, under any circumstances, a polymer must have interacted with a substrate before it can function as a catalyst. Therefore, it seems important to study this type of interaction systematically.

Generally, the interactions of chain molecules with low molecular weight species may be of two types.[1] In the first, the functional groups of the polymer interact with various reagents in much the same manner as would be expected of low molecular weight analogs of the repeating unit of the macromolecule. Of much more interest are macromolecular complexes of the second type, in which cooperative phenomena are essential to the stability of the complex, so that the polymer behaves in a manner which is qualitatively different from that of its low molecular weight analogs. The nature of the polymeric cooperative effect, if any, may be different for various systems, depending on the properties of interacting species. Generally, one might always obtain this type of information by studying the polymeric complexes as a function of molecular weight in the range where the cooperative effect is most sensitive to the chain length. Even the well-known starch–iodine complex has not been examined completely in the interesting molecular weight range.[2,3] To the best of our knowledge, no studies of polymer–substrate interaction have been made which completely cover the interesting transition range as a function of molecular weight of the polymer.[4] It is one of the purposes of this paper to present results of this type.

Poly(ethylene oxide), PEO, and potassium iodide were chosen in the present study for the following reasons: (1) highly purified oligomeric PEO's have been synthesized by us;[5] (2) the interaction of PEO with potassium iodide has been reported, although the authors were unsure of the species which directly interacts with the polymer.

Experimental Section

Fractions of high molecular weight PEO and various pure oligomers were the same materials previously reported.[5] Deuterated methanol was obtained from Merck Sharpe and Dohme of Canada. Potassium iodide was obtained from Baker and Adamson. Dimethoxyethane was obtained from Matheson Coleman and Bell, purified by distillation, and used as a monomeric analog.

Stock solutions were made either in pure deuterated methanol or in methanol containing 1% of cyclohexane (internal nmr reference). Various sample solutions were then mixed in the nmr sample tube. The spectra were obtained using a Varian A-60 spectrometer (Varian Associates, Palo Alto, Calif.). Dioxane (8%) in benzene was used as an external standard. The chemical shift is expressed in cycles per second (cps) downfield. Electrophoresis experiments were measured in a Perkin-Elmer Model 238 electrophoretic apparatus. Both ascending and descending boundaries were observed.

Results and Discussion

A PEO polymer molecule may generally be represented by the structural formula

$$\mathrm{HO{-}CH_2CH_2O{-}(CH_2CH_2O)_{n-2}{-}CH_2CH_2OH}$$

The ethylene groups in the parentheses are defined as internal ethylenes of the ether type (E_i), which are different from the end ethylene groups. All the E_i protons of PEO in methanol show a single nmr peak which overlaps the splitting nmr peaks of the end ethylene protons. For the monomeric analog, dimethoxyethane, the nmr peak of the two methyl end groups is displaced from that of the ethylene protons, and will not be shown in the present spectra.

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[3] M. A. Swanson, *J. Biol. Chem.*, **223**, 825 (1948).

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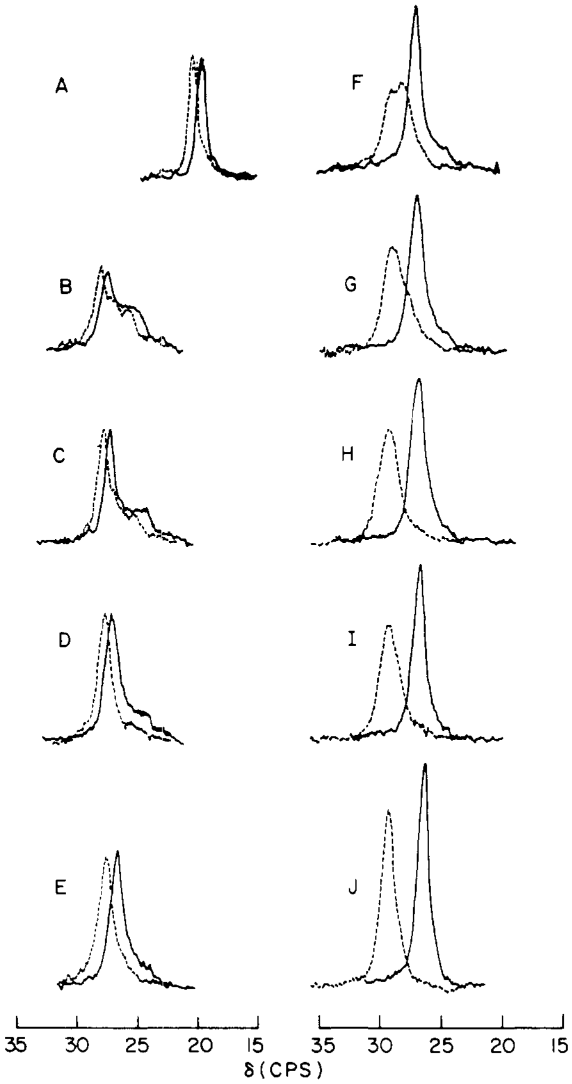

Figure 1. Representative nmr spectra of the ethylene protons of 1% PEO in deuterated methanol in the absence (———) and presence (- - - -) of 0.05 M potassium iodide: (A) dimethoxyethane, (B) triethylene glycol, (C) tetraethylene glycol, (D) pentaethylene glycol, (E) hexaethylene glycol, (F) heptaethylene glycol, (G) PEO-400 ($\bar{n}$ = 9), (H) PEO-600 ($\bar{n}$ = 13), (I) PEO-1000 ($\bar{n}$ = 22), (J) PEO-6000 ($\bar{n}$ = 140). Dioxane (8%) in benzene was used as an external reference, $\delta = 0$.

A set of representative nmr spectra of the ethylene protons of PEO's, 1% in deuterated methanol, with and without the presence of 0.05 M potassium iodide is presented in Figure 1. The introduction of potassium iodide into the PEO solutions has little effect on the nmr spectra of the E_i protons for oligomers ($n \leq 6$), but the spectrum of the heptamer is significantly changed into two partially resolved peaks. The nmr spectra of the higher members ($\bar{n} > 7$) of the series are all affected by potassium iodide, although the apparent influence becomes less pronounced for high polymers, because most of the E_i groups of a high molecular weight PEO are similarly affected. Therefore, it seems clear that there exists a transition of interactions between PEO and potassium iodide as the polymer chain grows to a length of seven monomeric units.

The differences (Δ) of chemical shifts of PEO with

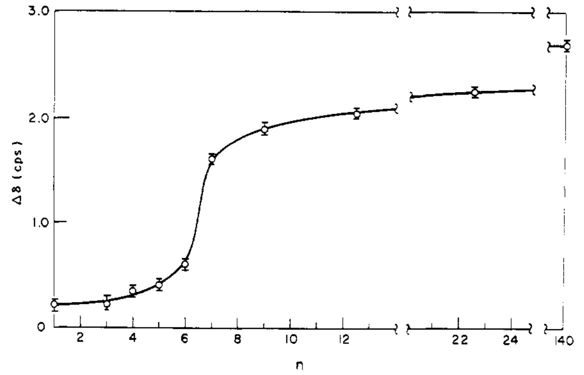

Figure 2. Plots of the difference of chemical shifts (with bulk magnetic susceptibility correction) of PEO (1%) in methanol with and without the potassium iodide (0.05 M) as a function of the chain length (n) at 35°.

and without the potassium iodide are plotted as a function of the chain length (n) in Figure 2. The concentrations of PEO and potassium iodide were kept constant for all measurements, and the bulk magnetic susceptibility correction (see later) was also applied. Again, a sharp change is observed at $n = 7$.

These results seem to suggest that the conformational structures of PEO's in these solution systems may change drastically at $n = 7$. It has been proposed that the association between PEO and potassium iodide is due to an ion–dipole interaction,[6] and only a drastic conformational change of PEO would cause a change of the dipole moment of the polymer segments and, consequently, of the interaction. From the present results, one cannot discriminate whether this conformationla change at $n = 7$ is provoked by the interaction of potassium iodide with PEO, or it is originally there even in the absence of the salt. We believe that the latter is more likely to be true, because our previous nmr results on the structures of oligomeric PEO's in some other solvents without the presence of salt also indicated a drastic structural change at $n = 7$.[5]

The positive Δ value (Figure 2) means that the nmr shift of PEO moves toward a lower magnetic field as a result of interaction with potassium iodide. For the present proton system, this seems to indicate that the charge density in the neighborhood of the E_i protons is reduced.[7] This can happen only when the positively charged potassium ion interacts with the etherate oxygen of PEO. From the chemistry point of view, it also seems reasonable to expect that a dimethoxyethane (the monomeric analog) should interact with the positive potassium ion rather than the negative iodide ion, and yet the general nature of the ion–dipole interaction in the present system is similar for all PEO's. Therefore, we believe that the potassium ion is actually the species which directly interacts with the polymer. We do not think that the negatively charged iodide ion would directly interact with the etherate oxygen of PEO as previously suggested.[6] Although it is not important for the purpose of present investigation to identify the exact species which interacts with the polymer, we would still

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

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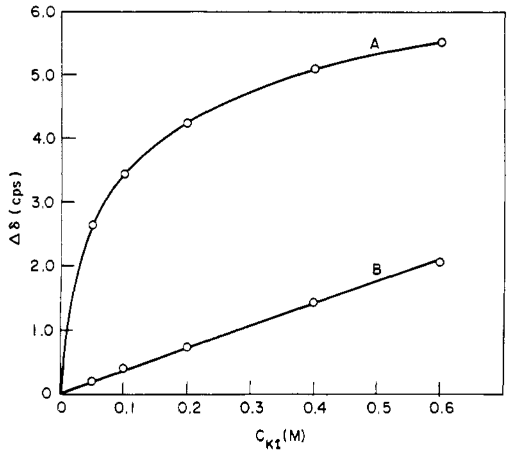

Figure 3. Plots of the difference of chemical shifts (with bulk magnetic susceptibility correction) of 1% PEO-6000 (A) or ethylene protons of dimethoxyethane (B) as a function of the concentration of potassium iodide in methanol at 35°.

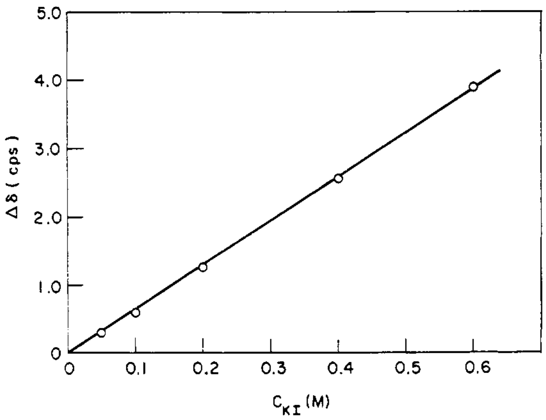

Figure 4. Plots of the difference of chemical shifts (without bulk magnetic susceptibility correction) of 1% cyclohexane in methanol containing 1% PEO as a function of the concentration of potassium iodide at 35°.

Table I

The Difference (Δ) of Chemical Shifts of PEO-6000 in Methanol in the Presence and Absence of Potassium Iodide at 35°

Polymer concn, %	Potassium iodide concn, *M*	Δ value, cps
2	0.05	2.7
2	0.10	3.7
2	0.20	4.5
2	0.40	5.5
2	0.60	5.7
5	0.05	1.5
5	0.10	2.7
5	0.20	3.9
5	0.40	4.8
5	0.60	5.2
10	0.05	0.9
10	0.10	1.7
10	0.20	2.8
10	0.40	4.3
10	0.60	5.1

like to clarify this problem. We have carried out further electrophoretic measurements on a sample solution containing 2% PEO (3 × 10^5) and 0.10 *M* potassium iodide in methanol, using a Perkin-Elmer 238 electrophoretic apparatus. Our preliminary results indicate unambiguously that the polymer in this solution is a polycation in nature. Of course, once the PEO becomes a polycation through its interaction with the potassium ion, its solution properties should also be expected to depend on the counteranions. Although it is not the purpose of the present paper to discuss the subject of polycations, we would still like to point out that the effects of counteranions on the solution properties of polycations are sometimes very specific and they are not as well understood as polyanions.[8,9]

Plots of Δ values (after the bulk magnetic susceptibility corrections) of 1% PEO-6000 and its monomeric analog, dimethoxyethane, as a function of potassium iodide in methanol are shown in Figure 3. It is obvious that the polymer and its monomeric analog interact differently with the potassium ion when the salt conconcentration is low; further associations of potassium ion with the polymer are reduced by the existing bound ion at higher salt concentrations. In other words, the apparent association constant of the potassium ion and PEO decreases as one increases the salt concentration. For the monomeric analog, the association is rather weak at low salt concentrations, but remains constant when the salt concentration is increased. The ratio of the Δ value of the polymer to that of the monomeric analog is more than 12 when the potassium iodide is 0.05 *M*: it decreases to less than 3 when the salt concentration is 0.5 *M*. Measurements were also made on PEO-6000 at other concentrations and the results are summarized in Table I.

Measurements of chemical shift were made on 1% cyclohexane, which was mixed with methanol and used as a solvent for preparing the previous samples. This was done because no association between cyclohexane and potassium iodide takes place in the present systems. The results are shown in Figure 4. No detectable difference was observed for Δ values of the PEO obtained in either pure methanol or methanol containing 1% cyclohexane. Therefore, it is reasonable to use the Δ values of the cyclohexane in various samples to correct the bulk magnetic susceptibilities.

The apparent association constants (*K*) of the potassium ion to PEO in methanol may also be computed from their chemical shift data. The free and bound units of PEO exchange rapidly to yield a single nmr resonance absorption which is an average of the chemical shifts of PEO in the two states. This can be expressed by eq 1, where δ_{obsd} is the observed chemical

$$\delta_{obsd} = X_f\delta_f + X_b\delta_b \qquad (1)$$

shift of PEO-6000; δ_f and δ_b are, respectively, chemical shifts of free and bound PEO; X_f and X_b are mole fractions of free and bound PEO, respectively. The δ_{obsd} and δ_f are obtained directly from experimental measurements; δ_b can be calculated by assuming that all the potassium ions are bound to the polymer when a large excess of the polymer is present,[6] an example of

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(8) K. J. Liu and H. P. Gregor, *J. Phys. Chem.*, **69**, 1248 (1965).

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TABLE II

APPARENT ASSOCIATION CONSTANT OF POTASSIUM IODIDE AND PEO-6000 IN METHANOL AT 35°

Polymer concn, %	Ratio of potassium iodide to PEO	Apparent association constant (K)
1	0.22	2.28
1	0.44	1.29
1	0.88	0.74
1	1.76	0.43
1	2.64	0.31
2	0.11	4.20
2	0.22	1.76
2	0.44	0.88
2	0.88	0.47
2	1.32	0.37
5	0.09	3.78
5	0.18	1.39
5	0.35	0.54
5	0.53	0.34
10	0.04	Very large
10	0.09	1.84
10	0.17	0.84
10	0.27	0.50

$$K = \frac{[\text{complex}]}{[\text{PEO}]_f[\text{K}^+]} \qquad (2)$$

this excess is 10% PEO (2.27 M) and 0.05 or 0.10 M potassium iodide. From these values, X_f and X_b may be calculated for all systems, and the K value may be obtained from eq 2, where $[\text{K}^+]$ is the concentration of the free potassium ion; the [complex] and $[\text{PEO}]_f$ are, respectively, the concentrations of the complexed and free PEO. These calculated formation constants are summarized in Table II. It is clearly shown that the apparent formation constant decreases as the ratio of the potassium iodide to PEO increases, while the total polymer concentration was kept constant. The K value also decreases as the polymer concentration increases at the same salt to polymer ratio. These phenomena are commonly found in polyelectrolyte solutions.[1,6,10]

The Δ values of PEO-6000 were also measured in aqueous solutions. They are all zero after the bulk magnetic susceptibility corrections using cyclohexane as standard. On this basis, it may be concluded that PEO does not form a complex with potassium iodide in water. Previous viscometric measurements in aqueous systems led to the same conclusion.[6]

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Polyoxamides. I. Preparation and Characterization of Cyclic Oxamides

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ABSTRACT: Cyclic oxamides of various diamines have been prepared and characterized. From hexamethylenediamine and oxalyl chloride the first three cyclic oligomers were obtained in pure form. These are designated *c*-62, *c*-6262, and *c*-626262. *c*-22, *c*-43, *c*-82, and 4-methoxy-*c*-62 were prepared from ethylenediamine, tetramethylenediamine, octamethylenediamine, and 3-methoxyhexamethylenediamine with oxalyl chloride.

Cyclic oxamides, notably the cyclic oxamides of hexamethylenediamine, have been prepared for polymerization studies. Poly(hexamethylene oxamide) is of interest because of its high melting point, stiffness, and low moisture sensitivity relative to common nylon resins. It is, however, thermally unstable at its melting point with gas evolution and loss of molecular weight. For this reason the possibility seemed attractive of making 62 polymer directly by polymerization of the cyclic monomer, 1,4-diazacyclodecanedione-2,3, hereafter referred to as *c*-62. This monomer had not previously been prepared nor had the ring-opening polymerization of cyclic oxamides been investigated.[2] This paper describes the preparation and characterization of cyclic oxamides and the following paper their polymerization.

Lactams with more than one amide group in the ring have been known for a long time. An excellent review was recently written by Dale.[3a] The best method for the preparation of cyclic diamides was described by Stetter;[3b] it is an extension and improvement of Ziegler[4] and Ruggli's[5] dilution technique for the preparation of

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(3) (a) J. Dale, *Angew. Chem.*, **78**, 1078 (1966); (b) H. Stetter and J. Marx, *Ann.* **607**, 59 (1957).

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(5) P. Ruggli, *Ann.*, **392**, 92 (1912).