Molecular Dynamics Simulation Study of Dielectric Relaxation in Aqueous Poly(ethylene oxide) Solutions

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Introduction

Aqueous solutions of poly(ethylene oxide) (PEO) are used in many important applications including protein crystallization,[1−3] modification of surfaces for biocompatibility,[4,5] control of particle aggregation in solutions,[6,7] modification of natural and artificial membranes,[8,9] and aqueous biphasic separations.[10] This wide range of applications, as well as the role of PEO as a model amphiphilic polymer, has inspired numerous experimental and simulation studies of PEO/water solutions. Experimental investigations of the OH-terminated poly(ethylene glycol) aqueous solutions[11−13] revealed some striking features in the dielectric relaxation behavior of these solutions including a linear dependence of the logarithm of the frequency of maximimum dielectric loss (f_m) and relaxation strength for $0.2 < $ PEO weight fraction (w_P) < 0.6 as well as a decrease in f_m with initial dilution of the PEO melt with a minimum in f_m at $w_P \approx 0.9$ followed by an increase with further dilution. This rather complex dependence of the dielectric relaxation behavior of PEO/water solutions on composition remains open to interpretation. In particular, the minimum in f_m at $w_P \approx 0.9$ has been attributed to slowing down of polymer dynamics with addition of water to the PEO melt due to hindered polymer segmental motion resulting from hydrogen bonds bridged between adjacent ether oxygens.[11] Such interpretations of experimentally observed phenomena rely on application of physical models or on “reasonable” assumptions that may not capture the underlying physics. Molecular dynamics (MD) simulations are able not only to predict physical phenomena but also can provide fundamental insight into underlying physical processes. Our MD simulation studies of PEO/water solutions revealed the rate of PEO conformational transitions is indeed slowed monotonically by PEO hydration.[14] However, as this slowing continues monotonically with dilution it is unclear how the minimum in f_m at $w_P \approx 0.9$ can be attributed to this effect.

In this note we extend our recent studies of structural[15,16] and dynamic[14,17,18] properties of PEO/water solutions in order to better understand the complex dependence of dielectric relaxation in these solutions on composition. Details of the MD simulations can be found elsewhere.[14,18] Here we mention that a quantum chemistry based force field for PEO/PEO[19] and PEO/water[20] interactions together with the transferable intermolecular four point potential (TIP4P) model for water[21] were used. MD simulations were performed at 318 K on aqueous solutions of 12 repeat unit PEO chains of the structure $H-(CH_2-O-CH_2)_{12}-H$ for compositions $w_P =$ 0.0, 0.17, 0.35, 0.52, 0.65, 0.78, 0.90, 1.0. Simulation box consisted of 3000−5000 atoms with linear box dimensions from 24.5 to 34.45 Å depending on composition.

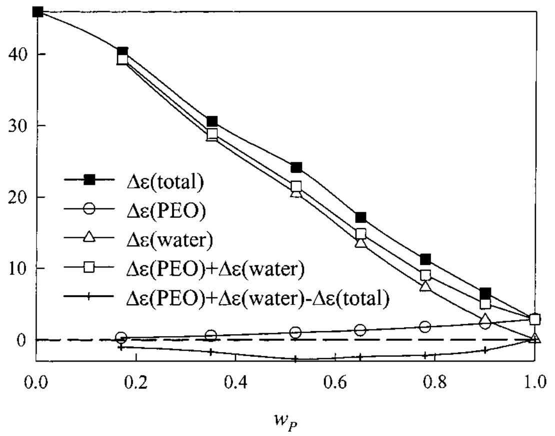

Figure 1. Dielectric strength $\Delta\epsilon$ due to dipole relaxation for PEO/water solutions (total), for collective PEO relaxation (PEO), and for collective water relaxation (water).

Results and Discussion

The frequency dependent dielectric constant ϵ' and dielectric loss ϵ'' normalized by the dielectric strength $\Delta\epsilon$ are obtained through the Fourier transform of the dipole moment autocorrelation function $P_1(t)$ and are given by[22]

$$\frac{\epsilon' + i\epsilon''}{\Delta\epsilon} = 1 - i\omega\int_0^\infty P_1(t)\exp(-i\omega t)\,dt \qquad (1)$$

where

$$P_1(t) = \frac{\langle \mathbf{M}(0)\mathbf{M}(t)\rangle - \langle \mathbf{M}(0)\rangle^2}{\langle \mathbf{M}(0)\mathbf{M}(0)\rangle - \langle \mathbf{M}(0)\rangle^2} \qquad (2)$$

and

$$\Delta\epsilon = \frac{4\pi\langle \mathbf{M}^2\rangle}{3Vk_BT} \qquad (3)$$

$\mathbf{M}(t)$ is the dipole moment of the simulation box at time t, V is the volume of the simulation box, k_B is the Boltzmann constant, T is the temperature, and $\langle\ \rangle$ denotes ensemble average. Note that dipole correlation function involves the average of the correlations between the dipole of a molecule at times t and 0 and correlations with the dipoles of its neighbor molecules. In this contribution, we monitored the dielectic relaxation of the whole simulation box and the contributions to this process due to the collective relaxation of all water molecules and the collective relaxation of all PEO molecules. In these cases $\mathbf{M}(t)$ is given by the collective dipole moment of the water molecules and PEO molecules, respectively. The strength of the dielectric process $\Delta\epsilon$ due to fluctuations of the simulation box dipole moment,[23,24] the collective dipole moment of all water molecules, and the collective dipole moment of all PEO molecules is shown as a function of polymer concentration in Figure 1. The relaxation strength for the solution, $\Delta\epsilon$(total), shows an almost linear drop with

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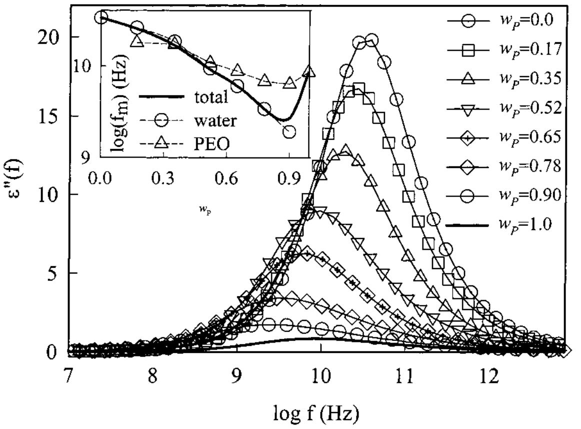

Figure 2. Dielectric loss for PEO/water solutions. The inset shows the concentration dependence of the maximum loss frequency for PEO/water solutions (total) as well as contributions from PEO and water.

increasing polymer weight fraction in agreement with time domain reflectometry experiments.[11] Due to the much larger dielectric constant of pure water compared to pure PEO, the water contribution dominates the dielectric relaxation process in PEO/water solutions for $w_P < 0.9$. For very high PEO concentrations ($w_P > 0.9$) contributions from water and PEO become comparable. Figure 1 shows that $\Delta\epsilon(\text{water}) + \Delta\epsilon(\text{PEO})$ deviates only slightly from $\Delta\epsilon(\text{total})$ with the largest deviation observed at $w_P = 0.52$, where the number of water/PEO contacts is the greatest. Due to the small deviation of $\Delta\epsilon(\text{water}) + \Delta\epsilon(\text{PEO})$ from $\Delta\epsilon(\text{total})$ the splitting of the dielectric relaxation of PEO/solutions into contributions from collective relaxation due to water and collective relaxation due to PEO is a reasonable approximation that we will utilize in the analysis of the dielectric loss spectra.

The dielectric loss spectra due to relaxation of the simulation box dipole moment, the collective dipole moment of all water molecules and all PEO molecules were calculated using eqs 1 and 2, where the decay of the dipole moment autocorrelation functions $P_1(t)$ from 0.95 to 0.04 was represented by the Kohlrausch−Williams−Watts (KWW) expression given as

$$P_{\text{KWW}}(t) = \exp[-(t/\tau)^{\beta}] \tag{4}$$

The resulting KWW fits were used in the Fourier transform in order to obtain the frequency dependent dielectric loss using eq 1. Dielectric loss for the PEO/water solutions is shown in Figure 2. In agreement with the experimental data,[11] the maximum loss frequency f_m(total) for the PEO/water solutions decreases with decreasing polymer weight fraction from $w_P = 1.0$ to $w_p = 0.90$ and then increases with further dilution, thus exhibiting a minimum at $w_P = 0.90$. In accord with our conclusions that water relaxation dominates the dielectric relaxation of PEO/water solutions for $w_P < 0.9$, f_m from water relaxation coincides with that of the PEO/water solutions for $w_P < 0.9$ as shown in the inset in Figure 2. The maximum loss frequency due to PEO relaxation is significantly different from that of water, being lower than that for water for $w_P < 0.35$ and higher for $w_P > 0.35$, indicating that the polymer collective dipole reorientation is slower than that of water for $w_P < 0.35$ and faster for $w_P > 0.35$. It is also interesting that the stretched exponential parameter β extracted from KWW fits to $P_1(t)$ exhibited a minimum at $w_P = 0.9$ for total PEO/water dipole relaxation and PEO collective dipole relaxation but showed a monotonic decrease for collective dipole water relaxation with increasing PEO concentration.

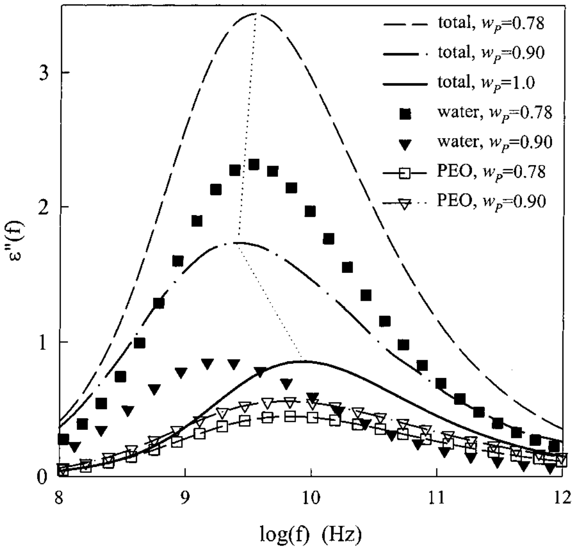

Figure 3. Dielectric loss spectra of PEO/water solutions (total) as well as contributions from PEO and water.

Now we will focus on the origin of the minimum in f_m at $w_P \approx 0.9$. Figure 3 shows the dielectric loss in PEO/water solutions as a function of frequency for $w_P = 0.78$, 0.9, and 1.0 as well as the contributions to the loss from water and PEO. At $w_P = 0.78$, f_m for the PEO/water solution coincides with that of water due to the relatively small contribution from PEO. At $w_P = 0.90$, contributions from water and PEO are very broad and comparable in magnitude, with water relaxation being slower and PEO relaxation being faster than that of the solutions. Figure 3 reveals that shift of f_m for the solution to lower frequency upon increasing polymer weight fraction from 0.78 to 0.9 is due to slowing down of water relaxation, not the PEO relaxation, as the PEO relaxation changes only slightly with increasing polymer concentration in this range. The shift of the f_m for the solution to higher frequency with further increase of polymer concentration from $w_P = 0.9$ to 1.0 is associated with a decrease in the contribution of water, which in this composition range has a much slower relaxation than PEO, and not with the speeding up of PEO dynamics upon increase of polymer concentration from $w_P = 0.9{-}1.0$ as a shift of f_m for the PEO contribution for this change in composition is much smaller than the shift of f_m(total).

The question remains as to why water relaxation slows so severely with increasing PEO concentration (see inset of Figure 2). In our recent paper dealing with water translational and rotational dynamics in PEO/water solutions from MD simulations,[18] we found that the slowing of water dynamics with increasing polymer concentration is due to (a) the correlation of the dynamics of water involved in hydration of PEO with PEO dynamics—the fraction of such "bound" water increases with increasing polymer concentration, (b) the disappearance of "free" water with bulk water-like dynamics with increasing polymer concentration, and (c) an increase in the fraction of water that forms multiple hydrogen bonds with PEO with increasing polymer concentration. Figure 4 shows the maximum loss fre-

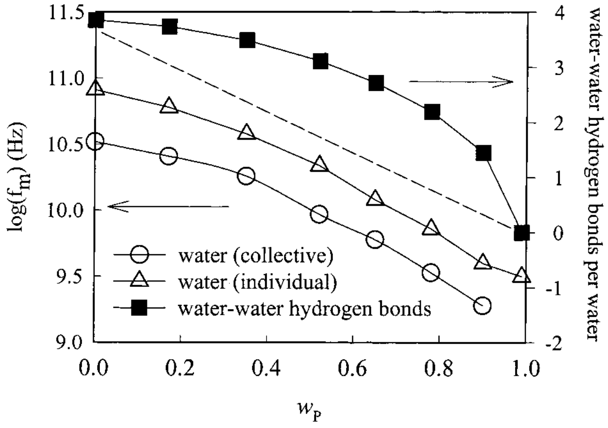

Figure 4. Concentration dependence of the maximum loss frequency fm for collective relaxation of water and for individual water molecule relaxation in PEO/water solutions. The number of water−water hydrogen bonds per water molecule is also shown. The dashed line indicates the expected number of hydrogen bonds per water molecule in the case of random mixing of PEO and water.

quency determined from the dipolar reorientation of individual water molecules. As expected from the composition dependence of the rotational relaxation times for water in PEO/water solutions,[18] f_m for individual water molecules decreases dramatically with increasing polymer concentration. Hence, the contribution of dipolar reorientation of individual water molecules to dielectric relaxation in PEO/water solutions slows with increasing polymer concentration for the reasons given above. However, as dielectric relaxation in pure water is highly cooperative,[25] the relaxation behavior of individual water molecules likely provides an incomplete picture of water relaxation in PEO/water solutions. Figure 4 also shows f_m for collective water motion, i.e., the contribution of water to the dielectric relaxation of the solution. In pure water, the cooperative nature of water motion is reflected in the $^1/_2$ order of magnitude decrease in f_m compared to the relaxation of individual water molecules. Interestingly, this difference remains constant in the PEO/water solutions throughout the entire composition range investigated, indicating that even in highly concentrated solutions with relatively little water, the water dynamics remain highly cooperative. This is a consequence of strong water clustering in concentrated PEO/water solutions[15] which is illustrated in Figure 4. Here, the number of water−water hydrogen bonds from our MD simulations is much higher in concentrated solutions than expected from random mixing of PEO and water.

Conclusions

Consistent with experimental observations, MD simulations of PEO/water solutions reveal that the maximum dielectric loss shifts to lower frequency with initial addition of water to PEO melts, with the lowest frequency occurring around $w_P \approx 0.90$. This initial decrease in the maximum loss frequency is attributed to the increasing contribution of water to the dielectric relaxation of the solution with increasing water content, as water in this composition range exhibits much slower dielectric relaxation than PEO. Upon further dilution beyond $w_P \approx 0.90$, the maximum loss frequency shifts to higher frequency due to decreasing water rotational relaxation times. Finally, highly cooperative dielectric relaxation of water is seen over the entire range of solution compositions investigated, indicative of strong water clustering at high polymer concentrations.

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