Temperature Dependence of the Anomalous Conformational Behavior of a Short-Chain Poly(oxyethylene) in Water Studied by Raman Spectroscopy

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The Raman spectra of aqueous solutions of $CH_3(OCH_2CH_2)_3OCH_3$ were measured for mole fractions 0.002–0.06 at five temperatures between 5 and 45 °C. The population of the *gauche* conformation around the C–C bond shows its maximum at about 0.01 mole fraction. The appearance of the maximum is less prominent at higher temperatures. The observed conformational behavior is consistent with the results of molecular dynamics simulations.

Poly(oxyethylene) (POE) is a polymer of great importance in scientific and industrial areas because of its high solubility in water.[1] At elevated temperatures, however, isotropic aqueous solutions of POE separate into two phases.[2] This peculiar phase behavior has attracted much attention of many investigators.[3] The hydrophilic nature of POE has been elucidated in terms of the chain conformation of POE in water.[4–7] The important results by vibrational spectroscopy are that the C–C bond in the POE chain prefers the *gauche* conformation in water and that the proportion of the *gauche* conformation increases with decreasing POE fraction.[5–7]

In the course of conformational analysis of POE by infrared and Raman spectroscopy, we have found interesting conformational behavior of short-chain POE compounds (dimer to hexamer) in water at low concentrations;[8,9] namely, the increasing tendency of the population of the *gauche* conformation around the C–C bond with decreasing POE fraction is reversed after passing a particular concentration. This anomalous conformational behavior was subsequently studied theoretically by molecular simulations.[10,11] In one of the simulation studies, Bedrov and Smith[11] have indicated that the anomalous conformational behavior disappears at higher temperature. As the previous vibrational spectroscopic measurements were performed only at room temperature,[8,9] we are urged to pursue experimental work at different temperatures to confirm the prediction by simulations.[11]

In this work, we have studied the temperature dependence of the anomalous conformational behavior of a short-chain POE compound, $CH_3(OCH_2CH_2)_3OCH_3$ (abbreviated as $C_1E_3C_1$), in water by Raman spectroscopy. The Raman spectra of aqueous solutions of $C_1E_3C_1$ were measured for mole fractions ranging from 0.002 to 0.06 at 5, 15, 25, 35, and 45 °C. The spectra were recorded on a JASCO NR-1800 Raman spectrometer equipped with a Princeton Instruments CCD detector. An NEC GLG 2162 argon ion laser operating at 514.5 nm was used for excitation. The temperature of the samples was held constant within ±0.2 °C during each measurement by an Oxford Instrument Optistat cryostat. In this work, we were able to obtain high-quality Raman spectra for mole fractions down to 0.002, in comparison with the mole fractions down to 0.005 in the previous work.[9] We studied in this work on the solutions of more than twice larger numbers of mole fractions than in the previous work.

The Raman spectra of aqueous solutions of $C_1E_3C_1$ at 5 and 45 °C for selected mole fractions are shown in Figure 1.

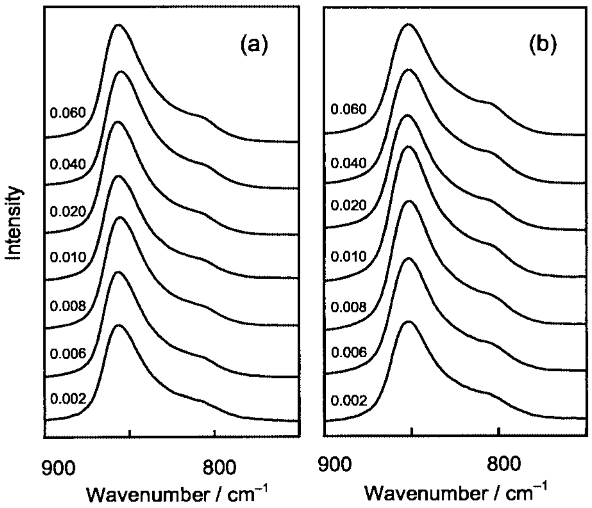

Figure 1. Raman spectra of aqueous solutions of $C_1E_3C_1$ at (a) 5 °C and (b) 45 °C. Mole fractions of $C_1E_3C_1$ are indicated in the figures. Intensities of the respective spectra have been normalized.

The observed spectral profiles in the 750–900 cm^{-1} region were resolved into three components with their maxima at 805, 830, and 850 cm^{-1} by fitting with the mixed 80% Gaussian and 20% Lorentzian function by the GRAMS/32 program (Galactic Industries). The integrated areas of the components at 805 and 850 cm^{-1} were taken as the relative spectral intensities for the *trans* conformation (I_{trans}) and the *gauche* conformation (I_{gauche}), respectively, around the C–C bond.[5,12] These components are the same as used in the previous analysis.[9]

In Figure 2, the intensity ratio I_{gauche}/I_{trans} is plotted against a mole fraction of $C_1E_3C_1$ at five temperatures. The plot indicates that the values of the ratio at higher temperatures are smaller than the values at lower temperatures in the whole concentration region studied. This observation implies that the *gauche* conformation around the C–C bond is more favored at lower temperatures, in agreement with the previous result for longer-chain POE compounds.[5] From the inverse temperature dependence of logarithm of I_{gauche}/I_{trans}, the apparent energy differences between the *gauche* and *trans* conformations, $E_{gauche} - E_{trans}$, were evaluated as −3.23, −3.37, −3.50, −3.84, −4.28, and −4.42 kJ mol^{-1} for mole fractions 0.004, 0.006, 0.008, 0.010, 0.030, and 0.050, respectively. These results indi-

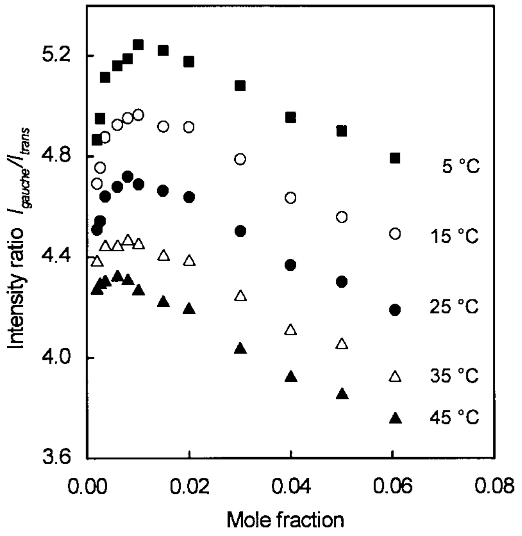

Figure 2. Intensity ratio I_{gauche}/I_{trans} for aqueous solutions of $C_1E_3C_1$ as plotted against a mole fraction of $C_1E_3C_1$ at five temperatures.

cate that the energy difference between the two conformations becomes smaller as the fraction of $C_1E_3C_1$ decreases.

As seen in Figure 2, the intensity ratio I_{gauche}/I_{trans} at each temperature shows its maximum in the 0.01 mole fraction region. The mole fraction x_{max}, at which the maximum of the intensity ratio is observed, is 0.010 at 5 °C, 0.009 at 15 °C, 0.008 at 25 °C, 0.007 at 35 °C, and 0.006 at 45 °C.[13] It is seen that x_{max} shifts to lower mole fraction as the temperature is increased. The plot in Figure 2 also shows that the appearance of the maximum of the intensity ratio is less prominent at higher temperatures.

The molecular dynamics simulations on $CH_3(OCH_2CH_2)_2OCH_3$ ($C_1E_2C_1$)[11] have indicated that the decrease in the *gauche* population for the C–C bond with decreasing $C_1E_2C_1$ mole fraction in concentration region lower than x_{max} can be explained by the decrease in the population of the *trans–gauche–trans* (TGT) conformation for the O–CH_2–CH_2–O segment and, in particular, by the pronounced decrease in the population of the TGTTGT conformation for the two-oxyethylene unit segment O–CH_2–CH_2–O–CH_2–CH_2–O. Bedrov and Smith[11] have suggested that the dipole orientation in the TGTTGT conformation is relatively unfavorable for interactions of the POE chain with the water molecules that complete the first hydration shell of the POE chain. The results of the simulations thus indicate that the anomalous conformational behavior, namely the decrease of the *gauche* population for the C–C bond with decreasing POE fraction, is reflected for the most part by the characteristic population behavior of the TGTTGT conformation with varying concentration.

The hydration structure around the POE chain is well defined and ordered at low temperatures, but it becomes less ordered with increasing temperature. The less prominent maximum of the *gauche* population for the C–C bond at higher temperatures is consistent with the expected hydration structure at these temperatures, and is in conformity with the results of molecular dynamics simulations,[11] which showed that the maximum of the *gauche* population disappears at higher temperature. The present experimental observation that the decrease in the *gauche* population begins at lower $C_1E_3C_1$ mole fraction at higher temperatures is also explained by the less ordered or less completed structure of the hydration shell, where the POE segment in the TGTTGT conformation can still interact favorably with water molecules.

A recent Raman spectroscopic study on a shorter compound $CH_3OCH_2CH_2OCH_3$ ($C_1E_1C_1$)[7] has shown that the population of the less hydrophilic TGG′ conformer decreases significantly with decreasing $C_1E_1C_1$ mole fraction and that the appearance of this conformation within the POE chain can be a basic mechanism of the phase separation of aqueous solutions of POE. Accordingly, the decrease of the population of the TGG′ conformation at low concentrations can be a factor of the overall decrease of the *gauche* population for the C–C bond and, in consequence, can be a second factor of the anomalous conformational behavior of the POE chain in water. The previous study has shown that the TGG′ conformer of $C_1E_1C_1$ is more populated at higher temperatures.[7] This conformational behavior should abate the decrease of the overall *gauche* population in the concentration region lower than x_{max} at higher temperatures, being consistent with the less prominent maximum of the *gauche* population at these temperatures.

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References and Notes

1 F. E. Bailey, Jr. and J. V. Koleske, “Poly(ethylene oxide),” Academic Press, New York (1976).
2 S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, *Polymer,* **17**, 685 (1976).
3 G. Karlström and B. Lindman, in “Organized Solutions,” ed. by S. E. Friberg and B. Lindman, Dekker, New York (1992), Chap. 5, p. 49.
4 G. Karlström, *J. Phys. Chem.*, **89**, 4962 (1985).
5 H. Matsuura and K. Fukuhara, *J. Mol. Struct.*, **126**, 251 (1985).
6 R. Begum and H. Matsuura, *J. Chem. Soc., Faraday Trans.*, **93**, 3839 (1997).
7 N. Goutev, K. Ohno, and H. Matsuura, *J. Phys. Chem. A*, **104**, 9226 (2000).
8 H. Matsuura and T. Sagawa, *J. Mol. Liq.*, **65**/**66**, 313 (1995).
9 S. Masatoki, M. Takamura, H. Matsuura, K. Kamogawa, and T. Kitagawa, *Chem. Lett.*, **1995**, 991.
10 O. Engkvist and G. Karlström, *J. Phys. Chem. B*, **101**, 1631 (1997).
11 D. Bedrov and G. D. Smith, *J. Chem. Phys.*, **109**, 8118 (1998).
12 H. Matsuura and K. Fukuhara, *J. Polym. Sci., Part B*, **24**, 1383 (1986).
13 The previous study[9] gave 0.03 for the value of x_{max} at room temperature. The higher-quality spectra and the more sophisticated band resolving method using the experimental data for more mole fraction points than in the previous work ensure that the present results are more reliable.