Solvent Effects on the Preferred Conformation of Poly(ethylene glycols)

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ABSTRACT: Solvent effects on the preferred conformation of poly(ethylene glycol), PEG, have been studied by high-resolution nmr and ir measurement. The nmr results indicate that the average segmental environment of PEG is very sensitive to water concentration up to about 50 vol %, and then remains almost constant for any further addition of water. Three molecules of water are required for the hydration of each ethylene oxide unit in a PEG chain. The temperature dependence of the hydrate formation in aqueous PEG solutions is small. Without specific interaction between the polymer and the solvent, the segmental environment changes linearly with the solvent content in chloroform or benzene over the entire composition range. In concentrated chloroform or benzene solution, PEG shows strong molecular association through intermolecular hydrogen bonds. The ir results contribute further information about the nature of the solvent effects on the conformational structures of PEG. The present ir spectra of PEG in the crystalline state and in benzene solution are similar to those previously obtained by other investigators. However, significant differences were observed in the ir spectrum of PEG in an aqueous medium as compared with that in benzene. The assignment of the ir absorptions of PEG under various sampling conditions is discussed in the light of this as well as previous studies. The conformation of PEG is in a more ordered form in an aqueous medium than in benzene solution or in the melt, and favors the TGT conformation for the COCCOC sequence.

Recently, in addition to the well-developed conformational studies of biopolymers, there has been an increasing interest in examining also the "preferential structure" of nonbiological macromolecules in solution. In a series of experiments, it has been shown that vinyl polymers, such as polystyrene and poly-β-vinylnaphthalene,[1–8] are in some sort of ordered form. Even the simplest chain molecule, polyethylene, has been found to exhibit interesting conformational adjustments in some "structure promoting" solvents when the chain units reach a certain number.[9,10]

Poly(ethylene glycol), PEG, is another polymer of interest. The persistence of some of the crystalline structural order of PEG in the liquid or in solution has been studied by ir and nmr spectroscopy and by ultrasonic and dipole moment measurements.[11–15] There is general agreement that the *gauche* conformation of the OCH_2CH_2O group in high molecular weight crystalline PEG remains largely unchanged in the molten state or in solution. When crystalline PEG is melted or dissolved, some disorder of the polymer chain must be involved. Also, the polymer chain is known to be less ordered for low molecular weight PEG oligomers. The interpretations of the nature of chain disorder in PEG by various authors, however, are not consistent. The influence of the solvent medium on the conformational structure of PEG has not been clearly explored[16] although certain peculiar viscosity results in aqueous PEG solutions have been reported.[17]

In this investigation, the segmental environments of PEG were examined by ir and nmr measurements to assess the role of water molecules on the conformational structure of PEG.

Experimental Section

Fractions of high molecular weight PEG and various pure oligomers were the same materials previously reported.[13] Deuterium oxide was obtained from Merck Sharpe and Dohme of Canada. All the other solvents used were purified in accordance with established procedures.

Nmr spectra were measured by using a Varian A-60 spectrometer with a temperature control attachment (Varian Associates, Palo Alto, Calif.). All chemical shifts reported are expressed in cycles per second (cps) relative to an external reference, cyclohexane (4%) in carbon tetrachloride.

The infrared spectra were recorded on a Perkin-Elmer Model 237 grating spectrometer. Alkali halide and silver chloride cell windows were used with appropriate Teflon spacers to obtain comparable band intensities from several concentrations of PEG in benzene and deuterium oxide. A variable path cell was used in the reference beam to compensate for solvent absorption in the spectra of benzene solutions with low concentrations of PEG. Deuterium oxide was used instead of water as a solvent because, in the spectral regions of interest, it contributed less background absorption. All solution compositions are given in volume per cent.

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Results

The internal ethylene protons (*i.e.*, all the ethylene groups, except for the two ethylene groups at the chain ends in the polymer) of all PEG's exhibit a single nmr peak in aqueous solutions. The chemical shift of this peak (δ_p) is not sensitive to the length of PEG chain.[13] Therefore, it was experimentally convenient to use low molecular weight liquid PEG for nmr studies of aqueous solutions. A representative plot of δ_p of PEG-400 at 35° as a function of water (D_2O) content is shown in Figure 1. The chemical shift of the OH proton is also included; δ_p increases linearly with water concentration until a certain composition (about 50%), and then remains almost constant for any further addition of water. The chemical shift of the OH protons behaves similarly: it increases rapidly with water concentration up to about 50%, and then changes very slowly with further increasing of water. Similar measurements in other solvents, such as chloroform and benzene, give very different results. The chemical shift of the main polymer peak changes linearly with the solvent content for the complete composition range. The change of the chemical shift of the OH protons is very slow in concentrated polymer solutions, and becomes very rapid when the polymer concentration is further diluted. A representative plot is shown in Figure 2. All the chemical shift measurements (Figures 1 and 2) were also carried out at other temperatures (4, 51, and 80° in aqueous system; 4 and 51° in chloroform solutions); the general features were found to be very similar to those shown in Figures 1 and 2.

In order to have a better understanding of the detailed segmental environments of PEG under various circumstances, we have carried out further studies by using ir measurements. In particular, the ethylene rocking modes in the 700–1000-cm^{-1} region have been shown by experiment[18] and calculation[18–22] to be most sensitive to the conformation of the repeating unit in PEG. Therefore, the ir absorptions of PEG in this spectral region have also been carefully examined in the present investigation.

Three representative ir spectra of PEG-4000, which include spectra of a high molecular weight PEG in the crystalline state, aqueous and benzene solutions, are shown in Figure 3. The present ir spectra of PEG-4000 in the crystalline state and in the benzene solution are similar to those previously obtained by other investigators.[19,23–26] However, significant differences were observed in the ir spectrum of the aqueous PEG solution as compared with that of the corresponding benzene solution. The ir spectrum of crystalline PEG has strong absorptions at 844, 947, and 960 cm^{-1}. In the spectrum of PEB-4000 in benzene, which is also known to be very similar to that of the melt, the corresponding absorptions were found at 844 and 947 cm^{-1}. In addition, a weak band of 886 cm^{-1} increases in intensity and new bands appear at 863, 993, and 1324 cm^{-1}. Most of the changes in the ir absorptions which appeared when the crystalline PEG was dissolved in benzene were not present in the spectrum of PEG in aqueous solution.

The effect of water molecules on the structure of PEG was systematically studied by measuring the ir spectra

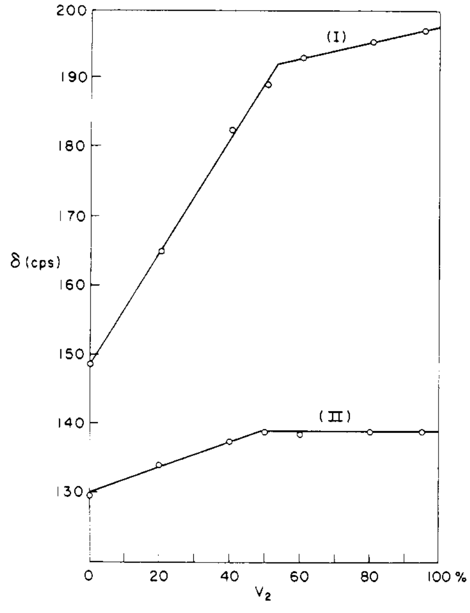

Figure 1. A representative plot of δ_p (chemical shift of the ethylene protons) of PEG-400 at 35° as a function of volume per cent water. V_2 (II). The chemical shift of the OH proton is also included (I).

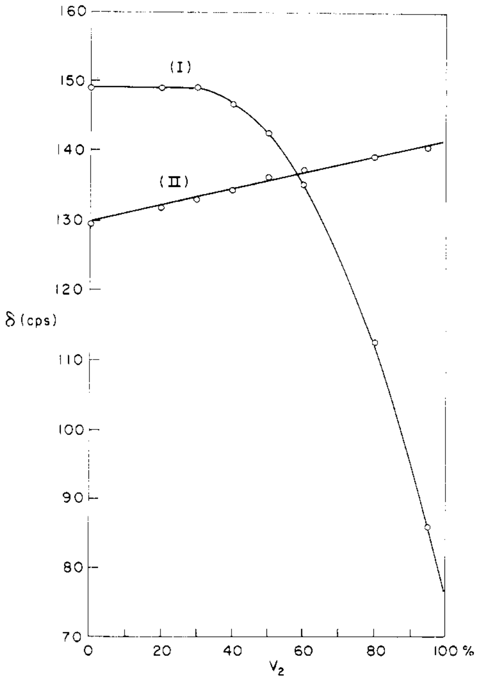

Figure 2. Plots of chemical shifts of the ethylene and hydroxy protons of PEG-400 at 35° as a function of chloroform content. The chemical shifts of OH and ethylene protons are represented by I and II, respectively.

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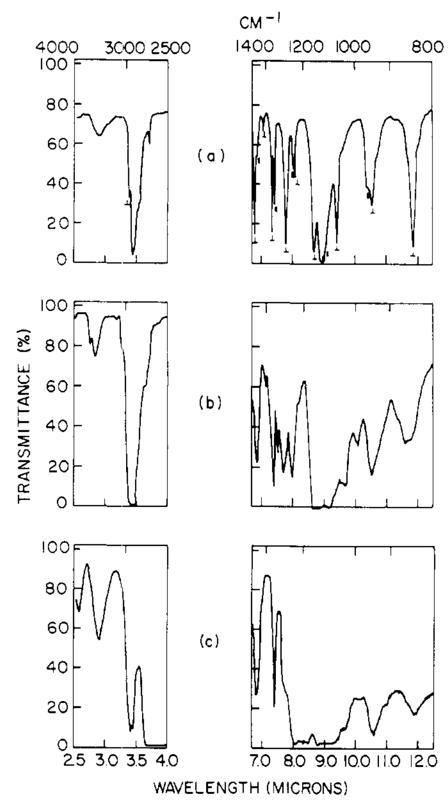

Figure 3. Representative ir spectra of PEG-4000: (a) crystalline state, (b) 20% in benzene solution, (c) 20% in aqueous solution.

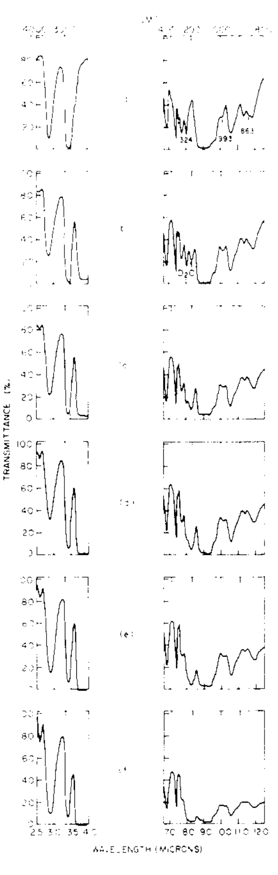

Figure 4. Ir spectra of PEG-600 in water with various concentrations: (a) 100% PEG, (b) 80%, (c) 60%, (d) 50%, (e) 35%, (f) 20%.

of PEG-600 in various aqueous solutions as shown in Figure 4. PEG-600 is a relatively low molecular weight liquid, and its ir spectrum is similar to that of high molecular weight PEG-4000 in benzene except for a stronger absorption at 886 cm^{-1}. The noncrystalline bands at 1324, 993, and 863 cm^{-1} may be observed to diminish in intensity or disappear as the D_2O content of the solution is increased. Residual absorption at 993 cm^{-1} is attributed to an OD bending vibration of $-CH_2CH_2OD$. At the same time, the decrease of the absorption at 886 cm^{-1} may clearly be observed. Also, the absorption at 2935 cm^{-1} was found to become stronger and narrower in the aqueous solutions.

Since it is known that the PEG molecules associate in concentrated solution,[18] we have also studied the concentration dependence of the ir spectrum of PEG in benzene. Three representative ir spectra of an oligomeric PEG, octamer, in benzene with various polymer concentrations (100, 50, and 5%) are shown in Figure 5. The spectrum of the concentrated solution (50%) is very similar to that of the pure liquid (100%). However, certain significant differences may easily be observed in the dilute solution (5%). The absorption peaks at 844 and 863 cm^{-1} merge into a broad unresolved peak at about 850 cm^{-1} in the dilute benzene solution. It is also clear that the intensity of the peak at 1324 cm^{-1} becomes stronger in the dilute benzene solution. A weak peak at 866 cm^{-1} and a sharp peak at 3600 cm^{-1} may also be observed in the dilute benzene solution. For high molecular weight PEG, the concentration dependence of the ir spectrum becomes less significant.

Discussion

The chemical shift of PEG in aqueous solution shown in Figure 1 provides some insight into the solvation of PEG in water. It seems to indicate that the average segmental environment of PEG changes linearly with water concentration until a certain amount of water is added. Any further addition of water causes a negligible effect on the segmental environment of PEG. These results suggest the formation of a stoichiometric hydrate containing about three molecules of water for each ethylene oxide unit in a PEG chain. This is consistent with previous speculation derived from viscosity results[17] and the change of chemical shifts of the OH protons in aqueous PEG solutions (Figure 1). The temperature dependence of the hydrate formation in these aqueous PEG solutions seems to be small, because no significant difference in plots such as that in Figure 1 was observed when the temperature was changed from 4° to 35, 51 and 80°.

Without specific interaction between the polymer and the solvent, the segmental environment changes linearly with the solvent content in chloroform or benzene over the entire composition range (Figure 2). The slow change of the chemical shift of the OH protons in the concentrated solutions is good evidence for the existence of strong molecular association through intermolecular hydrogen bonds. This dissociation would be expected to be favored by raising the temperature. The dissociation of PEG-400 was found to become rapid only after about 30, 40, and 55% of chloroform had been added to the solution at 51, 35, and 4°, respectively.

According to the present nmr results, the water molecules in aqueous PEG solution appear to exert a specific effect, in addition to that of dilution, on the segmental environment of PEG. The nature of this specific influence has been considered on the basis of valence theory.[27] We will base our interpretation on ir spectroscopy evidence.

The ir spectra of PEG in the liquid state or in solution may be interpreted by comparing them with the assigned bands in the vibrational spectra of crystalline PEG[19,25,26] and structurally related compounds such as 1,2-dichlorethane,[18,20–22] ethylene chlorohydrin,[28] metal–ethylenediamine complexes[29,30] ester and ether derivative of ethylene glycol,[31] crystalline polyesters,[32] and metal–ethylene glycol complexes.[33]

For crystalline PEG-4000, the strong ir absorption at 844, 947, and 960 cm^{-1} are assigned to vibration involving principally rocking motion of the ethylene group in the PEG repeating unit in the TGT conformation of the COCCOC sequence.[19,25,26] In order to account for the multiplicity of absorption bands in the 800–1000-cm^{-1} region of the ir spectra of PEG, particularly for those found in the spectra of oligomers, in the liquid state of benzene solutions, the *trans* form of the OCCO group has been proposed.[23,31,34,35] However, we do not believe that the *trans* form as a major structural unit has been well substantiated by the ir spectral evidence. Whenever observations have been made on OCCO groups definitely known to be in the *trans* form[18,20–22,30,32,36,37] or calculations made for this conformation around the C–C band,[20–22] the infrared active rocking frequencies have always been found in the 700–800-cm^{-1} region. A band at 845 cm^{-1} in the ir spectrum of crystalline poly(ethylene terephthalate) has been attributed to a rocking vibration of OCCO groups in the *trans* form,[38] but Tadokoro has shown[39] that this absorption has the wrong dichroic behavior for the ethylene rocking mode, so that such an assignment is questionable. A very weak band can be observed near 810 cm^{-1} in the ir spectra of PEG obtained in this, as well as other investigations.[23,24] This absorption could be assigned to ethylene groups in the *trans* form, but its persistence in the spectra of crystalline films[23] makes the assignment doubtful. In any case, since the absorption near 810 cm^{-1} is very weak when compared to the absorptions of the *gauche* form observed near 947 and 844 cm^{-1}, most of the ethylene groups in PEG, including both high and low molecular weight polymers, must be in the *gauche* conformation even in liquid or solution state.

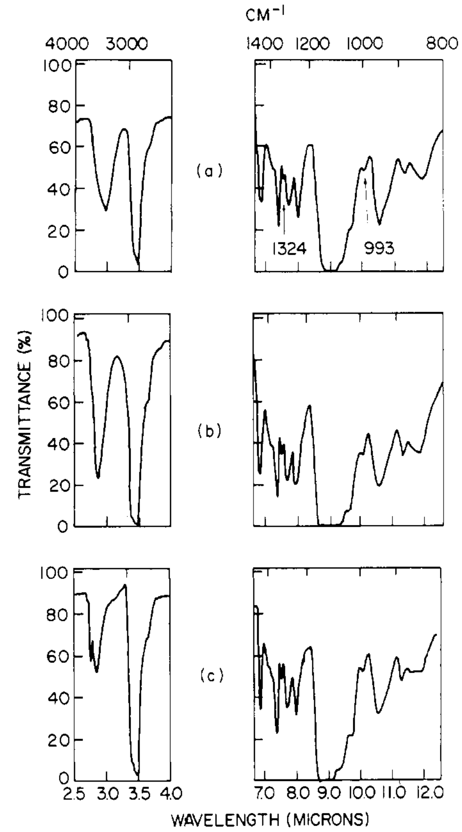

Figure 5. Ir spectra of oligomeric PEG, octamer, in benzene with various polymer concentrations: (a) 100% PEG, (b) 50%, (c) 5%.

The vibrational spectra of PEG in the liquid state or in solution should also be affected by the conformation around the C–O bond. Dioxane has the *gauche* conformation around the C–C bond as in PEG but the conformation around the C–O bond is *gauche* rather than *trans* as found for crystalline PEG. By using the same potential field to calculate the normal vibrations of dioxane as used for crystalline PEG, Miyazawa has shown that the conformation around the C–O bond can have a large effect on the ethylene rocking frequencies, and has emphasized the importance of this in the interpretation of PEG oligomer spectra.[24] These calculations and the infrared spectrum of dioxane show that the original bond found at 1324, 993, and 863 cm^{-1} in the benzene spectra of PEG oligomers could well be caused by a *gauche* conformation of the COCC groups as in dioxane. This interpretation is in agreement with Davison's suggestion[25] that rotation on melting of crystalline PEG occurs mainly at the C–O bonds where the energies of the *trans* and *gauche* conformations are closer to one another than for rotation around the C–C bonds.

The band at 886 cm^{-1} has been assigned to rocking vibration of the ethylene groups in both *trans* and the *gauche* conformations of PEG oligomers.[23,31,34] The band could, however, be associated with end groups since it disappears when the terminal hydroxyl is methylated[24] and becomes weaker as the chain length is ex-

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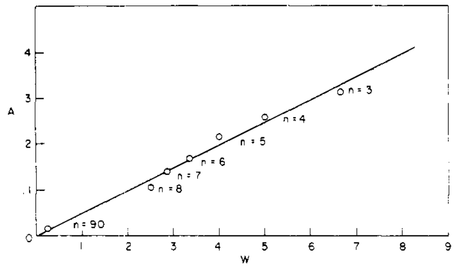

Figure 6. A plot of the ir absorbance (*A*) at 886 cm^{-1} *vs.* weight fraction (*W*) of CH_2CH_2OH in PEG.

tended (Figure 6). This band has been assigned to the *trans* conformation of the terminal $-CH_2CH_2OH$,[35] but we favor the assignment to the *gauche* conformation as suggested in the interpretation of the ethylene glycol spectrum.[33]

The weak band near 866 cm^{-1} is assigned to CH_2-CH_2OH groups which are not hydrogen bonded since it appears only in the spectra of oligomeric PEG in dilute benzene solutions which contain nonhydrogen bonded OH groups as shown by the appearance of a sharp band at 3600 cm^{-1} in the OH stretching region. The shift from 886 cm^{-1} to a lower frequency is to be expected when the hydrogen bonds are destroyed.[40]

The ir evidence of PEG in the crystalline form, the melt, and in benzene solutions indicated that (1) the conformation of the repeating unit in crystalline PEG is in the TGT form as previously suggested,[19,25,26] (2) in the melt or in benzene solution most of the ethylene groups in PEG remain in the *gauche* conformation, and the "disorder" of the polymer chain occurs mainly at the C–O bonds, (3) the conformations of the repeating unit of oligomeric PEG in benzene become more "disordered" in the dissociated state than in the associated form, and (4) the random conformations of PEG, which have been observed in the liquid state or in benzene solution, are greatly diminished in aqueous solution, with the appearance of relatively sharp bands at 844 and 2935 cm^{-1} corresponding to the perpendicular bands at 844 and 2950 cm^{-1} in the spectra of crystalline PEG.[19,25,26] We believe that the conformation of PEG in aqueous solution retains to a large degree the TGT sequence characteristic of crystalline PEB.

Finally, it should be pointed out that the nmr spin–lattice relaxation time (T_1) of PEG in aqueous solution is peculiarly short, only 0.65 sec at 35°.[15] The T_1 of PEG in methanol solution increases to 1.92 sec,[41] about three times that obtained in aqueous solution, whereas the viscosity of the methanol is only about 36% less than that of water. Conformational changes of PEG in aqueous solution could be involved to account for this peculiar difference. This is exactly consistent with what we have presently suggested for the special conformational structure of PEG in aqueous solution. Further work on nmr relaxation measurements is planned.

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Carbon-13 Nuclear Magnetic Resonance Analysis of Poly(propylene oxide)

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ABSTRACT: The white noise spin-decoupled, natural abundance ^{13}C nmr spectra of whole and fractionated poly(propylene oxide) have been obtained at 25.1 MHz. The spectra of the main-chain carbons are interpreted in terms of the structural and stereoregularities and defects in the chain backbone. The nmr analysis indicates that 89% of the crystalline fraction (mp 60°) and 49% of the noncrystalline fraction of this diethylzinc-catalyzed polymer consist of isotactic, structurally regular dyads.

The analysis of the chain structure of polymers by ^{13}C nmr has several advantages over analysis by ^1H nmr. First, all spin–spin interactions can be easily removed from the ^{13}C nmr spectrum by white noise heteronuclear decoupling techniques so that each nmr unique carbon produces just one line in the spectrum. Second, lines in the ^{13}C nmr spectrum are usually widely spaced because of the extensive range of relative ^{13}C chemical shifts. Finally, ^{13}C nmr resonances in polymers are not severely broadened by dipolar interactions because of the small ^{13}C nuclear magnetic moment. These advantages have already been demonstrated in the ^{13}C nmr determination of the monomer distribution in ethylene oxide–maleic anhydride copolymers.[1] The ^{13}C spectra were simple, well resolved, and provided information about both triads and pentads in the chain.

This paper reports the ^{13}C nmr analysis of the homopolymer of propylene oxide, $-[CH(CH_3)CH_2O]_x-$. Although the proton nmr analysis of this polymer is made intractable by small relative chemical shifts and over-

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