

Molecular Dynamics Simulations of Atomistic Hydration Structures of Poly(vinyl methyl ether)^{*}

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Abstract Molecular dynamics simulations have been performed on the aqueous solutions of poly(vinyl methyl ether) (PVME) at various concentrations. Both radial and spatial distribution functions are used to investigate the detailed hydration structures. The structures of water are found to get increasingly concentrated when polymers are introduced and the water motions are severely hindered by the polymer matrix. At low concentrations, larger populations of tt conformers in meso dyads than those at higher concentrations are found and this phenomenon is believed to be due to the increasing in bonding of water molecule to two ether oxygens in meso dyad. At higher concentrations, the size and conformations of polymers are quite similar to those in bulk. A transition of hydrogen bond fractions between PVME and water at around the concentration of 0.3 is observed and this value is perfectly in agreement with the results of conformational analysis and Raman spectra. Second neighbor hydrogen bond statistics revealed the domination of complicated hydrogen bond networks at low concentrations, but single hydrogen bonds as well as isolated clusters composed of 2–4 water molecules are usual around each polymer repeat unit.

Keywords: Molecular dynamics; Poly(vinyl methyl ether); Solvation structure; Hydrogen bonds.

INTRODUCTION

Aqueous solutions of poly(vinyl methyl ether) (PVME) exhibit lower critical solution temperature (LCST) miscibility behavior with moderate critical solution temperatures around 35–37 °C^[1–3]. The polymer dissolves below this temperature but phase separates when heated. In common cases, the LCST behaviors of aqueous polymer solutions can experimentally be sorted into three types^[2, 4]: type I represents the classical Flory-Huggins (FH) phase behavior, whose liquid-liquid phase separation critical composition shifts towards lower polymer concentrations for longer polymers; while the critical composition of type II hardly changes even for polymers with infinite molar masses; the LCST curves of type III are bimodal and have two stable critical compositions, one at lower polymer concentration (type I) and the other at higher polymer concentration (type II). The phase behavior of the PVME/H₂O system belongs to type III at physiological temperatures^[2].

This bimodal feature of the atypical phase behavior should, from the atomistic point of view, originate from the special hydrophilic and hydrophobic interactions between water and PVME^[3, 5]. The hydrophilic sites (ether oxygens) stabilize the aqueous solution by forming hydrogen bonds (HB) with neighboring water molecules

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while the hydrophobic groups (particularly the methyl groups due to the polarization of ether oxygens) destabilize the solution by altering the normal hydrogen bond network structure of water close to the polymer chains. The resulting structures of water around the hydrophobic groups were referred to as the “icebergs” by Nemethy and Scheraga^[6], and also by Frank and Evans^[7]. These two interactions compete with each other with increasing temperature until phase transition occurs^[3]. Wu *et al.* also utilized FTIR spectroscopy to investigate the microdynamics mechanism of the PVME aqueous solution, and they found the hydrogen bonds between hydrophilic groups and water and the hydration interactions between hydrophobic groups and water are completely reversible^[5].

There have been extensive investigations^[1, 3–5, 8–16] on the non-classical phase behavior and the above mentioned two sorts of interactions in the PVME/H₂O system. Basing on the changes in the near-infrared and calorimetric parameters observed with the variation of concentration, Maeda^[3, 10] proposed that an average of 2.7 water molecules per chain repeat unit in PVME solutions formed stable molecular complex through hydrogen bonding to the ether oxygens while additional 2.3 water molecules formed “icebergs” around the methyl groups whereas, over 5 water molecules were “free”, namely they had nearly no interaction with the polymer. Nies *et al.*^[1, 4, 14] concluded that experimental data from small angle neutron scattering did not support the existence of a stable molecular complex as the mixtures exhibited Ornstein-Zernike-like composition fluctuations even at the temperature as low as 10 °C. The bimodal LCST phase behavior of the PVME/H₂O system was also predicted, by way of the Wertheim Lattice Thermodynamics Perturbation Theory (Wertheim-LTPT), together with two adjacent narrow upper critical solution temperatures (UCST) miscibility gaps at low temperature, and these results were in agreement with experimental observations. The predicted solid-liquid equilibrium of the solvent showed a pronounced drop in melting temperature at intermediate weight compositions of 40 wt%–70 wt%. This peculiar concentration dependence of the melting line of water provided a new explanation for the double melting endotherm observed in (MT) DSC rather than being linked to the melting of bound and free water, namely the formation of a stable intermolecular complex.

The phenomenological results from experiments and theoretical predictions could not provide detailed molecular insights into the observed anomalous phase behavior. In an earlier work from our group^[12] quantum mechanical (QM) calculations were utilized to investigate the interactions between the PVME model compound and clusters of 2–5 water molecules, and as a result, the detailed molecular packing structures with relatively lower energies were obtained. The most stable configurations obtained were those with single HBs for clusters with not more than 3 water molecules and those with double HBs for clusters with more than 3 water molecules. The HBs between water and the ether oxygens were proved to be stronger than those between waters, namely these HBs are shorter in length and lower in energy. The hydrophobic interactions, called “QHBs” (quasi-hydrogen bonds), were found to coexist and associate with the HBs in many of those configurations. Different hydration features and mechanisms were analyzed and from the results an uneven distribution of water adsorption on the polymer was found to be preferred. It was also suggested that an average of 1.5 water molecules per repeat unit were required if all units of the polymer have to bound with water.

Despite the fact that the detailed configurations of possible packing structures can be successfully derived, QM calculations are still unable to describe the influence of polymer chain connectivity and conformation on the hydration structures. With the fast development of computational capabilities, atomistic molecular dynamics (MD) simulations have been extensively used to investigate the aqueous solutions of organic compounds, such as alcohols^[17], Urea^[18], amides^[19] and dimethylsulfoxide^[20]. Tamai and Nakanishi^[8] utilized the AMBER/OPLS force field^[21] and SPC/E water model^[22] to simulate the hydrogel model structures of poly(vinyl alcohol) (PVA), PVME and poly(*N*-isopropylacrylamide) (PNiPAM). It was found in the hydrophilic regions, the average number of hydrogen bonds between water molecules was smaller by 1.0–1.9 than those in pure water, and the defects of water-water hydrogen bonds were completely compensated by the water-polymer HBs for PVA but not for PVME and PNiPAM. On the other hand, in the hydrophobic regions, the average number of HB between water molecules was only slightly lower than those in pure water, the water-water HBs were stabilized in the hydrophobic regions especially for PVME and PNiPAM, and this was deemed to be due to the hydrophobic

hydration effects. It was also found that in the regions out of the first hydration shell, the HB numbers were not at all influenced by the polymer matrix. In their simulations, the stability of HBs was much more enhanced in the systems with lower water contents than those with more water, and this phenomenon was attributed to the constraints on the mutual orientation of water and polar groups imposed by the hydrophobic side group at higher polymer concentrations. But in their simulations, the concentration dependence of the hydration structures of PVME was not fully described.

In the present work, MD simulations have been performed on the aqueous solutions of PVME at concentrations varying from 0 wt% to 100 wt%. The OPLS-AA force field^[23, 24] and the TIP4P water model^[25] are used, for TIP4P is the only one with a realistic dimer structure and its quadrupole is the most realistic among the most frequently used water models^[26–28]. In addition, the most recent OPLS-AA force field parameters have been optimized with the TIP4P water model for better description of the interactions between water and organic substances^[27].

METHODS

Molecular Models and Force Field

Classical molecular dynamics simulations of aqueous solutions of PVME were carried out using the GROMACS simulation package^[29] with the OPLS-AA force field and the TIP4P water model. The potential functions adopt the form

$$V = \frac{1}{2}k_b(l-l_0)^2 + \frac{1}{2}k_\theta(\theta-\theta_0)^2 + \sum_{n=0}^5 C_n \cos^n(\phi) + 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}, \quad (1)$$

in which the former two terms represent the harmonic vibrations of bond lengths and bond angles, respectively; The third term stands for the dihedral potentials, whose OPLS parameters are translated into the Ryckaert-Bellemans^[30] type in GROMACS; The latter two are non-bonded interactions including the Lennard-Jones (L-J 12-6) and the electrostatic interactions. Table 1 lists the diagonal non-bonded parameters respectively for PVME and the TIP4P water, in which ε and σ are the well depth and collision diameter for the L-J 12-6 interaction, q is the polar charge, and m is the atomic mass. The standard combination rules^[24] are used for the off diagonal non-bonded atomic pairs

$$A_{ij} = \sqrt{A_i A_j}, C_{ij} = \sqrt{C_i C_j} \quad (2)$$

where $A_i = 4\varepsilon_i\sigma_i^{12}$ and $C_i = 4\varepsilon_i\sigma_i^6$. Intra-molecular interactions between all pairs of atoms separated by more than three bonds are regarded as ordinary non-bonded interactions, while the 1–4 interactions are monitored by both the dihedral potentials and the ordinary non-bonded interactions scaled by 0.5^[24].

Table 1. Non-bonded potential parameters for PVME and the TIP4P water model

Atom	ε (kJ/mol)	σ (nm)	q
PVME ^a			
C ₁	0.276	0.350	−0.12 (−0.18 ^b)
C ₂	0.276	0.350	0.17 (0.14 ^b)
C ₃	0.276	0.350	0.11
O _p	0.586	0.290	−0.4
H	0.126	0.250	0.06 (0.03 ^c)
TIP4P			
O _w	0.649	0.315	0.00
H _w	0.000	0.000	0.52
M _w ^d	0.000	0.000	−1.04

^a C₁ and C₂ are backbone carbons and C₂ connects with the side group; ^b Charges for carbons at chain ends;

^c Charge for hydrogens bonded to the carbon next to O_p; ^d The dummy atom in the TIP4P water model

Simulation Details

All PVME chains used in the current study contain 44 backbone carbons and all repeat units are connected head to tail. The atactic chains were generated according to the Monte Carlo method described below with steric ratio meso:racemic ($m:r$) = 1:1. First, 1000 configurations of chains, each with 10000 repeat units, are generated as prototypes (here we assume that so many polymer chains with such length are sufficient for the generation of the most probable steric sequences) with the specified steric ratio using the Monte Carlo method. The fractions of the continuous sequences of stereo dyads (such as mr , $mmrr$, ...) are counted, for efficiency only sequences with utmost 4 dyads are counted. The same method is used for the generation of 1000 chains with 44 backbone carbons, their fractions of the continuous sequences of stereo dyads are compared with those of the prototypes by the root mean squared deviation (RMSD), and the chain with the smallest RMSD (below 0.05) will be regarded as the most probable configuration at the limited chain length. Different numbers of such chains were generated using this method for systems at different concentrations, and each chain had different stereo sequences. Table 2 lists the number of PVME chains n_p , number of water molecules n_w , the number of water molecules each polymer repeat unit can ideally be assigned n_w/n_{mon} and the weight concentration c_p of each system.

Table 2. Simulated samples

n_p	n_w	n_w/n_{mon}	c_p (wt%)
0	2218	/	0
1	2060	93.6	0.03
4	1939	22.0	0.13
8	1585	9.0	0.26
12	1385	5.2	0.38
16	987	2.8	0.54
24	588	1.1	0.74
30	341	0.5	0.86
40	0	0	1.00

The initial amorphous structures were built using the Amorphous Builder in Accelrys Materials Studio, 20 structures were built for each system and the ones with the lowest potential energies were chosen for subsequent procedures. These chosen structures were then “solvated” in water using the “genbox” command in GROMACS and each system underwent hundreds of steps of energy minimization with the conjugate gradient (CG) method. The constant particle, constant pressure and constant temperature (NPT) MD runs were then carried out for 4–10 ns depending on the concentrations of the solution systems, and the equilibrium was monitored by the potential energies, densities, hydrogen bond numbers and polymer conformations. The canonical ensemble (NVT) sampling MD simulations were followed and extended for another 20 ns. The temperatures of all solution systems was maintained at 300 K with the Nose-Hoover^[31, 32] temperature coupling method, and the pressure was isotropically coupled to 0.1 MPa with the Parrinello-Rahman^[33] pressure coupling method. The bulk PVME system was initially equilibrated at 600 K under NPT to reach the equilibrium concentration. Then an annealing process of 3 ns was used to bring the temperature down to 300 K under the NPT ensemble. Further, another 10 ns further equilibration at 300 K was performed before NVT production runs. A cutoff of 1.2 nm was used for the van der Waals interactions. The Particle Mesh Ewald (PME) method^[34, 35] was used for long range electrostatic corrections and the long range dispersion corrections were also implemented for both energy and pressure. All bonds in polymers were constraint with the Lincs method^[36] and the rigid structure of water molecules was maintained with the Settle method^[37] during all MD simulations. A time step of 1 fs was used and the trajectories were recorded for every 1 ps.

Radial and Spatial Distribution Functions

The structure of liquid can often be well characterized by the radial distribution function (RDF) of atomic density,

$$g_{AB}(r) = \rho_B(r) / \langle \rho_B \rangle_{\text{local}} \quad (3)$$

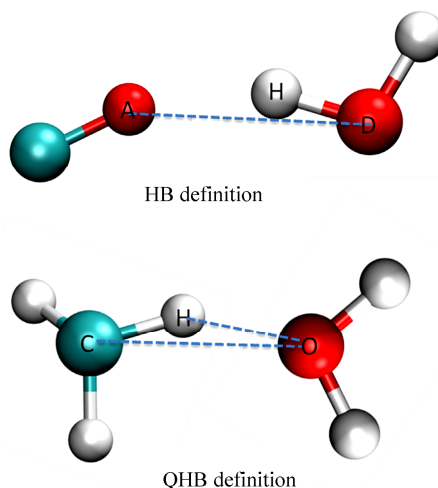
which represents the probability of finding particle B within the range $r + dr$ around particle A. The spatial distribution function (SDF) takes into account both radial and angular correlations between particles,

$$g_{AB}(\vec{r}) = \rho_B(\vec{r}) / \langle \rho_B \rangle_{\text{local}} \quad (4)$$

and allows three dimensional (3D) visualization of the local atomic densities, thus it provides much more detailed information on the local structural environment than RDF does. The visualization of SDF is often described by iso-surfaces, which show the distribution of particles with densities several times that of average around a reference atomic group. To calculate SDF, a local coordinate system has to be defined with a reference structure. For water, the local coordinate is defined so that oxygen remains at the origin and the whole molecule lies in the XY plane. For PVME repeat unit, the ether oxygen is set as the origin and the plane formed by the oxygen and the two connected carbons is regarded as the reference, so that the backbone configurations and conformations do not influence this local coordinate system.

Definitions for HB and QHB

The formation of a hydrogen bond needs an electronegative proton donor (D) and an acceptor (A) with at least one lone pair of electrons. The atomic pairs in our simulations are considered to be hydrogen bonded according to the Luzar and Chandler^[38, 39] criteria that if the distance between D and A is within 0.35 nm, and simultaneously the angle between the DA axis and one of the DH bonds is smaller than 30°. For QHBs, there exist various definitions in the literature and our definition refers to that of Zhang *et al.*^[19], which was based on the van der Waals diameter^[40] and quantum mechanics calculations^[12]. The QHBs between the methyl groups and water molecules are defined with the distance between the methyl carbon (C) and water oxygen (O), $r(\text{C} \cdots \text{O}) < 0.372$ nm and the angle $\text{C} \cdots \text{H} \cdots \text{O} > 150^\circ$. The definitions for HB and QHB are sketched in Scheme 1 for clarity, in which the white beads are hydrogen atoms (H) and the red beads are oxygen atoms (O) and the cyan beads are carbon atoms (C).



Scheme 1 The definitions of HB and QHB

The red beads are oxygen atoms, the cyan ones are carbon atoms and the white ones are hydrogen atoms as indicated. The denoted A and D on the hydrogen bond definitions designate the proton acceptor and proton donor, respectively

Diffusion Coefficient of Water

The diffusion of water can be estimated from the mean square displacement (MSD) within a time period of t

$$D = \lim_{t \rightarrow \infty} \langle |r(t) - r(0)|^2 \rangle / 6t \quad (5)$$

The experimental^[41] diffusion coefficient of pure water is $(2.11\text{--}2.66) \times 10^{-5} \text{ cm}^2/\text{s}$ at 298 K. The calculated value at 300 K is $3.78 \times 10^{-5} \text{ cm}^2/\text{s}$, which is slightly larger than the experimental result but still corresponds well with the simulation values^[27] ($3.73 \times 10^{-5} \text{ cm}^2/\text{s}$ at 298 K) using the same water model.

Measurements of the PVME Raman Spectra

Poly(vinyl methyl ether) with $M_w = 60.5 \text{ kg/mol}$ and $M_w/M_n = 3$ was synthesized in the group of Professor Eric Nies in the University of Leuven. Aqueous solutions with concentrations $c_p = 0.1, 0.3, 0.6$ and 0.8 as well as the bulk were prepared for use. The Raman spectra were recorded at room temperature using a JY-HR800 (JobinYvon) Raman micro spectrometer. A Nd:YAG laser (532 nm and 6 mW) was used as the excitation source. The Isotropic Raman scattering intensities were calculated from the parallel and perpendicular components of the experimentally measured Raman scattered light: $I_{//}(\nu)$ and $I_{\perp}(\nu)$.

$$I_{\text{iso}}(\nu) = I_{//}(\nu) - 4/3 I_{\perp}(\nu) \quad (6)$$

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%.

RESULTS AND DISCUSSION

Densities and Excess Volumes of Mixing

From NPT runs, the obtained equilibrium density of pure water ($0.993 \pm 0.006 \text{ g/cm}^3$) corresponds well with experimental results (about 0.997 g/cm^3). While the density of bulk PVME at 300 K is $(1.019 \pm 0.004) \text{ g/cm}^3$, slightly lower than the experimental value of 1.061 g/cm^3 ^[42]. This is probably caused by the relatively shorter chains simulated than used in the experiments^[43].

The binary mixtures exhibit strong non-ideal behavior as reflected by the excess specific volumes in Fig. 1. The values are calculated from the equilibrium densities of each solution system and those of pure water and bulk PVME. All excess specific volumes are negative and their standard deviations are smaller than the symbols shown in the Fig. 1. The largest excess specific volume is anticipated to be reached at $c_p = 0.5\text{--}0.7$, which corresponds well with the experimental values inferred by the Redlich-Kister^[44] polynomial^[13].

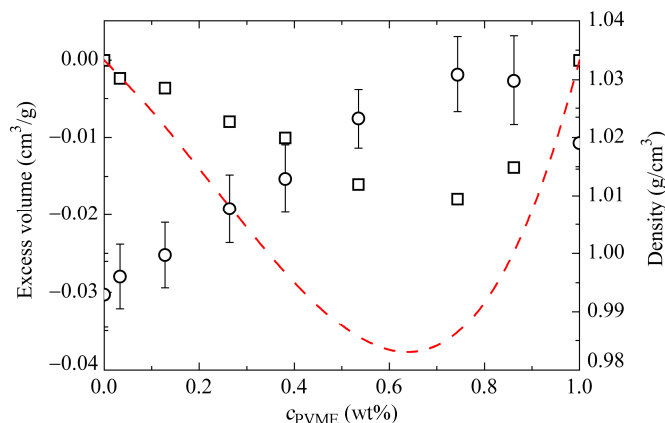


Fig. 1 Excess volumes ($\square$) and densities ($\circ$) obtained from NPT simulations at 300 K. The experimental excess volumes^[13] according to the Redlich-Kister polynomial^[44] are also plotted (...) for comparison. The densities correspond to the right y axis

Comparing with the experimental data in Fig. 1, all calculated excess specific volumes are smaller due to the conformations of the relatively short chains simulated. In aqueous polymer solutions, not only hard core volume packing and free volume effects are operational but also volume effects related to the directionality of the hydrogen bonds between water molecules and those between water molecules and PVME repeat units must

be considered^[13]. The conformations of the shorter chains simulated should in principle have led to the smaller excess volumes of mixing. Despite these differences, the simulated systems have in general well captured the essential features of PVME aqueous solutions.

Structure and Diffusion of Water in Solutions

Variation of local water structure with concentration

The results of RDF for atomic pairs O_w-O_w at all concentrations investigated are shown in Fig. 2. All RDFs have prominent first peaks at around 0.276 nm, and nearly no position changes are observed. The RDF of O_w-O_w for pure water (not plotted for clarity) is nearly identical with that for $c_p = 0.03$. All curves show clear peaks of HB, second neighbor HB and even third peaks of longer correlations, longer correlations are diminished because of the diffusion of water molecules. The near neighbor correlations show almost similar behavior for systems below $c_p = 0.6$, while in the water-poor mixtures namely $c_p = 0.74$ and 0.86 the $g(r)$ curves show sliding down beyond the second minimum. Together with the enhanced first and second peaks, these phenomena are deemed as the results from the association of water molecules as dimers or clusters^[45, 46], and such effects get stronger with the increase of concentration in these systems.

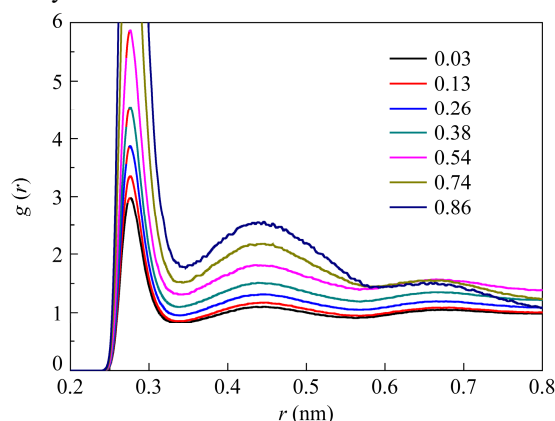


Fig. 2 Radial distribution functions of O_w-O_w for PVME solutions at the indicated concentrations

The SDFs in Fig. 3 provide more detailed and clearer manifests of the local water HB structures. The first neighbor HBs are characterized by the three density caps: two caps over the H atoms are due to proton accepting neighbors, and the single large density cap over the O atoms is due to proton donating neighbors. The density caps are plotted with the same iso-surface thresholds and the enhanced water-water correlations with concentration are clearly observed when more polymer chains are introduced. It is obviously shown in the Fig. 3 that the low concentration one has relatively thinner density caps while the high concentration one has thicker density caps. This indicates that in the high concentration, with small amount of water molecules, most are confined within the first neighbor shell of polymers, taking nearly all interaction configurations even with higher energies. Besides, in the low concentration, large amount of water molecules has huge interaction configurations to be selected according to lower energies, avoiding the small population configurations in the first neighbor shell.

Water diffusion in solutions

The mean square displacement curves of water molecules are plotted in double logarithmic scales in Fig. 4 for all systems including pure water, in which the linear function was also added for comparison. At low concentrations, these water molecules show diffusion behavior, for their MSDs show linear relation with time as compared with the green line. The slope of these MSD curves show monotonic decrease as the polymer concentration is increased, indicating stronger subdiffusive behaviors with concentration. At high concentrations, the MSD values are significantly smaller than those at lower concentrations, which suggest the possible presence

of polymer matrix significantly hindering the mobility of water molecules. The cages and HBs in polymers, discussed in the previous section, might have restricted the motion of these water molecules.

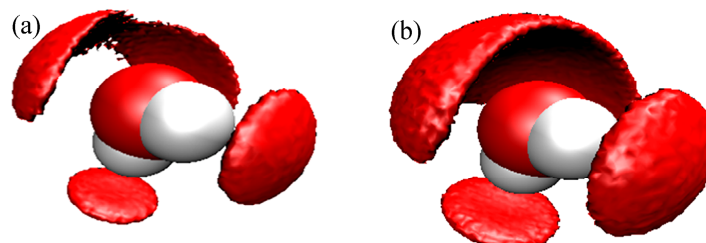


Fig. 3 SDF of local water density around water molecules for solutions with concentrations of (a) 0.13 and (b) 0.86 (Iso-surface thresholds are 4 for both)

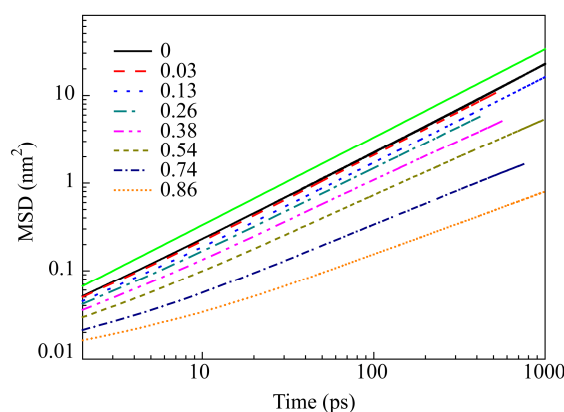


Fig. 4 Mean square displacement of water molecules at various concentrations. The green line is added for comparison with linear diffusion.

The Solvation Structures of the O_p and CH_3 Groups

For the investigation on the solvation structures of PVME repeat unit, the RDFs of atomic pairs O_p - O_w and C_3 - O_w at various concentrations were plotted and are shown in Fig. 5. With the increase of concentration, HBs between PVME and water also get increased beyond a concentration of 0.38. Only slight migration of the first peak is observed to increase from 0.269 nm to 0.273 nm (given in Fig. 6), which is smaller than that of O_w - O_w (see Fig. 2) which corresponds well with our previous quantum calculations^[12]. At higher concentrations, the HB having a relatively longer bond length is manifested by SDF for a concentration of 0.86 (Fig. 3) under confinement, taking the high energy configurations. While at low concentrations with abundant water molecules, the association between hydrophilic and hydrophobic interactions was found to shorten the HBs^[12]. But a small part of the ether oxygens have chances to form double hydrogen bonds, which makes the HBs longer and our later statistical results of HB will demonstrate that such double HBs are scarcely seen at all concentrations.

In addition, the first minima shift toward longer distances and the first peaks get broader at high concentrations, suggesting that there are changes of HB structures. The second peaks are much broader than the first ones at all concentrations, and their heights are even larger than those of the first peaks at lower concentrations. This indicates that the water molecules from the second hydration shell will form hydrogen bonds with the first shell water molecules, which have already donated their protons to the ether oxygen atoms in the polymer chains. But this is not necessarily the case as specific structures around adjacent atoms may also cause such well-defined peaks. Compared to the slight increase of peak positions of the O_p - O_w RDFs, the peaks of the C_3 - O_w RDFs decrease more significantly from 0.367 nm to 0.355 nm. These QHBs are much weaker than HBs, and the hydration effects will have much influence on their structures.

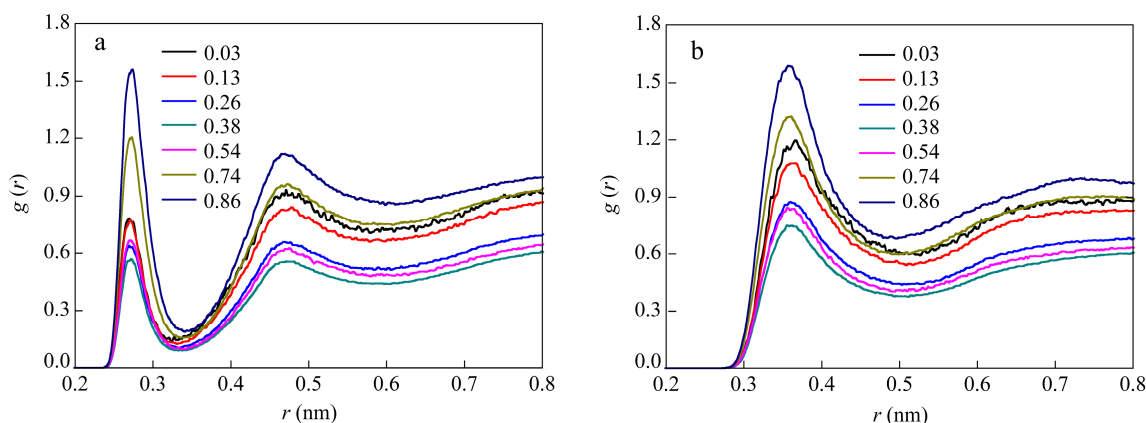


Fig. 5 Radial distribution functions of (a) O_p-O_w and (b) C_3-O_w at various concentrations

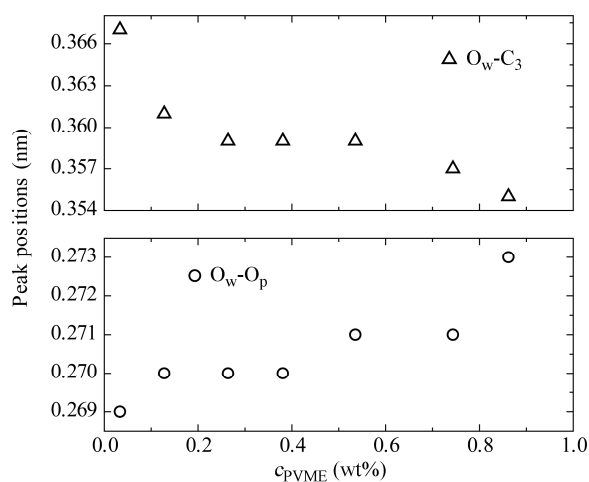


Fig. 6 Concentration dependence of RDF peak positions for O_w-O_p ($\circ$) and O_w-C_3 ($\triangle$)

For a clearer view of how water molecules are arranged around the PVME repeat units, SDF corresponding to the atomic pairs referred to above are plotted in Fig. 7. Only the SDF at the concentration of 0.54 is shown, for clear distinctions are not found at different concentrations since the peak height differences of $g(r)$ at other concentrations are much smaller than those of water as seen from comparisons between Fig. 5 and Fig. 2. With the polymer repeat unit as reference (C_1 is plotted just for reference), the density map of water around the repeat unit is shown. The iso-surface covering the reference ether oxygen represents the strong HBs between water molecules and the ether oxygens and such iso-surface corresponds to the first peak in Fig. 5(a). As for the second peaks in the O_p-O_w RDFs, there exit two sorts of interactions: the second neighbor HBs and the QHBs around the methyl group. It is also evident from Fig. 7 that the second neighbor HB iso-surface mixes with the QHBs, suggesting the cooperative association between HB and QHB, which results in complex water clusters around PVME. This result corresponds well with our previous quantum calculations^[12].

Polymer Backbone Conformations

The polymers in aqueous solutions often have significant conformational changes due to the specific hydrophilic and hydrophobic hydrations. As an overall estimate of the polymer conformations, the radii of gyrations of PVME in solutions are shown in Fig. 8. At low concentrations, the polymers adopt relatively extended conformations due to the specific hydrophilic and hydrophobic hydrations. With the increase of concentration, polymers aggregate and interpenetrate each other, and their sizes approach those in bulk.

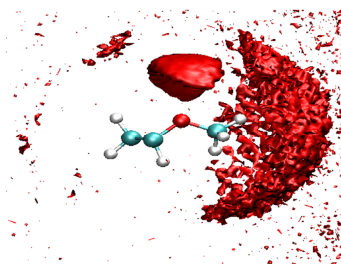


Fig. 7 SDF of water around PVME repeat unit with iso-surface threshold of 2 at the concentration of 0.54

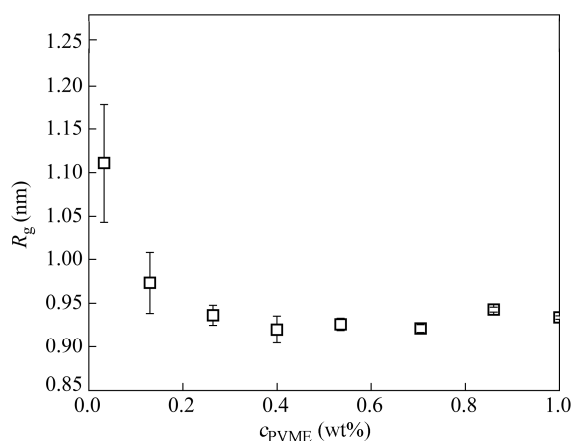


Fig. 8 Radius of gyration of PVME in solutions of various concentrations

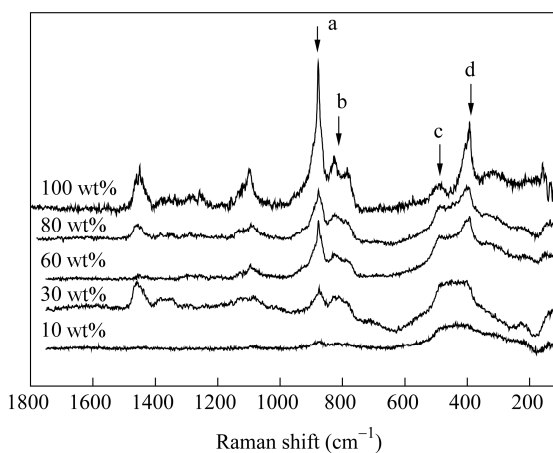


Fig. 9 The Raman spectra for PVME aqueous solutions of various concentrations

The Raman spectra of aq. PVME solutions of various concentrations are shown in Fig. 9. The peaks with most significant variations are denoted as a, b, c, d. Similar shapes of the peaks are observed for concentrations above 30 wt%, but for the spectra at low concentrations drastic differences are observed, the peaks of c and d level off and form plateaus. According to our previous interpretations^[12, 47, 48], the peaks of a and b are related to the stretching modes of C—C and C—O; while c and d are mainly caused by the bending modes. The bending modes of C—C—C are directly related to the backbone conformations and the spectra around 400–500 cm^{-1} have been regarded as the disordered longitudinal acoustic mode (D-LAM) regions which well represent the variations of the long sequence of PVME conformations^[47, 48]. As far as the radius of gyration is concerned, the Raman spectra are in good correspondence with our MD simulations.

In order to discover the detailed conformations of PVME in solutions, Figure 10 shows the fractions of the major isomeric dihedral pairs found for both meso and racemic dyads along the chains obtained in the simulation, and the ones with very small populations are not shown for clarity. For the meso dyads, the gt conformers are preferred and the drastic drop of tt conformers around the concentration of 0.3 are the most apparent. In the bulk state, the tt conformers in meso dyads are not at all preferred, which takes only ~5% in the conformer pairs in meso dyad. But in the hydration, the significant change of the tt conformer around 0.3 demonstrates that the hydration of PVME helps formation of the tt conformer through HB interaction of at least a water molecule bonding to two ether oxygens in meso dyads shown in Fig. 11. Compared with the meso dyads, the tt conformers are preferred in the racemic dyads, and the tt conformer pair show some increase when the concentration is above 0.3. In general, the polymer conformations are similar with those in bulk for solutions of high concentrations; but the conformations of dihedral pairs at low concentrations have more significant variations than those at high concentrations, and the conformations change at a critical concentration of 0.3. The

variation of this conformer change around the polymer concentration of 0.3 shows similar behavior of the Raman spectra, in which the emergence of peaks also occurs around this concentration.

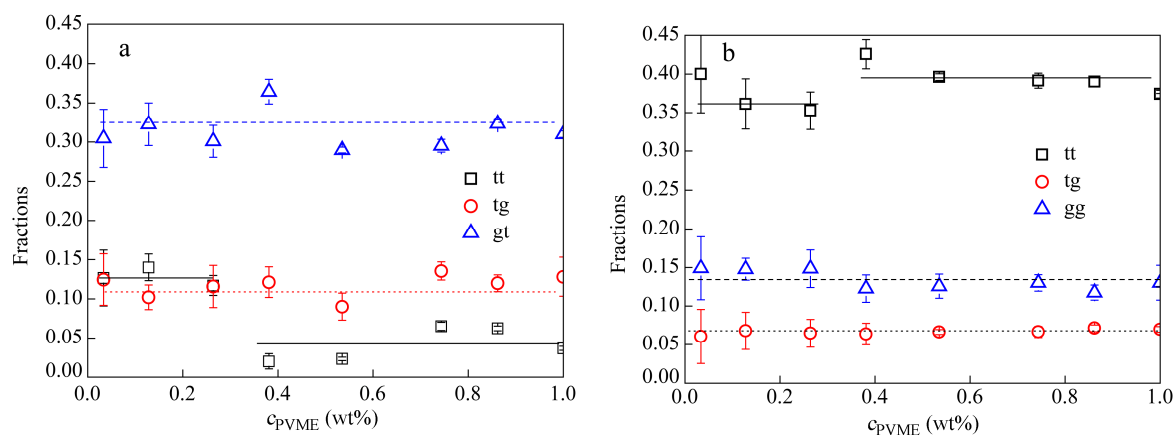


Fig. 10 Conformer fractions of dihedral pairs for (a) meso and (b) racemic dyads (The lines serve to guide the eye.)

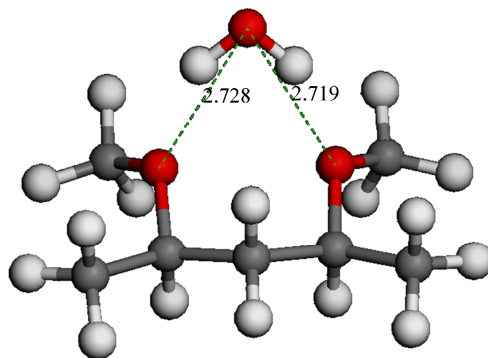


Fig. 11 A water molecule bonding to two ether oxygens in meso dyad

During the hydration of PVME, it has changes (1) in the radius of gyration, (2) in the conformational distribution for the tt conformers, and (3) in the Raman spectral profiles of D-LAM. Obviously, the three changes are correlated. The increase in global size is due to the local conformational variation, which is predominated by the tt conformation. Geometrically, it is reasonable, because among the end-to-end distances (within four backbone bonds) of various conformation dyads, the tt conformation dyad has the longest end-to-end distance. It leads to local structure expansion and the global size increase eventually. D-LAM shows the conformational structure transition occurs accordingly.

HB and QHB Statistics

For aqueous solutions of small compounds, water should be meanly distributed around the solute and the structure of the solute should not have much difference, but for polymers, the local chain conformation changes upon solvation. For PVME, each repeat unit can only form at most two hydrogen bonds with water, and the hydrogen bonding in polymers should not be uniform along the chains. In order to get more quantitative picture of the solvation structures of PVME solutions, we have counted the fractions of units forming i ($i = 0, 1, 2$) HBs or QHBs according to the geometrical definitions defined in section "Definitions for HB and QHB".

Figure 12(a) presents the fractions of O_p with i ($i = 0, 1, 2$) HBs with water. At low concentrations, most of the ether oxygens (over 90%) are able to form HB with water, but even at the lowest concentration investigated, there still exist about 10% ether oxygens which are not able to form efficient HBs with water due to the close contacts between local chain segments caused by the flexibility of the polymer chains. With the increase of

concentration, the fraction of such HBs decreases drastically, which is, in our opinion, due greatly to the conformational change as mentioned in the previous section. The conformational changes will cause significant variations of the solvation structures as HBs or the association between HBs and QHBs. The transition at around 0.3 matched perfectly well with the results of conformational analysis and Raman spectra as previously discussed. The further decrease of HB fractions at higher concentration is conceptually attributed to the deficient number of water surrounding the polymer chains. Due to the existence of negative cooperativity effect^[49] for HBs, the fractions of repeat units with double HBs are very small, but still possess a transition around the concentration of 0.3. Moreover, in recent work^[4] measured the demixing enthalpy of the aqueous solutions of a mono-dispersed low molecular weight (about 140 backbone carbones) PVME utilizing modulated temperature differential scanning calorimetry (MTDSC), and found there also exists a transition around the concentration of 0.3. But their results level off at low concentrations and decrease linearly over 0.3.

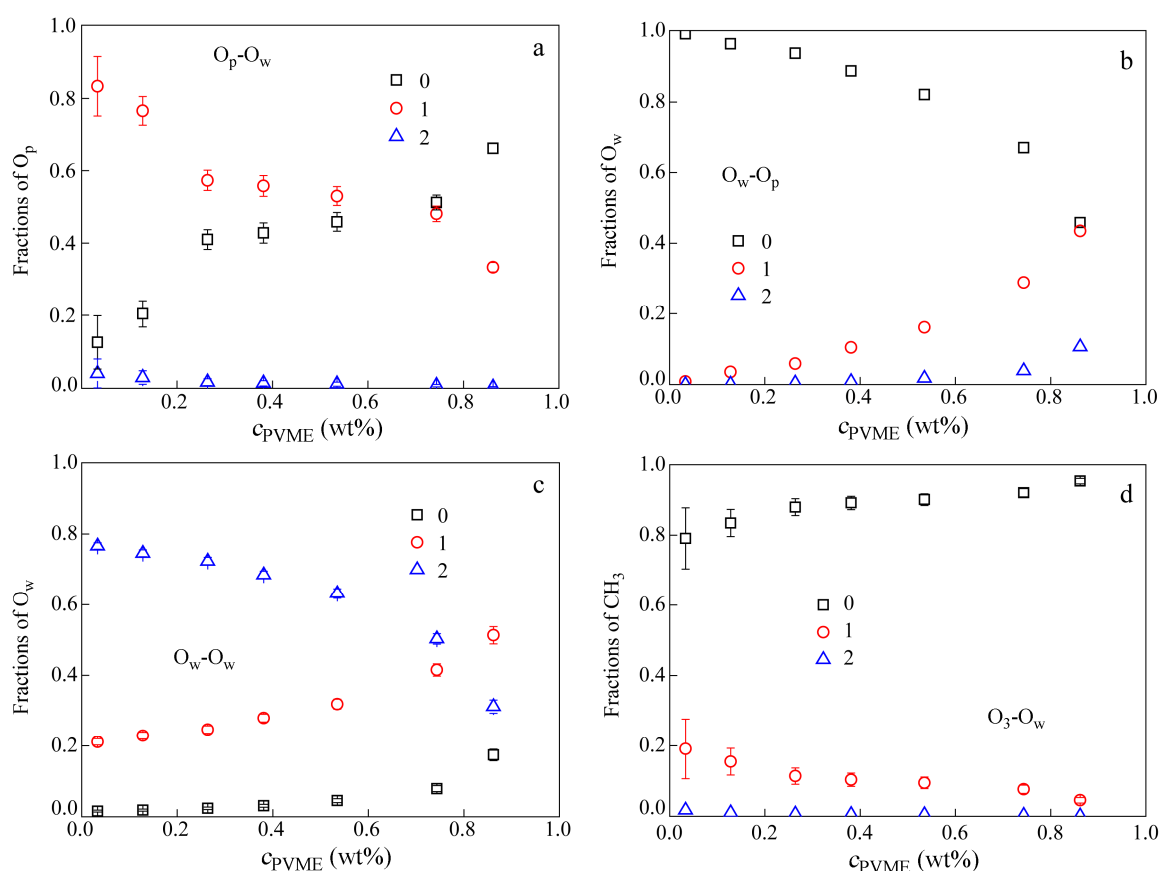


Fig. 12 (a) Fractions of O_p with i ($i = 0, 1, 2$) hydrogen bonds with water; (b) Fractions of O_w with i ($i = 0, 1, 2$) hydrogen bonds with PVME; (c) Fractions of O_w with i ($i = 0, 1, 2$) hydrogen bonds with water; (d) Fractions of C_3 with i ($i = 0, 1, 2$) QHBs with water

Figures 12(b) and 12(c) depict the fractions of O_w with i ($i = 0, 1, 2$) HBs with PVME and water respectively. With the increase of concentration, the fractions of HBs with PVME increase and at high concentrations significant amount of water has been observed to be hydrogen bonded to two polymer repeat units, which might be adjacent or from two different chains. Here, the numbers of double HBs have higher fractions at high concentrations. Water can serve both as acceptors and donors, but in Fig. 12(c) we just count those serve as donors or acceptors and thus the water molecules can also just form at most two HBs with water, so that they can be directly compared with those HBs between polymer and water. With the increase of

concentration, the fractions of water molecules that form only one HB with other water molecules increase while the fractions of those forming two HBs decrease, which indicates the severe interruption of normal water HB networks and the tendency to form isolated water clusters. Figure 12(d) describes the fractions of the CH₃ group with i ($i = 0, 1, 2$) QHBs with water, the fractions of QHBs are quite minor compared with those of HBs. The increased fraction of QHBs at low concentrations provides strong evidence that the association between HBs and QHBs has led to the increase of tt conformers in the meso dyads.

Cluster Analysis

The possible cluster structures with 1–5 water molecules around PVME repeat units have been surveyed with QM in our previous investigations^[12]. In this study we have taken into account the polymer chain connectivity and the dynamic features of real systems, the hydration structures might not well be completely the same with the cluster structures obtained in vacuum. Based on the statistical results in Fig. 12, we could make assumptions that all water molecules are within the clusters around the polymer, then at the concentration of 0.86 each repeat unit that has HB bonding with water can be assigned 1.56 water molecules, namely the clusters have on average 1.56 water molecules and this number is consistent with predictions (1.5) in our previous study^[12]. At low concentrations, the clusters could be assigned 2.77 and 5.18 water molecules at the concentrations of 0.74 and 0.54 respectively under the same assumption, thus at low concentrations there would be abundant water molecules except those in the clusters.

Through the RDFs and SDFs in previous sections, we have observed that around the polymer repeat units water molecules form at most two hydration shells. A representative snapshot of the HB bonded PVME-water cluster is shown in Fig. 13(a). Most ether oxygens form first shell HB with just one water molecule, namely very few form hydrogen bond with two water molecules as is the case for the negative cooperativity effect^[49]. As far as the second neighbor HB is concerned, some PVME repeat units form clusters with 2, 3 and 4 water molecules as noted by the circles, the oval-shaped circle designates the chain effect in HB between water molecules. The clusters inter-correlate with each other, forming relatively stable configurations.

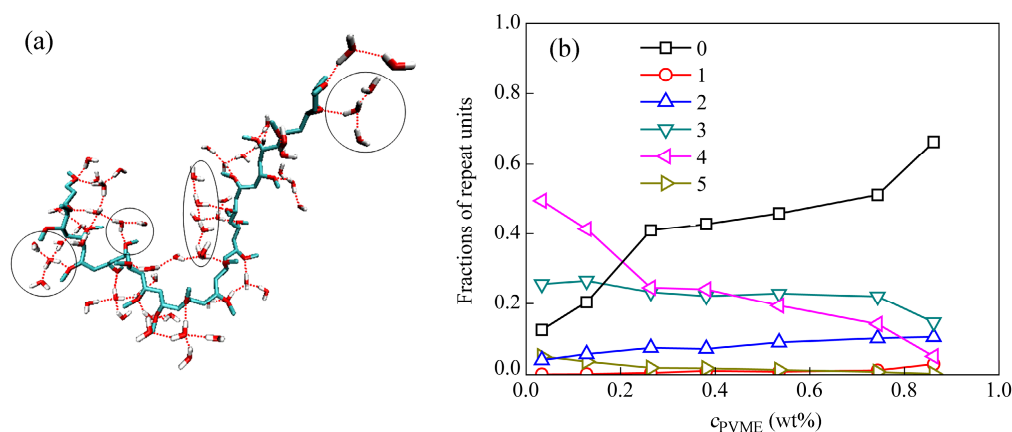


Fig. 13 (a) A representative snapshot of the HB bonded PVME-water cluster, the dotted lines represent the HBs; (b) Concentration dependence of the fractions of PVME repeat units with i ($i = 0-5$) water molecules in their surrounding clusters

The data for the squares are the same with those in Fig. 12(a). The lines serve to guide the eye.

We have also counted the fractions of repeat units with i ($i = 0-5$) water molecules which are hydrogen bonded to the first shell water molecules already donating their protons to the ether oxygen. These results are added to those shown in Fig. 12(a), and the resulting cluster size estimations are plotted against concentration in Fig. 13(b). Here, only clusters with no more than 5 water molecules are shown, because the fractions of clusters with more water molecules are negligibly small. At low concentrations, clusters with 4 water molecules take the

lead and in such structures all hydrogens and lone pairs of the first shell water molecules are hydrogen bonded and the entire structures form complicated 3D HB networks. The number of such structures decreases as the concentration increases due to the change of polymer conformations as demonstrated in section part "polymer backbone conformations", and they do not take overwhelming proportions at high concentrations. The fractions of clusters with 5 water molecules are barely perceivable at low concentrations and look very much similar with those of double HBs in Fig. 12(a), since only double HBs can form more than 3 second neighbor HBs. With increase of concentration, fractions of 3 water clusters show slight decrease while those of 2 water clusters obtained slight increase, at high concentrations the regional clusters composed of 2–4 water molecules are commonly seen, but in these systems most of the repeat units are wrapped in polymers due to inter-chain packing. We note that isolated HBs between water and ether oxygen are seen to take about 3% at the concentration of 0.86.

CONCLUSIONS

Through atomistic molecular dynamics simulations of the PVME solutions with various concentrations at 300 K, structure variations of water, polymer and their correlations were analyzed. The water structures get increasingly concentrated when polymers are introduced, and the water motions were severely hindered by the polymer matrix. The O_p-O_w RDFs show two well defined peaks, the first peaks represent the HBs between the polymer and water and they have shorter lengths than those between water molecules; the second peaks are much broader and are found to be contributed from both the second neighbor HBs and the QHBs around the CH_3 groups.

At low concentrations, the polymers adopt relatively extended conformations and the tt conformers in meso dyads undergo drastic decrease at the concentration of around 0.3, which is believed to be due to the increase of water molecule bonding to two ether oxygens in meso dyad at low concentrations; while other conformers have less apparent variations. At higher concentrations, the sizes and conformations are quite similar to those in bulk. And the structural variations of polymers are in qualitative agreement with the observations from the Raman spectra.

Solvation mechanisms different from small molecules are proposed for PVME solutions through the counting of HBs and QHBs. The transition of fractions of O_p with HBs with water at around 0.3 coincides perfectly well with the results of conformational analysis and Raman spectra, which indicates that the hydration structures are greatly influenced by the conformational changes in polymer. Fractions of water molecules hydrogen bonded to PVME increase with concentration and at high concentrations significant amount of water has been observed to be hydrogen bonded to two polymer repeat units which may be within the same chain or from two different chains.

The fractions of clusters around PVME repeat units with i ($i = 0-5$) water molecules are well designated and it is found that the 3D HB networks take the majority in solutions at low concentrations, and regional clusters composed of 2–4 water molecules are common and single isolated HBs between water and ether oxygens are also seen at high concentrations.

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