Raman Analysis of a Conformational Distribution of Poly(ethylene oxide) and Its Model Compound in the Liquid State

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ABSTRACT: Isotropic Raman spectra of poly(ethylene oxide) in aqueous solution and in the melt show differences in the skeletal stretching vibration bands near 800 cm^{-1} and in the disordered longitudinal acoustic mode feature in the 200−400 cm^{-1} region. These spectra may be simulated by superposing calculated spectra resulting from a series of normal coordinate calculations performed for an ensemble of conformers. The conformational distribution for poly(ethylene oxide) in the molten state appears to favor the tgg′ conformer, which dominates the spectrum calculated to match closely the observed isotropic Raman spectrum. It appears that the experimental data suggest that the tgg′ conformation is present by a greater amount than is predicted by previous simulation methods. On the same basis, it appears that the aqueous solution of poly(ethylene oxide) contains mostly tgt conformers. The results for poly(ethylene oxide) were supported by measurements and computations made using 1,2-dimethoxyethane as a model.

Introduction

Poly(ethylene oxide) (PEO) has a repeat unit consisting of three linkages along the backbone, the O−C, C−C, and C−O bonds. The structures of this family of polymers, either as homopolymers or as part of a copolymer, determine properties in a large number of applications, including thermoelastomers,[1,2] polymeric electrolytes,[3−5] or surfactants. Steric considerations alone suggest that the minimum-energy conformer is all trans, designated as ttt, in a notation that successively references the backbone O−C, C−C, and C−O bonds. However, the most stable conformation in the crystal includes a gauche conformation and is designated tgt.[6] Since the conformation present in the crystal must be the result of the interaction of a number of factors that include crystal field forces, there is no way to use the crystal structure to predict with certainty the dominant conformation present in the melt or in solution. An early facile explanation of the introduction of gauche conformations suggested that these may be due to electrostatic interactions between the net positive and negative charges that accumulate respectively on the backbone due to the introduction of the heteroatom into the chain.[6]

The structure of this polymer has continued to intrigue investigators over the years. The chain structure departs from tgt and changes to ttt when poly(ethylene oxide) is blended with poly(methyl methacrylate).[7] The structure of poly(ethylene oxide) was recently studied in solution, and it was found that the structure of adsorbed chains at the air−solution interface is very different from the disordered structure expected for the solution state.[8,9] In fact, the vibrational bands found for these adsorbed chains have characteristics similar to those observed in the crystalline state.[9] Various theoretical studies have led to quite different results for the chain conformations expected for poly(ethylene oxide).[6,10−19] Under certain experimental conditions, the tgg′ conformer may prove to have the highest relative population.[13] It must be mentioned that the relative population of various conformers, especially the tgg′ one, has yet to be confirmed by experimental techniques.

Although vibrational spectroscopy is widely used to determine localized chain conformations in polymers in a variety of physical states, the method has been infrequently used to obtain quantitative structural information for polymers in solution or in the melt. The frequency and relative intensity of observed vibrational bands are dependent on the relative concentrations of specific localized structures. For samples involving well defined structures and dependable band assignments, the method works well. However, when a broad distribution of a large variety of conformations is involved, the method is more difficult to apply with confidence, and it is often hard to relate observed spectroscopic differences to well defined structural changes.[20]

Traditionally, a detailed spectroscopic analysis of a complex molecular system is often achieved by use of a normal coordinate calculation based on solution of the equations of motion in the harmonic approximation, using force constants transferred from smaller molecules.[21−24] Since the vibrational spectrum is conformationally sensitive, different spectra are observed for different relative contributions of different conformations, these depending on the immediate molecular environment; a change in temperature, for example, will change the relative populations of the various conformers. Even in relatively short chain molecules, the problem involves some complexity. For example, the number of possible conformers for a C_{12} hydrocarbon is of the order of 10^4, each with a unique spectrum often only slightly different from that of another. In order to treat polymers lacking long range order, an approximate method due to Snyder is used.[25] The method consists

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essentially of specifying a conformation of high probability, calculating the spectrum of the conformation from force constant and intensity data transferred from smaller molecules, storing the result, changing the conformation to another of relatively high probability, repeating the calculation, adding the spectra to produce a composite for comparison with experimental data, and iterating until only conformations of low probability remain. Since so many conformations are possible, the conformations treated are generated by a *Monte Carlo* method that uses the relative energy of the conformation to estimate its probability of occurrence. With only a small number of structural and intensity parameters, in this way it has been possible to reproduce experimental infrared and Raman spectra of some *n*-alkanes with accuracy.[25−28] The method has been applied to more complicated polymers lacking long range order.[27,29]

In order to complete a normal coordinate treatment of poly(ethylene oxide) and of the model compound, 1,2-dimethoxyethane, a force field developed by Snyder and Zerbi for small ether molecules was transferred.[30] For the isolated molecule, the chain statistics is dependent on the relative energy of the various states of the rotational isomeric model. However, for the chains in condensed phases, bond dipole moments may well alter the relative populations due to the contribution to the total energy from interchain dipole−dipole interactions. It has long been established that poly(ethylene oxide) chains have a large fraction of bonds in the gauche conformation,[6] a fact supported by a number of experiments. In the case of 1,2-dimethoxyethane, the all trans conformation has C_{2h} symmetry, possesses a center of symmetry, and therefore lacks a molecular dipole moment. The gauche conformers all lack a center of symmetry and therefore possess finite dipole moments. For this reason, the conformation of 1,2-dimethoxyethane most stable in the gas phase should differ in population from that in a disordered condensed phase, as dipole−dipole interaction lowers the energy of the gauche conformers relative to that of the all trans conformer, and the gauche conformers are thereby stabilized in the melt. However, although several studies of 1,2-dimethoxyethane have reported the presence of gauche conformations, the relative amounts of tgt and tgg′ sequences differ considerably depending on the experimental conditions and the models used for the analyses.[10,12] In all cases, the ttt conformation accounts for less than 15% of the total population. Quantum mechanical and other simulation methods suggest that the energies of various conformers are not terribly different.[6,10−19] The statistical weight certainly suggests the chance for the gauche state to occur much more frequently than the trans conformer. The experimental evidence to date has not verified the exact structural distribution of 1,2-dimethoxyethane, and without such information, a detailed analysis of poly(ethylene oxide) is difficult.

In the present study, we have developed a method aimed at an approximate quantitative analysis of the conformational distribution in poly(ethylene oxide) and the model compound 1,2-dimethoxyethane in the liquid state. Although a detailed study of the molecular vibrations of 1,2-dimethoxyethane in all states of aggregation is clearly needed to form a basis for further development of the method utilized here, the results described below show fair agreement with the experimental spectra.

Table 1. Structural Parameters Used in the Simulation Studies of 1,2-Dimethoxyethane and Poly(ethylene oxide)

parameter	values	parameter	values
C−C	1.54 Å	m_C	12
C−O	1.41 Å	m_O	16
C−H	1.096 Å	trans (RIS)	180°
X−Y−Z[a]	109.5°	gauche (RIS) OC−CO	±77.14°
m_H	1.008 145	gauche (RIS) CC−OC	±67°

[a] *X*, *Y*, and *Z* can be used to designate any H, C, and O along the chain.

Experimental Section

Materials. Dimethoxyethane (99.9%, HPLC grade) and poly(ethylene oxide) (M_n *ca.* 4600) (Aldrich Chemical Co., Milwaukee, WI) were used as received. An aqueous solution of poly(ethylene oxide) was prepared by dissolving the polymer in water filtered through a Milli-Q purification system with a nominal resistivity of 18.2 MΩ cm^{-1}.

All Raman spectra were excited with 100 mW of 514.5 nm light produced by a Spectra-Physics 165-08 Ar^+ ion laser and collected at 90° using custom optics to focus the scattered light through a polarization analyzer followed by a polarization scrambler onto the horizontal entrance slit of an Instruments SA U-1000 double monochromator operated at 4 cm^{-1} resolution, equipped with an RCA C31034 photomultiplier and controlled by a Spectra Link interfaced to an IBM PC. The sample temperature was maintained within ±0.5 °C by passing nitrogen gas at the desired temperature through a Miller-Harney cell in which the sample capillary was mounted.

All experimental data were analyzed using *Lab Calc*. Isotropic Raman scattering intensities were calculated from the parallel and perpendicular components of the experimentally measured Raman scattered light: $I_{||}(\nu)$ and $I_{\perp}(\nu)$.

$$I_{iso} = I_{||}(\nu) - \frac{4}{3} I_{\perp}(\nu) \tag{1}$$

The 314 cm^{-1} band of carbon tetrachloride was used to verify the accuracy of the scattering geometry and light collection optics used, and gave the expected value of 0.75 within 2%.

Computations. The program used to generate a computed composite spectrum from a distribution of chain conformations was adapted from that developed by Snyder and co-workers.[25,26,28] The original code was designed for use with *n*-alkanes. In our laboratory modifications were introduced into the program that allow nonequivalent bonds along the chain. When a three-state rotational isomeric model was defined, the relative energy of each rotameric state was used to generate a conditional probability for the chain, using first- and second-order interaction rotational isomeric state (RIS) probabilities for 1,2-dimethoxyethane and poly(ethylene oxide) taken from the literature.[6,10,11] When a disordered chain was to be simulated, an ensemble of 1000 chains was used. The chain length used in the simulation reported here was 13 repeats, which required random choice of 41 torsion angles with rejection of the small class of self-overlapping and low probability chains. The isotropic Raman spectrum $S(\nu)$ for the liquid state was simulated as a composite of contributors from the ensemble of chains generated by a *Monte Carlo* procedure which assigned both a conformation and a total probability to each chain. The spectrum of each chain was calculated and multiplied by its relative probability, and the result was added to the composite consisting of all the chain spectra that had been previously run, until the probabilities became less than an assigned stopping criterion.

The force constants used in calculating the frequencies and the internal coordinates of the system were transferred from an earlier study.[30] The force constants were selected by the program from a force constant library by matching the atomic type and local geometry of each atom. The bond lengths, bond angles, dihedral angles, and masses of the atoms used are listed in Table 1.

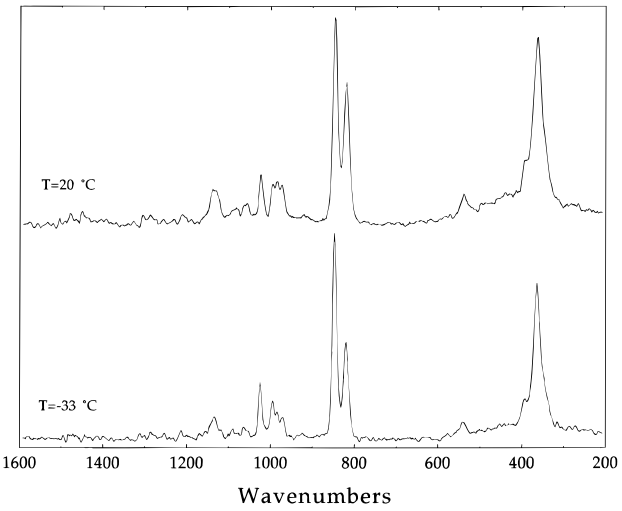

Figure 1. Observed isotropic Raman spectra of 1,2-dimethoxyethane at 22 °C (top) and at −30 °C (bottom).

The spectrum of the entire distribution of chains can be written

$$S(\nu) = \sum_{i=1}^{m} S^i(\nu) \tag{2}$$

where $S^i(\nu)$ is the contribution of the ith chain conformation and m is the total number of chains used in the simulation. The band shapes used in the simulation were a convolution of 9 parts Lorentzian and 1 part Gaussian band contours assigned a fixed half width of 8 cm^{-1}. The band intensities were calculated from simplified bond polarizabilities for C−C stretching, C−O stretching, C−O−C bending, and C−C−O bending internal coordinates. The scattering activity α_j of the jth mode of a chain calculated by the bond polarizability method is then proportional to

$$\alpha_j \propto (\sum_{\sigma=1}^{4} A_\sigma \sum_k L_{kj}{}^{\sigma}) \tag{3}$$

where A_σ is an intensity parameter which is proportional to the derivative of the mean polarizability of the αth internal coordinate and where $L_{kj}{}^{\sigma}$ is a normal coordinate element associated with the αth internal coordinate. The relative intensity parameters used for the C−C stretching, C−O stretching, C−O−C bending, and C−C−O bending internal coordinates were 1.0, 0.6, 0.2, and 0.2, respectively. Intensity contributions from the C−H stretching and torsion about the C−C or C−O bonds were ignored, as the interest in this investigation centers primarily on nontorsional skeletal modes. The simulated isotropic Raman spectrum was finally calculated from the relation

$$I_{\text{iso}} = \frac{S(\nu)}{\nu}\left[1 - \exp\left(-\frac{hc\nu}{kT}\right)\right] \tag{4}$$

where hc/k is the second quantization constant, which has the numerical value 1.4388 cm deg, T is measured in Kelvin degrees, and ν is in cm^{-1} units.

Results and Discussion

The isotropic Raman spectra obtained for 1,2-dimethoxyethane, a model compound for analyzing poly(ethylene oxide) conformation, at 22 and −33 °C are shown in Figure 1. These differ significantly from the normal Raman spectrum in that only the polarized component remains, since the depolarized component has been removed. Most of the strong bands above about 1000 cm^{-1} in the normal Raman spectrum have intense depolarized components and are much reduced in intensity in the isotropic Raman spectrum. Skeletal modes with polarizability changes along the main chain are expected to be intense in the isotropic Raman spectrum. Past studies have indicated that skeletal stretching vibrations such as the C−O stretching mode in the 800 cm^{-1} region are extremely sensitive to changes in chain conformation and can be used for analyzing the type and number of conformers in polyethers.[3−5] The relative intensities of several bands in this region are sensitive to temperature. The strong band located at 848 cm^{-1} has been assigned as C−O stretching for the tgt conformer, and its neighboring intense band at 822 cm^{-1} has been assigned to CH_2 rocking.[31] The intensity of the 848 cm^{-1} band increases relative to that of the 822 cm^{-1} band with decreasing temperature, suggesting an increase in tgt content for the sample at lower temperatures.

The 200−400 cm^{-1} region is also of interest in the spectrum of 1,2-dimethoxyethane and is associated with the backbone bond stretching and bending vibrations. In spectra of long chain molecules in disordered states a strong band assigned to the disordered longitudinal acoustic mode is found in the 200−400 cm^{-1} region. This band is related to the longitudinal acoustic mode found for straight chain segments with a well defined specific chain conformation and is associated with the backbone bond stretching and bending vibration of ordered chain molecules in the solid state. The disordered longitudinal acoustic mode is used for describing a similar set of motions associated with disordered chains in the liquid state, analogous to the corresponding motions of 1,2-dimethoxyethane with frequencies in the 200−400 cm^{-1} region.[20,26,32−34]

There are 27 possible conformers associated with the three dihedral angles of 1,2-dimethoxyethane, but 17 are degenerate. The 10 distinguishable rotameric states, together with the associated degenerate states given in parentheses, are ttt, ttg (ttg$^+$, ttg$^-$, g$^+$tt, g$^-$tt), tgt (tg$^+$t, tg$^-$t), tgg (tg$^+$g$^+$, tg$^-$g$^-$, g$^+$g$^+$t, g$^-$g$^-$t), tgg′ (tg$^+$g$^-$, tg$^-$g$^+$, g$^+$g$^-$t, g$^-$g$^+$t), gtg (g$^+$tg$^+$, g$^-$tg$^-$), gtg′ (g$^+$tg$^-$, g$^-$tg$^+$), ggg (g$^+$g$^+$g$^+$, g$^-$g$^-$g$^-$), ggg′ (g$^+$g$^+$g$^-$, g$^-$g$^-$g$^+$, g$^-$g$^+$g$^+$, g$^-$g$^-$g$^+$), and gg′g (g$^+$g$^-$g$^+$, g$^-$g$^+$g^{2-}). The last five conformers should have very low probabilities of occurrence in 1,2-dimethoxyethane. The total population of these five conformers has been variously estimated as 6%,[10] 8%,[35] or 4−8%.[13] The simulated Raman spectra for the most probable tgt, ttt, tgg, tgg′, and ttg conformers of 1,2-dimethoxyethane are shown in Figure 2. The 365 cm^{-1} band in the observed Raman spectrum of 1,2-dimethoxyethane has been assigned primarily to C−O−C bending in the tgt conformer.[31] There is a barely resolved component at 396 cm^{-1} on the high frequency side of the 365 cm^{-1} band shown in Figure 1. Inspection of Figure 2 shows that this region of the spectrum is populated by bands from all of the conformers. Simulated spectra for both the ttt and ttg conformers show a band at ∼400 cm^{-1} due to a C−C−O skeletal bending mode. All simulated spectra show a contributor at lower frequencies, and those for ttg and tgt conformers each have a band at very nearly 365 cm^{-1}. If the ttg conformer is present in an appreciable amount, a band at 440 cm^{-1} would be expected according to the simulated Raman spectrum, but inspection of Figure 1 shows little evidence of a Raman band at 440 cm^{-1}. If the tgg or tgg′ conformers were present, there should also be a component at 550 cm^{-1}, which is not found experimentally. The spectra shown in Figure 1 do not reveal

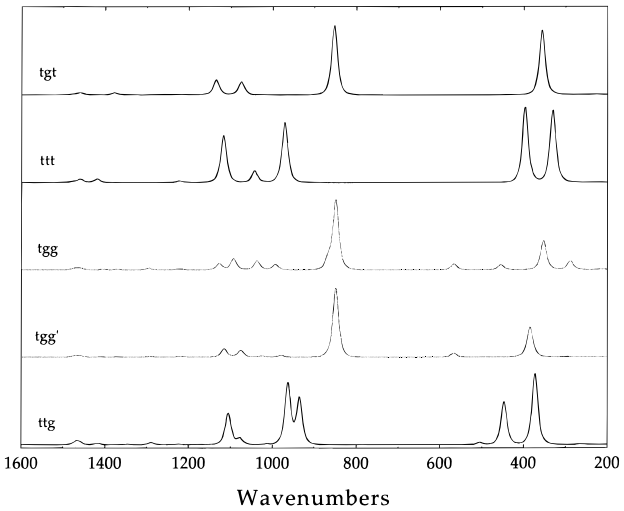

Figure 2. Simulated isotropic Raman spectra of 1,2-dimethoxyethane using different conformers.

Table 2. Conformational Distribution of Different Samples of 1,2-Dimethoxyethane Used in Simulation Studies

sample	ttt	ttg	tgt	tgg	tgg′	others
A	0.16	0.05	0.27	0.04	0.43	∼0.05
B	0.12	0.08	0.51	0.16	0.09	∼0.04

observable changes in the 400−600 cm^{-1} region with temperature, and the simulated spectra therefore suggest that the ttt and tgt conformers entirely dominate the aqueous solution. The decrease in intensity of the 396 cm^{-1} band with decreasing temperature then measures a decrease in the amount of ttt conformer present in the liquid at lower temperatures, which establishes the tgt conformer as the most stable in the liquid, in agreement with results reported by earlier workers.[13,31]

The conformations of 1,2-dimethoxyethane change remarkably with state of aggregation, and the temperature dependence of the conformational distribution in any liquid state remains an open question. Recent electron diffraction[35] and molecular dynamics simulations[11] indicate that the tgg′ conformer is the most stable in the gas, while the crystal consists of the tgt conformer which dominates the solution.[13,31] Isolated in an argon matrix at 35 K, the ttt conformer is the most stable.[36] The gas and aqueous solution state populations may be crudely approximated by assuming two sets of energies, as shown in Table 2. Distribution A is dominated by the tgg′ conformer and roughly corresponds to the gas, while distribution B is dominated by the tgt conformer and approximates the aqueous solution. These two sets of energies lead to very different simulated spectra shown in Figure 3, together with the observed room-temperature isotropic Raman spectrum of melt 1,2-dimethoxyethane. An obvious difference between the simulated spectra and the observed Raman spectrum of the melt is the presence of a band at 822 cm^{-1} in the observed spectrum. This band has been assigned to a CH_2 rocking mode of the ttg conformer.[31] Since the simulated spectra are based only on the four skeletal internal coordinates (C−C and C−O stretch, C−O−C and O−C−O bend), no hydrogenic modes are included in the simulation and the absence of the 822 cm^{-1} band is expected. Otherwise, the simulated isotropic Raman spectrum for distribution B agrees fairly well with the observed one, especially in the skeletal bending region below 600 cm^{-1}. Ogawa et al.[31] found

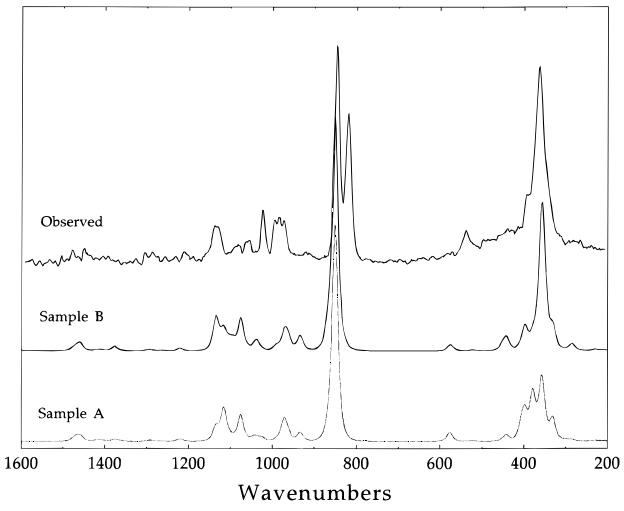

Figure 3. Comparison of observed and simulated spectra with different conformational distributions of 1,2-dimethoxyethane (see text and Table 2).

that the band in the 365 cm^{-1} region is broader in the Raman spectrum of 1,2-dimethoxyethane gas than it is in the Raman spectrum of solution 1,2-dimethoxyethane. The simulated Raman spectrum of distribution A has a broader contour in the 365 cm^{-1} region than shown by distribution B and corresponds more closely with the gas phase Raman data reported by Ogawa et al. A slightly different distribution of various conformers will not change the dominant features of the simulated spectra.

The short 1,2-dimethoxyethane molecule has too few conformers and vibrations to produce the complicated composite of a true D-LAM band of a polymer. This model compound really is not appropriate for analyzing poly(ethylene oxide) conformation, since interactions between well separated structural units also exist.[6] The determination of the conformational distribution for poly(ethylene oxide) either in the solution or melt is a much more difficult problem. Several liquid systems of poly(ethylene oxide) have been investigated, including the molten state,[37−39] solutions in organic solvents[37,38,40] and solutions in water.[37,40] Koenig and Angood[37] have reported the Raman spectrum of poly(ethylene oxide) in the melt and in both chloroform and aqueous solution, and concluded that the conformations of poly(ethylene oxide) in aqueous solution retain the tgt conformation that occurs in the crystalline solid but that the Raman spectrum of the chloroform solution resembles more closely that of the melt than it does the spectrum of the aqueous solution. The conformational distribution was not deducible from the spectra due to uncertainty in band assignments.

The conformational distribution is broadly reflected in the characteristic ratio, C. C was found for poly(ethylene oxide) to be 5.2 for aqueous solution and for solutions in some organic solvents and 6.9 for the melt and for solutions in other organic solvents. Although C varies sensitively with the parameters E_ρ and ϕ_{CC}^{g} assigned to the C−C bond and used in Flory's rotational isomeric state analysis, Abe, Tasaki, and Mark were unable to reproduce the characteristic ratio $C = 6.9$ found by small angle neutron scattering for polydisperse samples ($M_w/M_n = 1.5$) of molten poly(ethylene oxide) samples with reasonable values of these parameters, but they had no difficulty in matching the $C = 5.2$ value.[41] These authors stated that they found no plausible explanation for the large enhancement of the C value

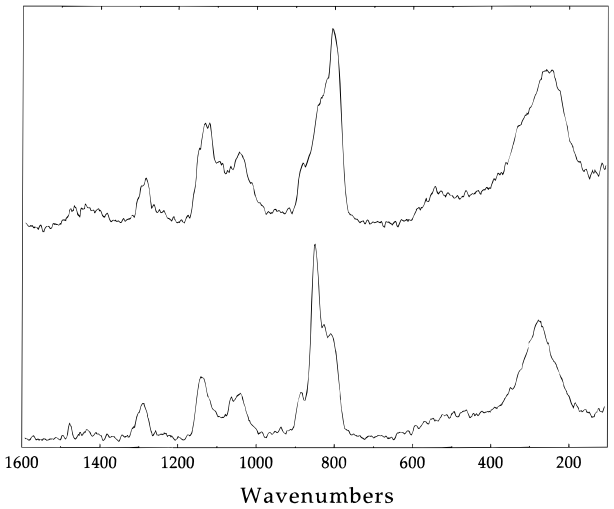

Figure 4. Observed isotropic Raman spectra of poly(ethylene oxide) in the melt state (top) and in water (bottom).

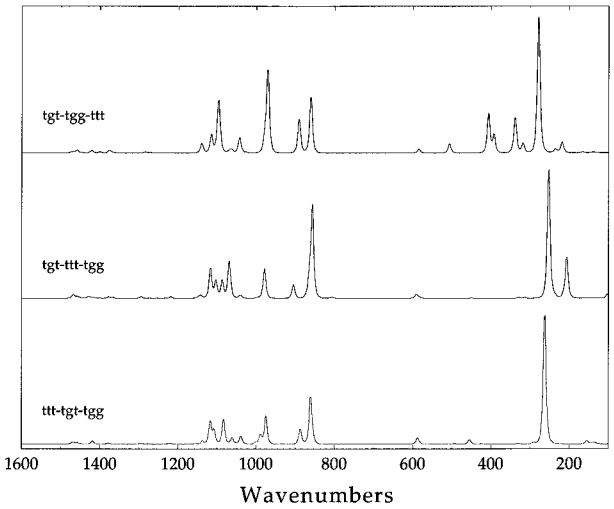

Figure 5. Simulated isotropic Raman spectra of three-repeat-sequences of poly(ethylene oxide).

in the melt. Evidently, the source of the enhancement must be sought in other factors than the parameters E_ρ and $\phi_{CC}{}^g$. Very recently, Smith et al. reported small angle X-ray scattering results for a more nearly monodisperse sample of molten poly(ethylene oxide) ($M_w/M_n = 1.04$) and found a characteristic ratio of 5.7.[15]

The isotropic Raman spectrum of poly(ethylene oxide) in the melt and in aqueous solution shown in Figure 4 suggests new indicators for characterizing the conformational distribution. Considerable differences are evident in the band shape for the 850 cm^{-1} band and for the D-LAM region near 365 cm^{-1}. Although the differences are insignificant in the normal Raman spectrum, the shape and position of the features in these two regions differ substantially in the isotropic spectrum. The strong bands in the 850 cm^{-1} region are almost mirror images for the two experiments carried out. The most intense feature in the 800 cm^{-1} region for the aqueous solution is located at 880 cm^{-1}. In contrast, the intense feature for the melt center is at 830 cm^{-1}. The shapes of the D-LAM bands observed for the two poly(ethylene oxide) samples are also quite different. The band observed for sample A is somewhat broader than the band observed for sample B. The shoulder on the high-frequency side of the D-LAM band in sample A proves to be an important feature that may be used to differentiate the two sets of data. These differences are to be correlated with differences in conformational distributions in the melt and in the aqueous solution of poly(ethylene oxide).

The conformational distribution must be reflected in the contour of the D-LAM band, since the underlying vibrations involve mechanical coupling of skeletal coordinates that are different for each conformational sequence. The same three conformational sequences, ttt, tgt, and tgg, connected differently to each other yield very different simulated spectra. All three simulated spectra in Figure 5 have a backbone stretching vibration that produces a strong band near 860 cm^{-1}. The D-LAM region is entirely different for each sequence of nine rotameric states and is dominated by the presence of an intense band at different frequencies flanked by various weaker bands.

The conformational distribution for poly(ethylene oxide) most likely always contains the conformer sequences ttt, tgt, tgg, tgg′, ttg.[6,11,41] Sequences of nine rotameric states constructed from three identical rotameric triple sequences have simulated Raman spectra

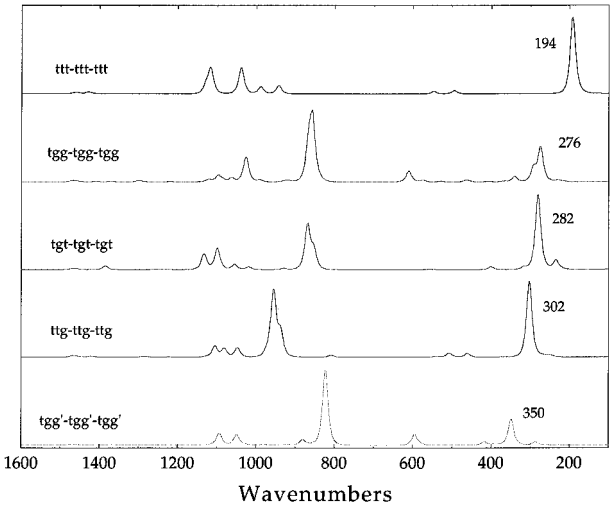

Figure 6. Simulated isotropic Raman spectra of three-repeat-sequences of poly(ethylene oxide).

shown in Figure 6. The strong band in the D-LAM region occurs for these sequences in the broad range from 194 to 350 cm^{-1}. The strong band for the three conformer sequences has frequencies in the order tgg′ > ttg > tgt > tgg > ttt. For the backbone stretching mode, the tgttgttgt and tggtggtgg sequences have a strong simulated band around 860 cm^{-1}, the tgg′tgg′tgg′ sequence has one at 830 cm^{-1}, and the ttttttttt and ttgttgttg sequences lack a substantial contributor in the 850 cm^{-1} region.

Such highly ordered sequences are unlikely in a disordered chain, and the less orderly sequences shown in Figure 7 were then considered. Each of these simulated spectra were computed for two identical triples of high probability, such as tgttgt, connected to another one of relatively high probability, such as ttt. Comparison of the results shown in Figure 6 with those in Figure 7 suggests that regular sequences of identical triples, such as tgttgttgt, have higher skeletal vibrational frequencies in the D-LAM region. Connecting two identical triples with a third of a different type may yield a frequency intermediate between the two types of identical triples. For example, the sequence ttttgttgt has a simulated band at 262 cm^{-1}, which is lower than the simulated 282 cm^{-1} band produced by the tgttgttgt sequence but higher than the simulated 194 cm^{-1} band due to tttttttt. The simulated spectra are strongly

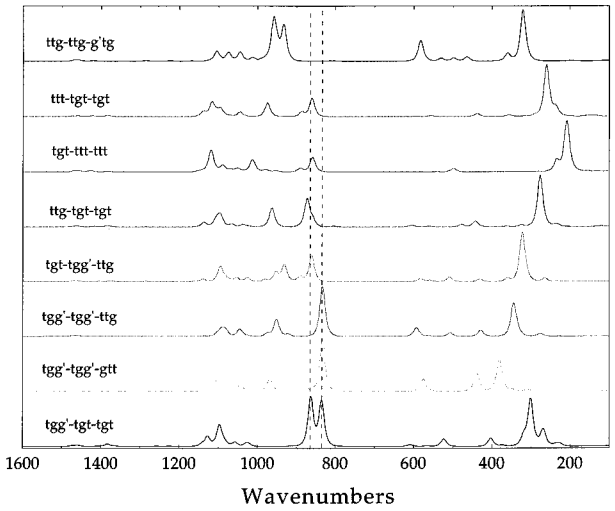

Figure 7. Simulated isotropic Raman spectra of three-repeat-sequences of poly(ethylene oxide).

Table 3. Conformational Distribution of Different Samples of Poly(Ethylene Oxide) used in Simulation Studies

sample	ttt	ttg	tgt	tgg	tgg′	gg′g	
C	0.105	0.085	0.466	0.149	0.122	0.003	for 22 °C
D	0.107	0.061	0.599	0.156	0.060	0.002	for 22 °C
E	0.131	0.066	0.259	0.040	0.354	0.108	for 70 °C
C′	0.106	0.091	0.440	0.190	0.104	0.006	for 22 °C
D′	0.108	0.057	0.596	0.157	0.056	0.001	for 22 °C
E′	0.119	0.061	0.204	0.052	0.354	0.153	for 70 °C

dependent on the exact sequence of rotameric states, rather than on the fractional content of t, g, and g′ states. For example, the two conformers tgg′tgg′ttg and tgg′tgg′gtt differ only in the placement of the g rotameric state in the terminal triple but have very different simulated spectra. Indeed, the tgg′tgg′gtt sequence has a simulated band at 382 cm^{-1}, which is a higher frequency than found for any other sequence in Figures 6 or 7. In the higher frequency backbone bond stretching region around 850 cm^{-1}, the simulated spectra are much less sensitive to the details of rotamer order. Any of these conformers containing the tgt sequence has a simulated band at 860 cm^{-1}, and when the sequence contains tgg′ as the terminal group, a simulated band occurs at 830 cm^{-1}.

A *Monte Carlo* method was used to generate three conformational distributions of poly(ethylene oxide) chains incorporating the energy terms of Flory's model ($E_s = -0.430$, $E_\rho = 0.900$ and $E_\omega = 0.338$ kcal/mol),[6] Abe's model ($E_\sigma = -0.5$, $E_\rho = 0.9$ and $E_\omega = 0.338$ kcal/mol),[41] and Smith's model ($E_\sigma = 0.1$, $E_\rho = 1.4$ and $E_\omega = -1.3$ kcal/mol).[11] The percentages of various conformers are listed in Table 3 as simulations C, D, and E, respectively. The equilibrium fractions of the conformational distribution are listed in the last three rows of Table 3, where C′ designates the equilibrium fraction for simulation C, and similarly for D′ and E′. The three RIS models can be divided into two groups: (1) Flory's (simulation C) and Abe's (simulation D) produce conformational distributions with the largest percentage of tgt conformer; (2) Smith's simulation E is dominated by the tgg′ conformer.

The simulated isotropic Raman spectrum for each of these distributions is shown in Figure 8. Simulation E fits the Raman spectrum observed for the molten state fairly well. In contrast, the simulated spectra obtained using distributions C and D match the observed isotropic Raman spectrum of the aqueous poly(ethylene oxide) solution. The similarities between the simulated and observed spectra can be found not only in the D-LAM pattern but also in the backbone bond stretching region. As shown in Figures 6 and 7, the tgg′-dominated distribution produces a D-LAM with a maximum at approximately 350 cm^{-1} and a skeletal stretching vibration at 830 cm^{-1}. The distribution having mostly tgt conformers is associated with a D-LAM centered at approximately 282 cm^{-1} and having the skeletal band at 860 cm^{-1}. Such simulated spectra from the two groups fit the two different observations, one for poly(ethylene oxide) in aqueous solution and the other in the melt.

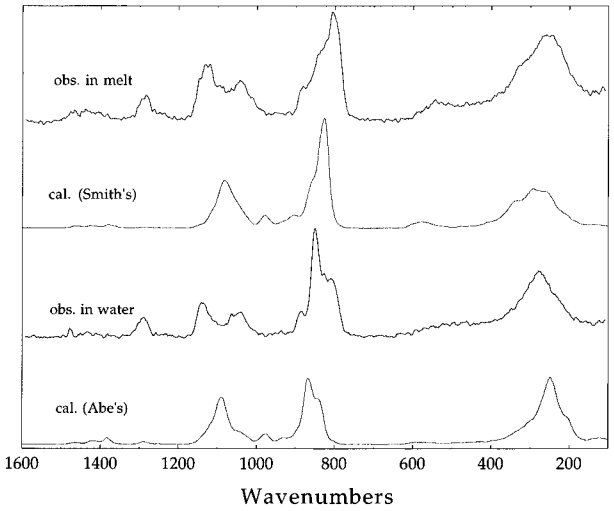

Figure 8. Simulated and observed isotropic Raman spectra of poly(ethylene oxide). Different conformational distributions are described in text and Table 3.

Although the simulated spectrum for distribution C fits the data obtained from poly(ethylene oxide) in aqueous solution well, there are minor departures. The band maximum is about 20 cm^{-1} lower than the observed value. This difference is possibly caused by adopting a specific force field refined to 1,2-dimethoxyethane type model compounds.[30] This set of force constants yields a frequency of 398 versus the 396 cm^{-1} observed value for the ttt conformer of 1,2-dimethoxyethane. For the tgt-conformer, a value of 356 cm^{-1} was obtained, which is 9 cm^{-1} lower than the observed value. Therefore, the D-LAM frequency for the tgt dominated distribution would be expected to have a slightly lower calculated value than observed. This difference, in contrast, is very small compared to the D-LAM frequency shift that results on changing a conformational distribution. The contribution to D-LAM for a regular sequence of tgttgttgt has a frequency of 282 cm^{-1}, and that associated with a sequence of tgttgttgttgttgt has one as low as 264 cm^{-1}. As shown in Figure 7, even two connected tgt conformers, if linked to ttt (the case of the ttttgttgt sequence), will have a frequency of 262 cm^{-1} or, if linked to a ttg conformer (the case of the ttgtgttgt sequence), will still have a rather low frequency at 276 cm^{-1}. Simulation D has a pronounced shoulder on the low-frequency side of the calculated D-LAM, since its larger population of tgt conformer leads to a higher probability of long tgt sequences connected to a ttt conformer along the chain.

The tgg′ conformer has been found for 1,2-dimethoxyethane trapped in an argon matrix of 1,2-dimethoxyethane.[36] The reason this conformer is stable in an argon matrix is that there are strong attractive interac-

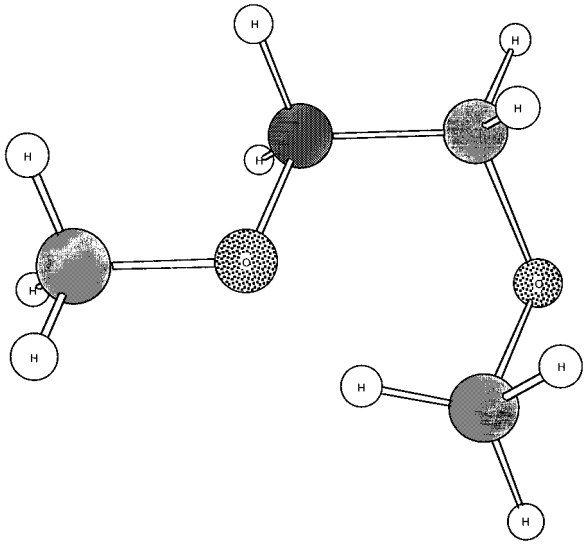

Figure 9. Schematic representation of the tgg′ conformation of 1,2-dimethoxyethane and poly(ethylene oxide), caused by the O···H attraction effect.

tions between an oxygen atom and a hydrogen opposite the methyl group five bonds away, as shown in Figure 9. This phenomenon has been investigated by *ab initio* calculation using a D95+(2df,p) basis set and an MP2 approximate electron correlation,[11] and the existence of this conformer has been shown in NMR experiments.[39,41]

These results have demonstrated that the conformational distribution of poly(ethylene oxide) in the melt is reasonably predicted by a set of statistical weights which include the so-called O···H attraction effect.[11] These results also indicate that for the system poly(ethylene oxide) in water the O···H attraction effect is lost. The simulated and experimental data suggest that, by changing intermolecular interactions, it is possible to change the conformational distribution in poly(ethylene oxide) significantly.

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