

# 1P105      Hydration of short-chain poly(oxyethylene)s: A quantum chemical study

○ Shaheda A. Wahab, Takanori Harada, Toshiaki Matsubara and Misako Aida  
Center for Quantum Life Sciences, and Graduate School of Science, Hiroshima University

## Introduction

Poly(oxyethylene) (POE) is an excellent candidate for both experimental and computational studies aimed at gaining a better understanding of polymer-water interactions. POE is an important polymer for the various biotechnical and biomedical applications. Because of its significant behavior, a number of studies have been performed so far on the peculiar properties of POE in water. Hydration is in particular a key factor responsible for the emergence of the hydrophilic nature. We therefore focused on the hydration of the oxyethylene ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ ) unit of POE and studied the role of a water molecule on the stabilization of the POE. We have investigated the stability of POE with the various conformations and the interaction of the short-chain POE with a water molecule in the gas phase and in the several solvents with the various dielectric constants using the quantum chemical methods. We used  $\text{CH}_3(-\text{OCH}_2\text{CH}_2-)_m\text{OCH}_3$  ( $\text{C}_1\text{E}_m\text{C}_1$ ) as a model of POE.

## Computational Methods

All the calculations have been carried out using the GAUSSIAN 03 program. The geometry optimizations were performed by the second-order Møller-Plesset perturbation (MP2) method using the basis set at the 6-311G\*\* level. The quadratic configuration interaction method with single and double substitutions (QCISD) in addition to the MP4 method were used to obtain more reliable energies. The thermochemical parameters, enthalpy, entropy and Gibbs free energy, were also calculated by the MP2 method with a scale factor of 0.9496 for calculated vibrational frequencies at the temperature of 298.15K. The solvent effects were investigated by the polarized-continuum-model (PCM) approximation using the solvents, water ( $\text{H}_2\text{O}$ ), dimethylsulfoxide ( $(\text{CH}_3)_2\text{SO}$ ), methanol ( $\text{CH}_3\text{OH}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), chloroform ( $\text{CH}_3\text{Cl}$ ), and carbon tetrachloride ( $\text{CCl}_4$ ) with the dielectric constants,  $\epsilon = 78.4, 46.7, 32.6, 8.93, 4.9, \text{ and } 2.2$ .

## Results and Discussion

We have found the monodentate and the bidentate H-bonding interaction of a water in the hydration, which leads to three hydration modes, type I, II, and III, as shown in Figure 1. In type I, one hydrogen of water is attached to one of the POE oxygens. On the other hand, in type II and III, two hydrogens of water are attached to the two oxygens of POE that are in the 1,2- and 1,3-position. We investigated the stability of POE with three hydration modes that are closely related to its solubility, using the model of POE,  $\text{C}_1\text{E}_1\text{C}_1$  and  $\text{C}_1\text{E}_2\text{C}_1$ .

**C<sub>1</sub>E<sub>1</sub>C<sub>1</sub>:** The stability of the conformers of C<sub>1</sub>E<sub>1</sub>C<sub>1</sub> in the gas phase decreased in the order, TTT (0.0 kcal/mol) > TGG' (0.02 kcal/mol) > TGT (0.52 kcal/mol). When one water molecule is added, the conformer TGT is especially largely stabilized by the H-bonding with the water with the bidentate mode. As a result, this tendency is reversed. The tendency in the stability with a water molecule, TGT > TGG' > TTT were not changed, even if the solvent effect is taken into account.

**C<sub>1</sub>E<sub>2</sub>C<sub>1</sub>:** For C<sub>1</sub>E<sub>2</sub>C<sub>1</sub>, we calculated three essentially important conformers, i.e., TTTTTT, TGTTGT and TGTTG'T. One water molecule interacts with the bidentate mode in both conformers, TGTTGT and TGTTG'T. In contrast, it interacts with the monodentate mode in the conformer, TTTTTT.

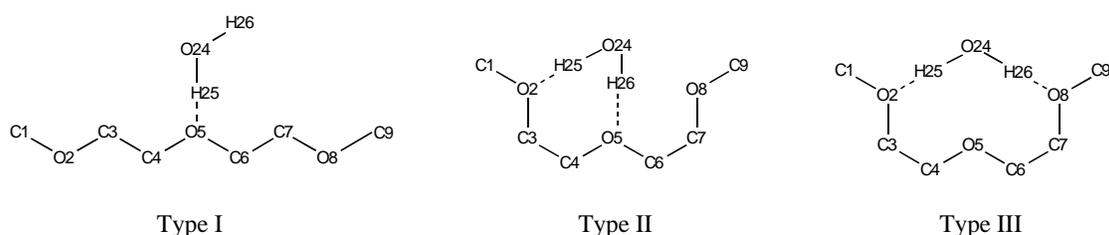


Fig.1. Three types of hydration modes of one water molecule on the POE chain of C<sub>1</sub>E<sub>2</sub>C<sub>1</sub> with the various conformations. Type I: monodentate, Type II: bidentate, Type III: bidentate.

The H-bonding with type III more stabilized the conformers compared to that with type II in both gas phase and solution. The O(POE)–H(water) distances of the H-bonding are in the range from 2.05 Å to 2.48 Å. In type III, especially two dihedral angles O<sub>2</sub>–C<sub>3</sub>–C<sub>4</sub>–O<sub>5</sub> and O<sub>5</sub>–C<sub>6</sub>–C<sub>7</sub>–O<sub>8</sub> were reduced due to the strong H-bonding. Without a water molecule, TTTTTT was more stable in energy than TGTTGT and TGTTG'T. However, this tendency was reversed with a water molecule, because both conformers, TGTTGT and TGTTG'T, are significantly stabilized by the H-bonding with a water molecule. These computational results are in good agreement with the experimentally observed results<sup>1</sup> that the H-bonding with type III obviously more stabilizes the conformers compared to that with type II. The H-bonding with the bidentate mode is further strengthened in the solution. The H-bonding becomes weaker with the increase in the dielectric constant of the solvents. TGTTG'T with type III was more stable in energy compared to TGTTGT with type III in the solution, which is in accordance with the experimental result.<sup>2</sup> It is also suggested by the natural bond orbital (NBO) analysis that type III is more stable in energy than type II. Thus, we successfully verified by the computations the hydration mode speculated experimentally.

## References

1. H. Matsuura, Md. R. Matin, and K. Okura, *Chem. Lett.*, **32**, 122–123 (2003).
2. M. R. Matin, S. A. Wahab, Y. Katsumoto, H. Matsuura, and K. Ohno, *Chem. Lett.*, **34**, 502-503 (2005).