9548 *J. Am. Chem. Soc.* **2000,** *122,* 9548−9549

Conformations and Chain Dimensions of Poly(ethylene oxide) in Aqueous Solution: A Molecular Dynamics Simulation Study

Grant D. Smith,* Dmitry Bedrov, and Oleg Borodin

Department of Materials Science and Engineering
122 S. Central Campus Drive Rm. 304
University of Utah, Salt Lake City, Utah 84112

Received March 27, 2000

We have performed a molecular dynamics (MD) simulation study of the conformations and chain dimensions of poly(ethylene oxide) (PEO) in aqueous solution. Local conformations were found to depend on temperature and composition in agreement with spectroscopy; in particular, an increase in the C−C dihedral gauche (*g*) population with decreasing temperature and polymer concentration was observed. In concentrated solution chains were compact relative to the melt due to a decrease in the C−C *g* dihedral angle and an increase in C−C *g* population. With dilution chains became more extended. A rotational isomeric state (RIS) model was utilized to examine the influence of local conformations on the dimensions of ideal chains. The RIS chains did not extend with dilution, indicating that this effect is not attributable to changes in local conformations. Additionally, the dimensions of solution chains were found to depend only weakly on temperature despite changes in local conformations that significantly influence RIS chain dimensions. These differences between solution and ideal chains can be attributed to excluded volume and other chain extensional effects in solution.

PEO is an excellent candidate for experimental and simulation studies aimed at gaining a better understanding of polymer−water interactions. Our previous simulations[1] revealed that the conformations of glyme and diglyme depend strongly upon temperature and solution composition. To determine if the same behavior holds for longer PEO chains and to investigate the influence of local conformations on PEO chain dimensions we have performed MD simulations of HCH$_2$−O−CH$_2$H (PEO-530) using quantum chemistry based atomistic potentials shown to accurately reproduce the properties of PEO melts[2] and aqueous solutions of PEO oligomers.[1] NVT ensembles consisting of approximately 4000 atoms with at least eight polymer molecules were studied using methods described previously.[1] After equilibration, sampling runs of 10−40 ns (depending on temperature and composition) were performed for each system.

We classify the PEO local conformations (O−C−C−O dihedral sequences) *tgt* and *tgg* as hydrophilic since their populations increase with dilution and the remaining conformations as hydrophobic. Figure 1 shows the population of hydrophilic and hydrophobic conformers. Consistent with spectroscopy,[3] the PEO solutions were found to exhibit nearly the same compositional dependence of conformational populations as glyme and diglyme.[1] Also consistent with experiment,[4] the C−C *g* population is seen to increase with dilution; simulations reveal that this is accompanied by an increase in hydrophilic conformers. Note that the C−C *g* population does not correspond to the total hydrophilic conformer population as has been supposed in some models for PEO solutions[5] because the important tg^+g^- conformer is actually hydrophobic. Despite the increase in C−C *g* population with dilution, a nonnegligible trans population can be seen in good agreement with spectroscopic studies[3,4] and in stark contrast to previous simulations of PEO-660 in aqueous solution,[6] where C−C *t* conformations were completely absent at all temperatures investigated. The *tgt* conformer is intrinsically low in energy (comparable to the *ttt* conformer) and is stabilized in both the melt and solution by intermolecular polar interactions[1,2] (see Table 1). Consequently, the *tgt* conformer is strongly preferred in both the melt and solution resulting in a decreasing *tgt* population with increasing temperature and a corresponding increase in populations of all other conformers.

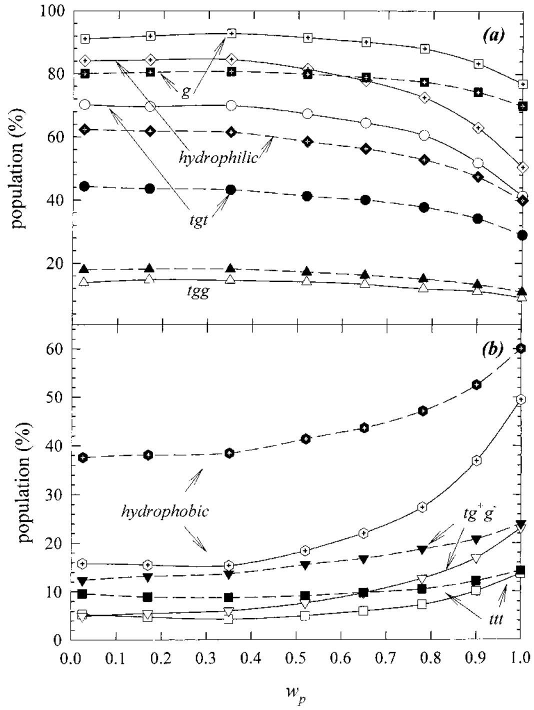

Figure 1. Population of important PEO (a) hydrophilic and (b) hydrophobic conformations in aqueous solution as a function of weight fraction polymer: solid lines, open symbols at 318 K; dashed lines, filled symbols at 450 K. Lines serve to guide the eye.

The dimensions of the PEO chains reflect the influence of water on local conformations and, since water is a good solvent for PEO, swelling effects with increasing dilution due to excluded volume. The mean-square radius of gyration $\langle R_g^2\rangle$ for PEO-530 chains as a function of composition is shown in Figure 2. For all temperatures, $\langle R_g^2\rangle$ increases with decreasing polymer concentration for $W_p < 0.5$. For semidilute solutions scaling laws predict[7] $\langle R_g^2(W_p)\rangle \sim W_p^{-m}$, where $m = {}^1/_4$. We find that for $W_p < 0.5$, $m \approx 0.10$. As the PEO-530 chains are too short for excluded volume effects on chain dimensions to be fully manifested, a reduce scaling exponent is reasonable.

To investigate the influence of the temperature and composition dependent local conformations on chain dimensions separately from excluded volume effects, we parametrized an RIS model for melt and solution chains based upon our third-order model for unperturbed PEO chains.[8] While the latter was parametrized to reproduce the local conformations of PEO oligomers as determined from gas-phase quantum chemistry calculations, the

---

[1] Bedrov, D.; Pekny, M.; Smith, G. D. *J. Phys. Chem. B.* **1998**, *102*, 996. Bedrov, D.; Smith, G. D. *J. Chem. Phys.* **1998**, *109*, 8118. Bedrov, D.; Smith, G. D. *J. Phys. Chem. B* **1999**, *103*, 3791.

[2] Smith, G. D.; Yoon, D. Y.; Jaffe, R. L.; Colby, R. H.; Krishnamoorti, R.; Fetters, L. J. *Macromolecules* **1996**, *29*, 3462.

[3] Matsuura, H.; Sagawa, T. *J. Mol. Liq.* **1995**, *65*, 313.

[4] Björling, M.; Karlström, G.; Linse, P. *J. Phys. Chem.* **1991**, *95*, 6707.

[5] Karlström, G. *J. Phys. Chem.* **1985**, *89*, 4962.

[6] Tasaki, K. *J. Am. Chem. Soc.* **1996**, *118*, 8459.

[7] Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannick, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.

[8] Smith, G. D.; Yoon, D. Y.; Jaffe, R. L. *Macromolecules* **1993**, *26*, 5213. For melt and solution calculations, a preexponential factor of 0.51 was used for the C−C *g* statistical weight. The corresponding reduced entropy is consistent with increased ordering resulting from the polar interactions in the condensed phases that reduce the energy of the C−C *g* state (see Table 1).

10.1021/ja001053j CCC: $19.00

Table 1. Principal RIS Energies (kcal/mol) for PEO Chains

interaction	unperturbed[a]	$W_p = 1.00$[b]	$W_p = 0.90$[c]	$W_p = 0.78$[c]	$W_p = 0.65$[c]	$W_p = 0.52$[c]	$W_p = 0.35$[c]	$W_p = 0.17$[c]	$W_p = 0.025$[c]
C−C *g*	0.10	−0.64	−0.94	−1.20	−1.35	−1.51	−1.54	−1.52	−1.49
C−O *g*	1.40	1.30	1.34	1.38	1.37	1.39	1.38	1.37	1.39
C−C−O g^+g^-	−1.30	−0.41	−0.09	0.12	0.31	0.48	0.60	0.66	0.69

[a] From ref 8. [b] From fit to melt chain local conformational populations. [c] From fit to solution chain local conformational populations

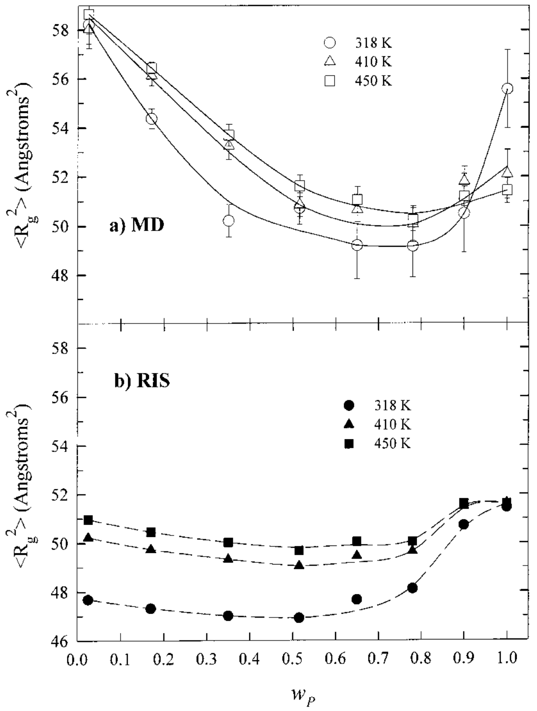

Figure 2. Radius of gyration of PEO chains in aqueous solution as a function of weight fraction polymer from (a) RIS predictions and (b) MD simulations. Lines serve to guide the eye.

melt and solution models were parametrized to reproduce local conformations determined from condensed-phase MD simulations. The RIS energies, which reflect the conformational energies of dihedrals or dihedral pairs relative to the *t* conformation, are given in Table 1. The large increase in *tgt* population in the melt over unperturbed chains[8] and the further increase in aqueous solution is reflected in the energy of the first-order C−C *g* energy; this polar arrangement is stabilized in the melt and solution by polar interactions. The reduction in the tg^+g^- population in the melt and further in solution is reflected in a dramatic increase in the energy of the second-order C−C−O interaction.

Using standard RIS techniques[8,9] $\langle R_g^2\rangle$ for the ideal RIS chains in the melt and solutions were calculated and are shown in Figures 2 and 3. Average bond lengths, valence angles, and dihedral angles were taken from melt and solution simulations. As with simulations, the RIS model predicts a reduction in chain dimension for the most concentrated solutions ($W_p > 0.7$) relative to the melt. This effect is small at higher temperature and is due primarily to a reduction in the equilibrium C−C *g* dihedral angle in solution relative to the melt. The reduction in chain dimensions for the ideal chains is greater at 318 K due the greater C−C *g* population. Both the RIS and MD solution chains show an increase in $\langle R_g^2\rangle$ with dilution for ($W_p < 0.5$). The effect for the ideal RIS chains reflects the influence of local conformations only, and is relatively small, and is due mainly to the decreasing C−C−O g^+g^- population with dilution. The expansion of the MD solution chains with dilution ($W_p < 0.5$) relative to RIS predictions reflects the excluded volume effects discussed above.

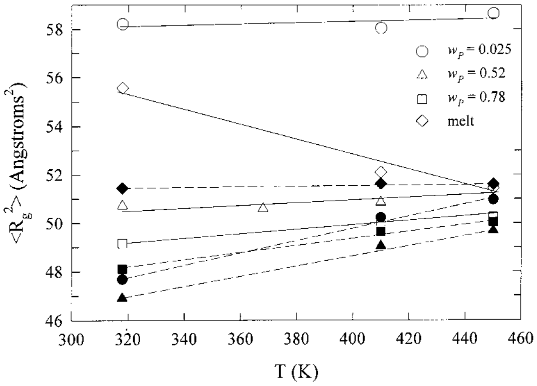

Figure 3. Radius of gyration of PEO chains in aqueous solution as a function of temperature: dashed lines, filled symbols indicate RIS predictions; solid lines, open symbols indicate MD simulations. Lines serve to guide the eye.

Despite large changes in local conformations with increasing temperature, particularly a decreasing C−C *g* and C−C−O g^+g^- population, that led to expansion of the RIS chains, MD solution chains show relatively weak temperature dependence as shown in Figure 3. For dilute solutions the reduced dependence of chain dimensions on temperature compared to RIS predictions may be due to decreasing solvent quality with increasing temperature;[10] swelling effects in the MD solution chains can be expected to be greatest at lower temperature. For the more concentrated solutions, where excluded volume effects are relatively unimportant, the reduced temperature dependence of the MD chain dimensions compared to ideal chains is consistent with the behavior of the melt chains. Figure 3 shows that the melt chains become more extended with decreasing temperature, an effect in agreement with SANS measurements[2] that is not reproduced in the ideal melt chains. Hence, intermolecular interactions in concentrated solution may mimic those seen in the melt, influencing chain dimensions in a fashion counter to changes engendered by the temperature-dependent local conformations.

Finally, it has been reported in a simulation study of a PEO-660 solution[6] and speculated in various experiment works[11] that PEO in aqueous solutions assumes extended *tgt* helical conformations reminiscent of the crystal. No direct evidence for these was found; rather it was assumed that the increase in C−C *g* and *tgt* conformer populations with decreasing temperature observed in solution must reflect formation of such sequences. We have examined our PEO solution and melt chains for evidence of C−C *g* (g^+ or g^-) sequences. For both melts and solutions at all temperatures the probability of long same-sign *g* sequences is not significantly greater than that found for Bernoulli (uncorrelated) chains. Hence, while simulations predict large C−C *g* and *tgt* populations in agreement with experiment, this does not translate into extended helical chain conformations. The extended helical conformations observed in previous simulations[6] are a result in part of a zero C−C *t* population, which is inconsistent with both experiment[3,4] and our simulations.

Acknowledgment. Support of this work through NSF DMR 9624475 is gratefully acknowledged.

JA001053J

---

(9) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1969.

(10) Bekiranov, S.; Bruinsma, R.; Pincus, P. *Phys. Rev. E* **1997**, *55*, 577.

(11) Schaefer, J. *Macromolecules* **1969**, *2*, 533. Matsuura, H.; Fukuhara, K. *J. Mol. Struct.* **1985**, *126*, 251.