

Hydration of Poly(ethylene oxide)s in Aqueous Solution As Studied by Dielectric Relaxation Measurements

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Received: January 18, 2006; In Final Form: March 21, 2006

The hydration state of poly(ethylene oxide)s (PEOs) in aqueous solutions was investigated using dielectric relaxation measurements at 25 °C over a frequency range up to 20 GHz, which is the relaxation frequency of water molecules in a bulk state. The dielectric relaxation spectra obtained indicated decomposition into two major and one minor relaxation modes with relaxation times of 8.3, 22, and 250 ps, respectively. The two major modes were attributed to rotational relaxation of water molecules belonging to the bulk state and water molecules hydrogen bonded to ethylene oxide (EO) monomer units. The number of hydration water molecules per EO unit depended on the molar mass of PEO (M) and reached a constant value of 3.7 at $M > 1500$, which agrees with the value obtained by other experiments.

Introduction

The physicochemical features of water-soluble polymers in aqueous solution are highly dependent on the strength of interaction between water molecules and monomers of the polymers. Poly(ethylene oxide) (PEO) is a typical water-soluble polymer with water solubility that exhibits unique temperature dependence; the solubility of PEO decreases with increasing temperature. Eventually, the PEO segregates from the solution above a certain critical temperature, namely the *lower critical solution temperature* (LCST), which depends on molar mass (M), in contrast to the normal behavior of other water-soluble polymers.^{1–4} This temperature-dependent solubility is unusual for water-soluble polymers whose solubility is due to hydrogen bond formation between water molecules and the monomer units. These hydrogen bonds may break above the LCST. Recent advancements have been made in the experimentally and theoretically derived understanding of such complicated temperature dependence of polymer solubility.^{4–9}

In the study of the hydration structure of PEO in aqueous solution, the number (n) of hydrated water molecules per ethylene oxide (EO) monomer unit is a critical feature. The number, n , ranges from 1 to 6 depending on the method used to calculate it and on the M value of the PEO.^{4,10–18} Recently, Huang et al.¹⁷ investigated the maximum n value of PEO in aqueous solution as a function of M from eutectic point composition data determined by differential scanning calorimetry (DSC). The reported n values for $M = 400$, 1540, and 70000 were 1.6, 2.4, and 3.3, respectively. The n value for $M = 400$ was identical to that reported by Sato et al.¹⁸ via dielectric relaxation measurements based on a time domain reflectometric technique. Most methods employed for the determination of n identify break points in the composition, i.e., molar fractions of EO monomer units relative to water molecules at which measured physical variables, such as phase transition temperature determined by DSC, exhibit sharp breaking points. Thus, the n value determined by these methods implies the average critical molar ratio where free (or bulk) water molecules not involved in hydrogen bonding with PEO disappear. However, PEOs have an intrinsic hydration state represented by the

number (n_1) of water molecules involved in hydrogen bonding with PEO and surrounded by a large number of bulk water molecules in dilute aqueous solution. The value of n_1 may be different from that of n due to the difference in the definition.

In this study, we used a frequency (ω) domain dielectric relaxation technique that provides accurate electric permittivities consisting of real and imaginary functions (ϵ' and ϵ'') of ω for the determination of n_1 for PEOs with varying M values in dilute aqueous solution. Because water molecules have a relatively large electric dipole moment, ca. 1.8 D, the results of dielectric measurements conducted over a wide ω range covering the relaxation frequency of bulk state water molecules, ca. $1.3 \times 10^{11} \text{ s}^{-1}$, are quite sensitive toward changes in the mobility of water molecules due to hydration induced by the presence of PEOs.

More than two decades ago, Kaatz et al.¹⁹ published precise dielectric relaxation data for aqueous solutions of water soluble polymers, including PEOs. They reported a value for n_1 of 5.5, which is much greater than that obtained in this study, ca. 3.7. We discuss the reason for this difference.

Experimental Section

Materials. PEOs with varying M values from 300 to 7500 were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and were used without further purification. Highly deionized water with a specific resistance greater than $15 \text{ M}\Omega \text{ cm}$ was generated by an Elix-UV3 system of Millipore (Billerica) and used as a solvent. The concentration (c) of PEOs was 0.5–2.5 M based on the monomer unit. Deuterium oxide (D_2O) with a purity of 99.9% was purchased from Sigma-Aldrich (St. Louis, MO) as the solvent for ^{13}C NMR measurements. The c of PEO with $M = 3000$ dissolved in D_2O for ^{13}C NMR measurements was 2.0 M.

Methods. Dielectric relaxation measurements were conducted over a ω range of 6.28×10^6 to $1.26 \times 10^{11} \text{ rad s}^{-1}$ (1.0×10^6 to $2.0 \times 10^{10} \text{ Hz}$) using two types of systems. A lower ω range from 6.28×10^6 to $6.28 \times 10^9 \text{ rad s}^{-1}$ was covered by an Agilent, RF LCR Meter 4287A (Palo Alto), equipped with a custom-made electrode cell with the vacant capacitance of ca. 0.23 pF. Primary electric capacitance (C) and conductance (G) were determined in a parallel coupling equivalent circuit as functions of ω . Real and imaginary portions of relative electric

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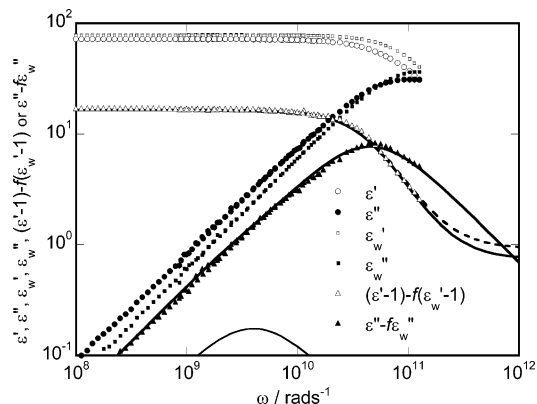


Figure 1. Frequency (ω) dependencies of dielectric spectra (ϵ' and ϵ'') for an aqueous solution of PEO with $M = 7500$ at $c = 2.49$ M and 25 °C. Dielectric spectra for bulk water (ϵ_w' and ϵ_w'') and differential spectra for the solution, $(\epsilon' - 1) - f(\epsilon_w' - 1)$ and $\epsilon'' - f\epsilon_w''$, evaluated assuming $f = 0.70$ are also plotted. Solid and broken lines represent calculated curves via eq 2 using fit parameters ($\Delta\epsilon_1$, τ_1 , $\Delta\epsilon_2$, τ_2) summarized in Table 1 and n_i ($i = 3$ and 4 ; solid and broken lines). A thin solid line represents a dielectric loss curve of the relaxation mode of EO ($i = 2$).

permittivity, ϵ' and ϵ'' , were calculated using $\epsilon' = CC_0^{-1}$ and $\epsilon'' = (G - G_{dc})(C_0\omega)^{-1}$; G_{dc} , indicating direct conductance, is due to the presence of ionic impurities in sample solutions. A Hewlett-Packard Material Probe System 85070B consisting of an S-Parameter Network Analyzer 8720ES (Palo Alto) was employed in the ω range of 3.14×10^8 to 1.26×10^{11} rad s $^{-1}$. In this system, ϵ' and ϵ'' were automatically calculated as functions of ω through a program supplied by Hewlett-Packard. Measurement details have been reported elsewhere.^{20,21}

To determine the partial (monomer unit) molar volumes (\bar{V}_m) of PEOs in aqueous solution, densities of aqueous PEO solutions were measured at 25.0 °C using an Anton Paar digital density meter DMA5000 (Graz).

Longitudinal relaxation time (T_1) of ^{13}C NMR for a D_2O solution of PEO with $M = 3000$ was determined at 25 °C under D_2O locked mode via an Inversion Recovery pulse sequence technique using a Varian UNITY plus 600-NMR spectrometer (Palo Alto) at resonance frequency of 603.2 MHz for proton nuclei (150.8 MHz for ^{13}C).

Results and Discussion

Dielectric Behavior. Typical ω dependence of ϵ' and ϵ'' for an aqueous solution of PEO with $M = 7500$ at $c = 2.49$ M (based on monomer unit) and 25 °C is shown in Figure 1. Real and imaginary parts (ϵ_w' and ϵ_w'') obtained for pure water using the same measurement system are also shown for comparison. The dielectric spectra contain obvious differences. Spectra for the solution are broader than those for pure water, especially near $\omega = 5 \times 10^{10}$ rad s $^{-1}$. In some reports^{18,22} of the dielectric behavior of aqueous PEO systems, adjustable parameters were determined to express the broadness of dielectric spectra by fitting data to semiempirical dielectric relaxation functions such as Cole–Cole,²³ Davidson–Cole,²⁴ and Havriliak–Negami²⁵ formulas.

However, this study involved the summation of Debye-type functions for spectral analyses because physical meanings for the semiempirical adjustable parameters were not clear. The ω dependence of ϵ_w' and ϵ_w'' for bulk water (BW) molecules are well described with only one relaxation mode as given by eq 1 with relaxation time, strength, and the permittivity values of infinitely high ω , $\tau_w = 8.3$ ps, $\Delta\epsilon_w = 73.3$, and $\epsilon_{\infty w} = 5.1$,

TABLE 1: Summary of Dielectric and Related Parameters, \bar{V}_m , f , $\Delta\epsilon_1$ ($= \Delta\epsilon_{\text{HW}}$), τ_1 ($= \tau_{\text{HW}}$), $\Delta\epsilon_2$ ($= \Delta\epsilon_{\text{EO}}$), τ_2 ($= \tau_{\text{EO}}$), n_1 , and $55.6\Delta\epsilon_{\text{HW}}(cn_1)^{-1}$, for Aqueous PEOs Solutions Examined in This Study

M	c/M	$\bar{V}_m/\text{cm}^3 \text{ mol}^{-1}{}^a$	f	$\Delta\epsilon_1$	τ_1/ps	$\Delta\epsilon_2$	τ_2/ps	n_1^b	$55.6\Delta\epsilon_1 \times (cn_1)^{-1}{}^c$
300	1.30	37.31	0.840	9.2	20.0	0.10	250	3.4	112.2
	1.71		0.810	10.5	21.0	0.20	250		97.8
	2.09		0.750	14.0	21.0	0.30	250		106.6
	2.48		0.710	16.0	21.0	0.40	250		102.4
400	0.891	37.07	0.890	6.0	20.0	0.15	250	3.5	110.2
	1.73		0.800	10.7	21.0	0.25	250		101.4
	2.48		0.705	16.2	21.0	0.40	250		111.4
1500	1.32	36.64	0.840	8.8	22.0	0.15	250	3.7	100.1
	1.70		0.800	10.5	22.0	0.20	250		92.7
	2.10		0.745	13.5	22.0	0.25	250		96.6
	2.49		0.700	16.5	22.0	0.30	250		99.7
3000	1.30	36.84	0.840	8.50	22.0	0.25	250	3.7	100.9
	1.74		0.796	10.8	23.0	0.33	250		96.0
	2.10		0.740	14.0	22.0	0.42	250		102.8
	2.48		0.690	16.5	21.0	0.50	250		102.8
7500	0.492	36.64	0.940	3.10	22.0	0.08	250	3.7	97.4
	0.683		0.915	4.45	22.0	0.10	250		100.7
	0.978		0.880	6.40	22.0	0.12	250		101.0
	1.32		0.835	8.50	22.0	0.20	250		103.0
	1.70		0.800	10.0	22.0	0.25	250		100.8
	2.10		0.750	12.8	22.0	0.30	250		101.5
	2.49		0.700	15.3	22.0	0.35	250		94.9

^a Determined from density measurements and coincident with literature data.³⁰ ^b Average values. ^c Identical with $55.6\Delta\epsilon_{\text{HW}}(cn_1)^{-1}$; n_1 is assumed to be the average value.

respectively, at 25 °C.²⁶ The total ϵ' and ϵ'' are described by eq 2 by introducing (rotational) relaxation strength ($\Delta\epsilon_i$), time (τ_i), and polarizability (δ_i) for the relaxation mode of each component ($i = 1$ and 2);^{20,27} although the factor of -1 in eq 2 is not necessary in most cases, we retained it for a more precise analysis. When the molar polarizability of i was β_i , δ_i is calculated to be $3\beta_i c_i (2\epsilon_v)^{-1}$ using the concentration of i , c_i , and the electric permittivity of vacuum, ϵ_v .^{20,27} The factor (f) of the first term of eq 2 indicates the fractional contribution of the bulk state water molecules: $f = 1$ indicates pure water. The additional relaxation modes of components $i = 1$ and 2 are attributed to the rotational mode of hydrated water (HW) molecules ($i = 1$) to PEOs and that of EO monomer units ($i = 2$), respectively. This is an advantage of using a summation of the Debye type relaxation functions instead of empirical parameters to express the broadness of the dielectric spectra.

$$\epsilon'_w = \frac{\Delta\epsilon_w}{1 + \omega^2\tau_w^2} + \epsilon_{\infty w} \quad \epsilon''_w = \frac{\Delta\epsilon_w\omega\tau_w}{1 + \omega^2\tau_w^2} \quad (1)$$

$$\left. \begin{aligned} \epsilon' - 1 &= f(\epsilon'_w - 1) + \sum_{i=1,2} \left(\frac{\Delta\epsilon_i}{1 + \omega^2\tau_i^2} + \delta_i \right) \\ \epsilon'' &= f\epsilon''_w + \sum_{i=1,2} \frac{\Delta\epsilon_i\omega\tau_i}{1 + \omega^2\tau_i^2} \end{aligned} \right\} \quad (2)$$

Figure 1 also involves differential spectra, $(\epsilon' - 1) - f(\epsilon'_w - 1)$ and $\epsilon'' - f\epsilon''_w$, evaluated assuming $f = 0.70$. Lines for $(\epsilon' - 1) - f(\epsilon'_w - 1)$ and $\epsilon'' - f\epsilon''_w$ were calculated using the parameters summarized in Table 1. The value of $3\beta_2(2\epsilon_v)^{-1}$ ($= 3\beta_{\text{EO}}(2\epsilon_v)^{-1}$) was calculated to be 0.076 M^{-1} from data of bulk PEO in liquid state at room temperature.¹⁸ On the other hand, the value of $3\beta_1(2\epsilon_v)^{-1}$ ($= 3\beta_{\text{HW}}(2\epsilon_v)^{-1}$) was 0.074 M^{-1} , as determined from the relation $\epsilon_{\infty w} = 5.1$ for pure water, since even hydrated water molecules presumably possess the same

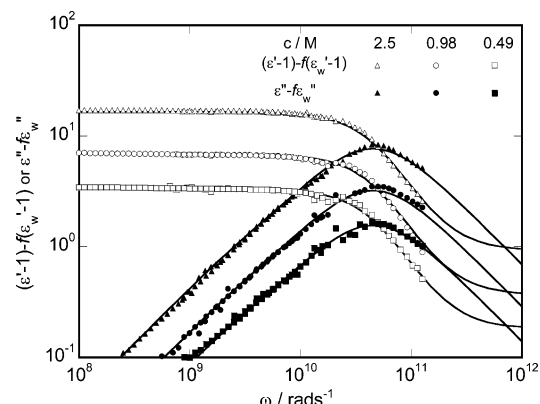


Figure 2. ω dependencies of differential spectra, $(\epsilon' - 1) - f(\epsilon'_w - 1)$ and $\epsilon'' - f\epsilon''_w$, for aqueous solutions of PEO with $M = 7500$ at various c values and 25 °C. Solid lines represent calculated curves via eq 2 using fit parameters summarized in Table 1.

polarizability as bulk water molecules. The relation $c_{\text{HW}} = cn_1$ is simply assumed in this case. Although the value of n_1 is assumed to be 3 (thick solid line) and 4 (broken line) for the curves reproducing $(\epsilon' - 1) - f(\epsilon'_w - 1)$ in Figure 1, the shape of the lines for $(\epsilon' - 1) - f(\epsilon'_w - 1)$ were not sensitive to n_1 until it reached a value of 5 in the ω range of the experimental data. The assumed magnitude of $\Delta\epsilon_2 (= \Delta\epsilon_{\text{EO}})$ as seen in Table 1 is much less than that of $\Delta\epsilon_1 (= \Delta\epsilon_{\text{HW}})$, and the value of $\Delta\epsilon_{\text{EO}}$ is not always necessary for ϵ' and ϵ'' , especially in low c solutions. A thin solid line in Figure 1 represents a dielectric loss curve of the relaxation mode of EO ($i = 2$), $\Delta\epsilon_{\text{EO}}\omega\tau_{\text{EO}}(1 + \omega^2\tau_{\text{EO}}^2)^{-1}$ (cf. eq 2), to show how small the contribution of the relaxation mode of EO in the system is.

Because the experimental data and generated curves are in agreement, the use of ϵ' and ϵ'' in eq 2 appears to provide a successful solution. All other sample solutions examined also show successful decomposition into three (two major and a minor) relaxation modes: BW, HW, and EO. Figure 2 shows the ω dependencies of $(\epsilon' - 1) - f\epsilon'_w$ and $\epsilon'' - f\epsilon''_w$ for an aqueous PEO system with $M = 7500$ for various c values. A large relaxation mode caused by HW ($i = 1$) around 5×10^{10} rad s^{-1} with relaxation strength dependent on c was clearly found irrespective of the value of c , and a very small relaxation mode of EO ($i = 2$) also was observed near 4×10^9 rad s^{-1} in sample solutions. Solid lines represent the best fit $(\epsilon' - 1) - f\epsilon'_w$ and $\epsilon'' - f\epsilon''_w$ curves for data calculated with eq 2 assuming parameters summarized in Table 1. Reasonable agreement between the calculated curves and data observed in Figure 2 confirms the validity of eq 2 for the analysis in this aqueous system of PEOs.

Hydration Number. Because the c value set in this study was not so high, hydrated EO monomer units of PEOs in aqueous solution are sufficiently surrounded by a number of bulk-state water molecules. Thus, we can discuss intrinsic hydration state and number, n_1 , based on the data obtained. According to previous studies^{20,21,28,29} assuming separated relaxation modes in aqueous solutions, the value of f is directly related to the volume fraction ($\phi = c\bar{V}_m$) of solute molecules as shown in the first term of eq 3. The \bar{V}_m values obtained for each PEO, which are tabulated in Table 1, coincide well with those found in the literature.³⁰

$$f = \frac{1 - \phi}{1 + \frac{1}{2}\phi} - \frac{cn_1}{55.6} \quad (3)$$

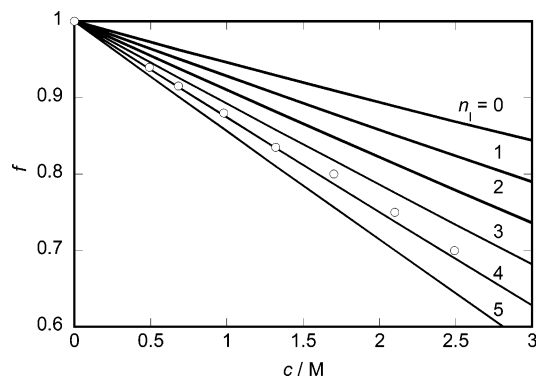


Figure 3. c dependence of f used to make Figure 2 for aqueous solutions of PEO with $M = 7500$ at various c values and 25 °C. Lines represent calculated curves via eq 3 assuming n_1 values from 0 to 5.

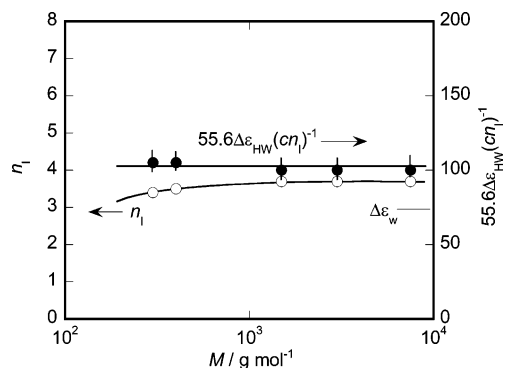


Figure 4. Dependence of the determined n_1 and $55.6\Delta\epsilon_{\text{HW}}(cn_1)^{-1}$ on M for aqueous solutions of PEOs at 25 °C.

The second term of eq 3 represents the contribution of hydrated water molecules (HW) to solute molecules; the value of 55.6 indicates the molar number of BW molecules per liter. The HW molecules no longer behave as bulk-state water molecules with $\tau_w = 8.3$ ps; their molecular motion is detected as the mode of $i = 1$ in aqueous systems of PEOs.

The dependence of f on c for the system shown in Figure 2 is presented in Figure 3. Lines in the figure represent the c dependence of f calculated using eq 3 with n_1 values from 1 to 5. Since f data lie between the lines calculated at $n_1 = 3.0$ and 4.0 , we conclude that $n_1 = 3.0$ – 4.0 for the PEO with $M = 7500$. The average value of $n_1 = 3.7$ was used in Table 1, which gives the best fit curve for the experiments represented in Figure 3. Essentially, the same procedure shown in Figure 3 to determine the n_1 value has been successfully applied to other PEOs. The n_1 value obtained depends slightly on M as shown in Figure 4. Because the number ratio of terminal hydroxyl groups (OH) relative to EO units increases with decreasing M value, the slight decrease in the n_1 values seen in Figure 4 suggests that the intrinsic hydration number of water molecules to OH is smaller than n_1 to oxygen atoms of the EO units. The n_1 value approached a constant value of 3.7 at $M > 1500$, while the n value previously determined using DSC measurements¹⁷ was thought to continue a steep increase from 1.6 ($M = 400$) to 3.3 ($M = 70000$) with increasing M ; the physical meanings of n_1 and n as determined by DSC¹⁷ are different, especially at low M values such as 400. The value of $n_1 = 3.7$ is similar to that of n previously reported using methods^{13–15} other than DSC. A value of $n = 3$ is most commonly reported in the literature.^{13–15} In most cases, the value of n was approximated from a molar fraction of EO units at which measured physical parameters, such as NMR chemical and Raman shifts, exhibit breaking points indicating critical thresholds for the presence of BW

molecules. If changes in the measured parameters are not sensitive to molar fraction, n values will be slightly underestimated.

Moreover, the value of $n_1 = 3.7$ is close to the number of water molecules near the oxygen atoms of EO units, ca. 3.0, determined by integration of the pair distribution function of EO oxygen to water oxygen calculated by molecular dynamics simulations for PEO with $M = 660$ in aqueous solution at 27 °C;³¹ the physical meaning of this number appears to be identical to n_1 . Since integration with respect to radial distance was cut off at the first minimum distance of 0.35 nm of the pair distribution function, the value of 3.0 might be a slight underestimation.³¹

Because an oxygen atom of EO units bears two lone-pair electrons, two water molecules directly hydrate to the oxygen atom at maximum, forming hydrogen bonds using the two lone-pair electrons. Subsequently, one (or two) additional water molecule(s) have the ability to form additional hydrogen bonds to the two hydrated water molecules, sometimes bridging the two hydrated water molecules. The optimized structure of diethyl ether tetrahydrate, a typical model for tetrahydrated EO units, can be reasonably determined by ab initio quantum chemical calculations. Consequently, a value for n_1 close to 4 would be natural.

Kaatze et al.¹⁹ reported a value of 5.5 for n_1 for PEOs based on precise dielectric data. The difference between the value of n_1 obtained here and the n_1 reported by Kaatze et al., ca. 1.8, is beyond the magnitude of experimental uncertainty. The analytical method employed in their dielectric study¹⁹ was not essentially different from our methods. However, they assumed that the relaxation strength of hydrated water molecules to EO units is identical to that of bulk water molecules without any basic evidence, whereas we did not make the same assumption. This explains the difference in the n_1 values.

Relaxation Times. The major relaxation mode caused by HW ($i = 1$) near 5×10^{10} rad s⁻¹ has a relaxation time (τ_{HW}) of ca. 22 ps irrespective of M and c values as summarized in Table 1. Molecular motions of the EO unit in PEOs are found near 250 ps, a much greater value than that of τ_{HW} . Motions of HW molecules are not simple rotational motions at hydration positions, but are highly restricted by hydrogen bonding among hydrated EO and HW molecules. Thus, the most important process may be the detachment of HW molecules into the bulk water phase with freedom of rotational motion after the lifetime (τ_{life}) of the hydration or hydrogen bonding to the EO units. In this case, the value of τ_{HW} should correspond directly to that of τ_{life} .

Recent molecular dynamics simulations^{31,32} have provided realistic results for molecular parameters such as τ_{life} , of hydrogen bond formation of water molecules to EO units. Tasaki³¹ obtained a value of 25 ps for τ_{life} via molecular dynamics simulation; this τ_{life} value is close to the value of τ_1 ($= \tau_{\text{HW}}$) as shown in Table 1.

The small relaxation mode of EO ($i = 2$) observed near 4×10^9 rad s⁻¹ ($\tau_2 \approx 250$ ps) in sample solution was assigned to the rotational relaxation mode of EO units. Because a conventional method to determine the relaxation time of the dipole moment belonging to EO units is not available, we employed correlation time (τ_c) of ¹³C nuclei of EO groups as a reference for τ_2 ($= \tau_{\text{EO}}$). A ¹³C nucleus covalently bonded to a ¹H nucleus always exhibits a magnetic dipole–dipole interaction, which makes the magnetization of the ¹³C nucleus relaxed due to molecular motion agitating the magnetic field (with a time constant given as the correlation time, τ_c).³³ Since the T_1 value determined for ¹³C of PEO with $M = 3000$ in D₂O was 0.73 s

and the resonant signal of the nuclei was involved under the extremely narrowing conditions, the τ_c value was determined to be 57 ps via eq 4, assuming a bond length (r_{HC}) of 0.110 nm between hydrogen and carbon

$$\frac{1}{T_1} = \frac{h^2 \gamma_{\text{H}}^2 \gamma_{\text{C}}^2 \tau_c}{4\pi^2 r_{\text{HC}}^6} \quad (4)$$

where, h , γ_{H} , and γ_{C} are Planck's constant and magnetogyric ratios of ¹H and ¹³C, respectively. To convert the value of τ_c to that of a time constant with the same rank as the dielectric relaxation time of the methylene groups (τ_d), the relation of $\tau_d = 3\tau_c \sim 170$ ps was used. The rate of motion of dipoles belonging to EO units is governed by the motions of adjacent methylene groups. Therefore, the value of τ_2 is close to that of τ_d from the viewpoint of the order of magnitude.

The published dielectric relaxation behavior of bulk PEOs in liquid state at 25 °C with low M values (e.g., 200 and 400) shows the relaxation of the dipoles belonging to EO units at the relaxation time of 160 ps.¹⁸ This value means the relaxation time of EO units without the contribution of hydrogen bond because bulk PEOs contain no water molecules. However, in the case of dilute aqueous solutions of PEOs, the presence of hydrogen bonds with finite lifetimes such as τ_{HW} of 22 ps between EO units and water molecules possibly depresses the rate of molecular motions of the EO units due to much higher friction coefficients of the hydrogen bonded EO units than those of non-hydrogen-bonded EO units in the bulk liquid state. It has been well-known that most of solvent molecules accelerate the rate of molecular motion of solutes, whereas water molecules in aqueous PEOs solutions likely possess unusual effects to dynamics of dissolved PEOs because of the strong hydrogen bond formation. Consequently, the τ_2 ($= \tau_{\text{EO}}$) value determined in this study, ca. 250 ps as seen in Table 1, has been assigned to the relaxation time of dipoles of the EO units. As pointed out above the volume fraction of PEOs in the condition of the present study is sufficient low, and EO units are surrounded by a great number of water molecules, the relaxation time of EO units does not depend on the c value essentially. Moreover, the molecular motion of EO units in PEOs is of a fast one on the order of a monomer size, it hardly depends on the M value as seen in Table 1. Because the magnitude of $\Delta\epsilon_2$ ($= \Delta\epsilon_{\text{EO}}$) is much smaller than that of $\Delta\epsilon_{\text{HW}}$, the contribution of EO to the total dielectric relaxation behavior is negligibly small in strength. However, the much slower rate of molecular motion of the EO units compared to the HW molecules was recognized.

Relaxation Strength of Hydrated Water Molecules. Relaxation strength of hydrated water molecules is reduced to the value $55.6\Delta\epsilon_{\text{HW}}(cn_1)^{-1}$. This is expected to occur at the molar amount identical to that for bulk water, i.e., 55.6 M, which is a constant value of ca. 105, irrespective of c and M as summarized in Table 1 and shown in Figure 4. The $\Delta\epsilon_w = 73.3$ value for bulk water molecules is significantly smaller.

Distinctive differences between HW and BW molecules should reside in values for their rotational relaxation times, τ_{HW} and τ_w . Therefore, the greater value for $55.6\Delta\epsilon_{\text{HW}}(cn_1)^{-1}$ results from the longer relaxation time of HW water molecules, $\tau_{\text{HW}} \approx 22$ ps, compared to the $\tau_w \approx 8.3$ ps for BW. The generality that HW water molecules with relaxation times longer than that of coexisting bulk water molecules keep dielectric relaxation strength considerably greater than that of the bulk water molecules is not known at present. The validity of the findings must be tested in other aqueous systems, including hydrated solutes such as water-soluble polymers. If the findings are

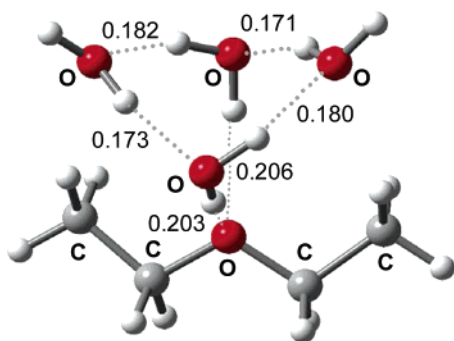


Figure 5. Optimized geometry of diethyl ether tetrahydrate obtained at the B3LYP/6-31G** level in the gaseous phase. The formation energy for the hydrate is calculated at the same level as the optimization with the self-consistent reaction field based on the SCI-PCM model³⁵ bearing the dielectric constant of bulk water to take account of the presence of bulk water molecules surrounding. The numbers in the figure show some hydrogen bond distances in nm.

generalizable, a technique to control the value of dielectric constants of aqueous systems could be developed using the hydration effect of solutes.

Hydration Structure. To realize a specific hydration structure of PEOs in aqueous solution, we performed ab initio quantum chemical calculations using Gaussian 03³⁴ for a model system that describes non- and tetra-hydrated EO units in aqueous phase. We first started semiempirical quantum chemical calculations to determine rough optimized geometries for non- and tetrahydrated diethyl ether in gaseous phase as the simplest model for non- and tetrahydrated EO units of PEOs dissolved in aqueous solution. Then, further optimization of the hydrate geometries in gaseous phase by ab initio calculation was done based on a density functional theory at the level of B3LYP/6-31G**. The formation energy calculation takes into account the effects of the bulk water molecules surrounding the diethyl ether hydrates and was performed with a self-consistent reaction field possessing a dielectric constant of bulk water assuming an SCI-PCM model.³⁵ Then, the magnitudes of the total formation energies ($E_T(0)$ and $E_T(4)$) were obtained for the optimized geometries of diethyl ether non- and tetrahydrates.

The final optimized geometry obtained for the diethyl ether tetrahydrate in aqueous phase is shown in Figure 5 with hydrogen bond distances between hydrogen and oxygen atoms given in nm. At the same level of B3LYP/6-31G**, we also calculated the optimized geometry for a water molecule with the same self-consistent reaction field, SCI-PCM model, to determine the magnitude of formation energy (E_{BW}) of a BW molecule. Then, the formation energy difference, $\Delta E_f = E_T(4) - (E_T(0) + 4E_{BW})$, was roughly calculated as $\Delta E_f = -136 \text{ kJ mol}^{-1}$. Consequently, the negative value of ΔE_f suggests that the EO tetra-hydrate is naturally generated in aqueous systems. Zeng et al.³⁶ also performed ab initio calculations for some dimethyl ether hydrates as model systems to describe the hydration geometries of poly(vinylmethyl ether) in aqueous systems. A dimethyl ether tetrahydrate, which has optimized geometry quite similar to that for the diethyl ether tetrahydrate shown in Figure 5, possesses the lowest formation energy of all the optimized dimethyl ether tetrahydrates.³⁶

Concluding Remarks

Poly(ethylene oxide)s dissolved in aqueous solution at 25 °C have an intrinsic hydration number, ca. 3.7 per ethylene oxide monomer unit, irrespective of concentration and molar mass, when the molar mass is greater than 1500.

The lifetime of hydrogen bonding or hydration of water molecules to ethylene oxide units is 22 ps and considerably

longer than the rotational relaxation time of bulk water molecules. Because the rotational relaxation time of ethylene oxide units is much longer than the lifetime of water molecules hydrated to them, the lifetime can be determined accurately.

The water molecules hydrated to ethylene oxide units possessing the lifetime of hydration significantly longer than the relaxation time of coexisting bulk water molecules, presumably keep dielectric relaxation strength considerably greater than that of the bulk water molecules.

Acknowledgment. We express special thanks to Canon, Inc. (Tokyo) for their kind financial support of this study.

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