

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231438739>

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

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · SEPTEMBER 2000

Impact Factor: 12.11 · DOI: 10.1021/ja001053j

CITATIONS

71

READS

53

3 AUTHORS, INCLUDING:



Dmitry Bedrov

University of Utah

164 PUBLICATIONS 3,108 CITATIONS

SEE PROFILE



Oleg Borodin

Army Research Laboratory

182 PUBLICATIONS 4,079 CITATIONS

SEE PROFILE

submitted to JACS as a Communication to the Editor

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, UT 84112*

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. Finally, in contrast to previous simulations and interpretation of some experiments, no tendency for extended helical conformations of the PEO chains was observed despite the large O-C-C-O *tgt* conformer population.

Its wide use, prototypical behavior and simple chemical structure make PEO an excellent candidate for experimental and simulation studies aimed at gaining a better understanding of polymer-water interactions. Our previous simulations¹ revealed that the conformations of glyme and diglyme depend strongly upon temperature and solution composition. In order 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 $\text{H}-[\text{CH}_2-\text{O}-\text{CH}_2]_{12}-\text{H}$ (PEO-530) using quantum chemistry based atomistic potentials shown to accurately reproduce the properties of PEO melts² 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 approximately 10 ns were performed for each composition.

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. The fraction of hydrophilic conformations, the total *g* populations for the C-C dihedral and the populations of the hydrophilic conformations are shown in Figure 1a, while the equivalent are shown for hydrophobic conformers in Figure 1b. Consistent with spectroscopy,³ the PEO solutions were found to exhibit nearly the same dependence of conformational populations on composition 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 solutions⁵ because the important tg^+g^- conformer is actually hydrophobic. Despite the increase in C-C *g* population with dilution, a non-negligible 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 *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 while the populations of all other conformers increase.

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 $W_p \leq 0.52$. For semi-dilute solutions scaling laws predict⁷

$$\langle R_g^2(W_p) \rangle \sim W_p^{-m} \quad (1)$$

where $m = 1/4$. We find that for $W_p \leq 0.52$, $m \approx 0.10$. As the solutions are too concentrated even at $W_p \approx 0.5$ to be considered truly semi-dilute and the PEO-530 chains are too short for excluded volume effects on chain dimensions to be fully manifested, a reduced scaling exponent is reasonable.

In order to investigate the influence of the temperature and composition dependent local conformations on chain dimensions separately from excluded volume and other non-ideal 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 melt and solution models were parametrized to reproduce local conformations determined from condensed-phase MD simulations. The corresponding RIS energies, which reflect the conformational energies of dihedrals or dihedral pairs relative to the *trans* conformation, are given in Table 1. The large increase in *tgt* population in the melt over unperturbed chains⁸ and further in 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 with the solvent. Similarly, the reduction in the *tg⁺g⁻* population 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. As with simulations, the RIS model predicts a reduction in chain dimension for the most concentrated solution relative to the melt. This effect is small at higher temperature and is due primarily to a slight reduction in the equilibrium C-C *g* dihedral angle. The reduction in chain dimensions for the ideal chains is greater at 318 K due to an increase in C-C *g* population. The expansion of the MD solution chains with dilution relative to RIS predictions reflects the excluded volume effects discussed above. Despite large changes in local conformations for solution chains with increasing temperature, particularly a decreasing C-C *g* population, that lead to expansion of the RIS chains, MD solution chains show relatively weak temperature dependence (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 highest polymer concentration, 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 measurements² 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. Note that simulation and RIS predictions are in best agreement for the most concentrated solution at the higher temperatures, where excluded volume effects and other chain extensional effects are least important.

Finally, it has been reported in a simulation study of a PEO-660 solution⁶ and speculated in various experiment works¹¹ that PEO in aqueous solutions assumes extended *tgt* helical conformations reminiscent of the crystal. In the experimental works propounding extended helical conformations, 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 a first-order Markov chain, the sequence length (*n*) distribution is given by

$$P_g(n) = (1-P)^2 n P^{n-1} \quad (2)$$

where *P* is the probability that a *g* C-C dihedral will be followed by a gauche dihedral of the same sign. 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 with $P = f_g/2$ where f_g is the total *g* fraction for the C-C dihedral. Hence, while simulations predict large C-C *g* and *tgt* conformer populations in agreement with experiment, this does not translate into extended helical chain conformations. The extended helical conformations previously observed in solution simulations⁶ are a result in part of a zero C-C *t* population, which is inconsistent with both experiment^{3,4} and our simulations, and hence is an artifact of those simulations.

Acknowledgments

The authors would like to express their appreciation to the National Science Foundation for support of this work through CAREER award NSF DMR 9624475.

References

- (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. Liquids* **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.
- (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

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

Energy	Unperturbed ^a	$W_p = 1.00^b$	$W_p = 0.78^c$	$W_p = 0.52^c$	$W_p = 0.17^c$
C-C <i>g</i>	0.10	-0.76	-1.34	-1.64	-1.66
C-O <i>g</i>	1.40	1.29	1.38	1.39	1.38
C-C-O g^+g^-	-1.30	-0.28	0.26	0.61	0.78

^aFrom Ref. 8. ^bFrom fit to melt chain local conformational populations. ^cFrom fit to solution chain local conformational populations.

Figure Captions

Figure 1. Population of important PEO (a) hydrophilic and (b) hydrophobic conformations in aqueous solution as a function of weight fraction polymer, dashed lines = 318 K, solid lines = 450 K.

Figure 2. Radius of gyration of PEO chains in aqueous solution as a function of weight fraction polymer, dashed lines, filled symbols = RIS predictions, solid lines, open symbols = MD simulations.

Figure 3. Radius of gyration of PEO chains in aqueous solution as a function of temperature, dashed lines, filled symbols = RIS predictions, solid lines, open symbols = MD simulations.

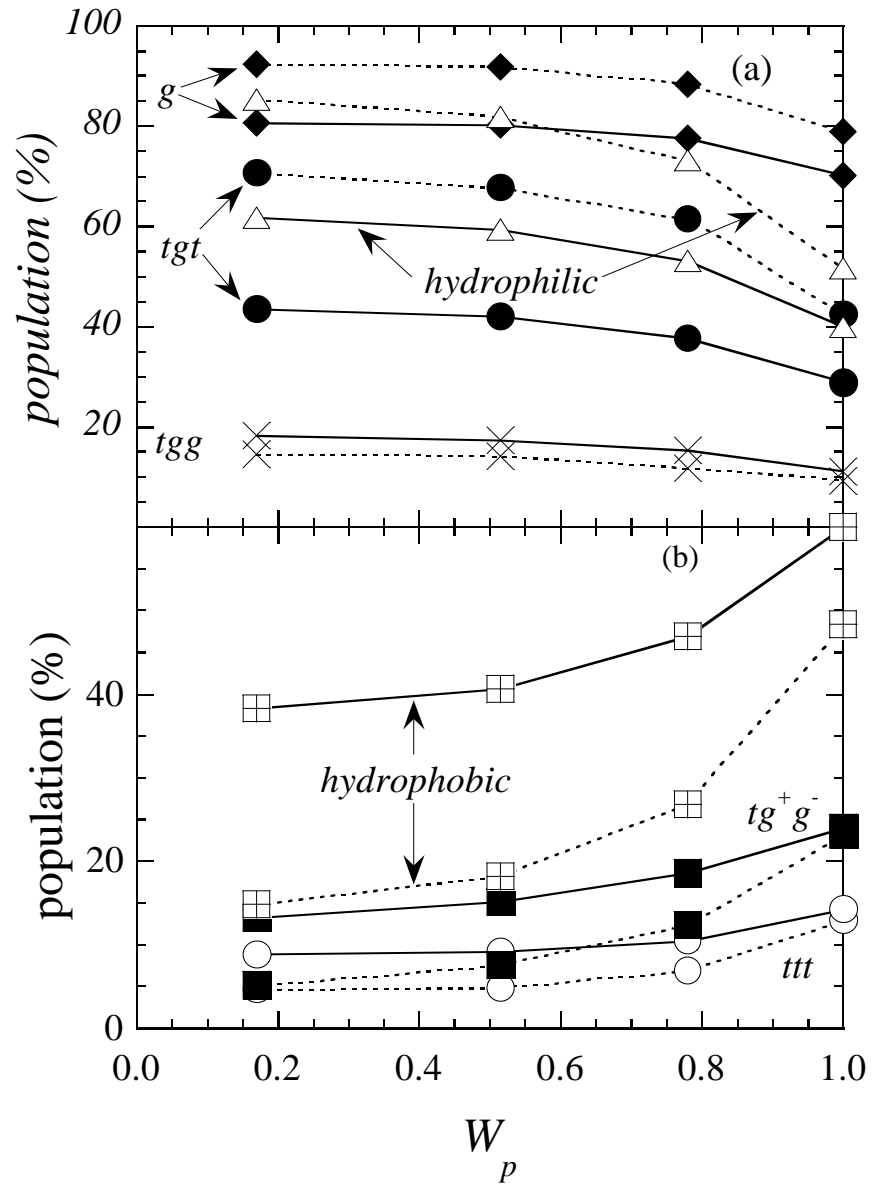


Figure 1

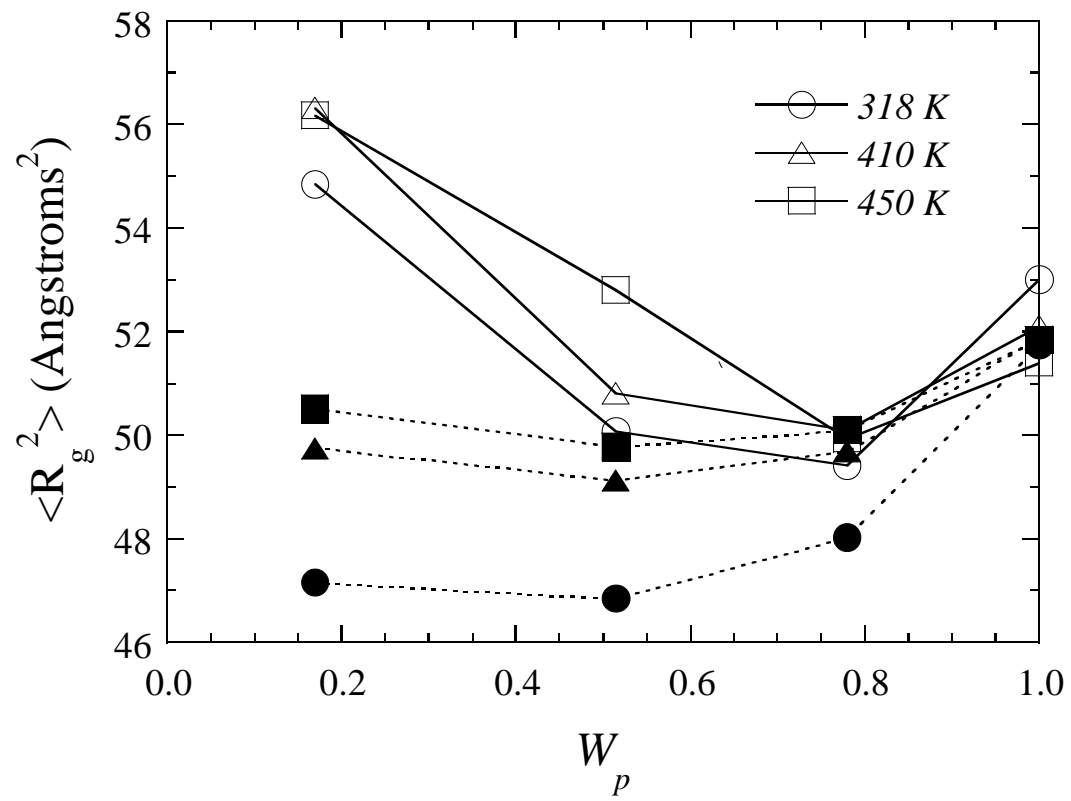


Figure 2

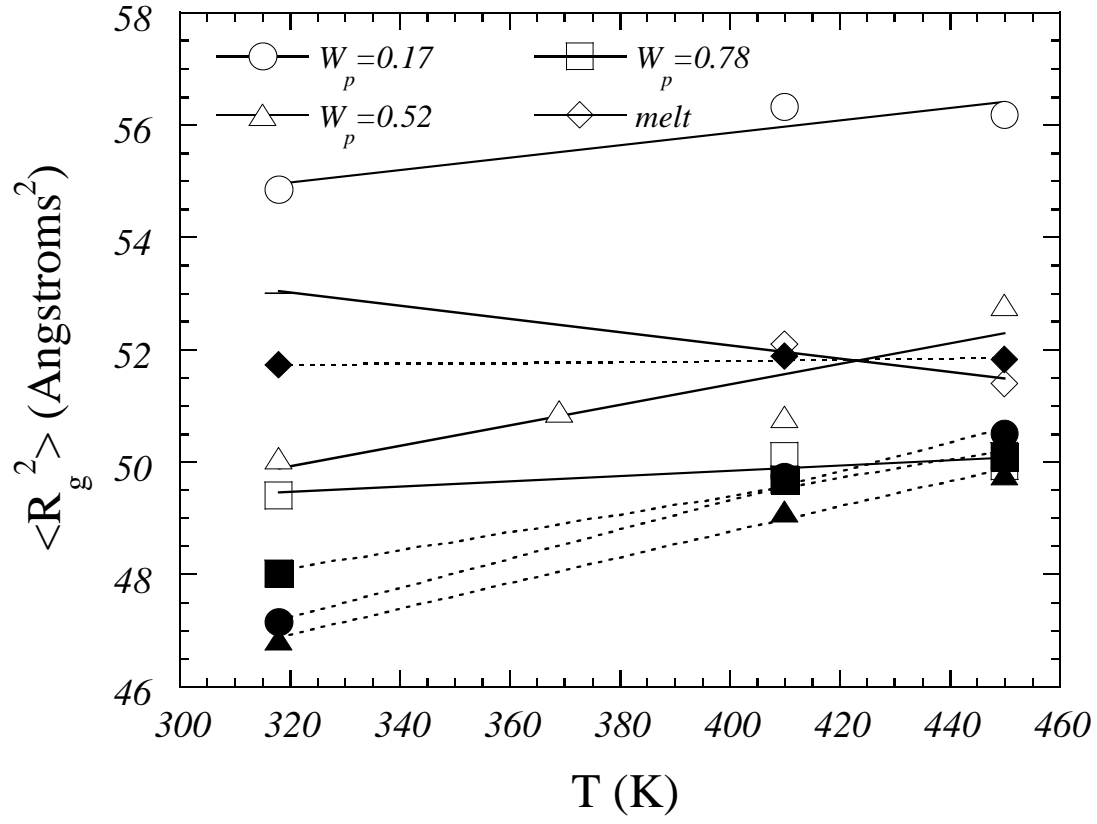


Figure 3