

## Thermal Stability of the Hydration Structure of Short-chain Poly(oxyethylene) in Carbon Tetrachloride: An Infrared Spectroscopic Observation of the Breakdown of Hydrogen Bonds

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(Received December 6, 2004; CL-041489)

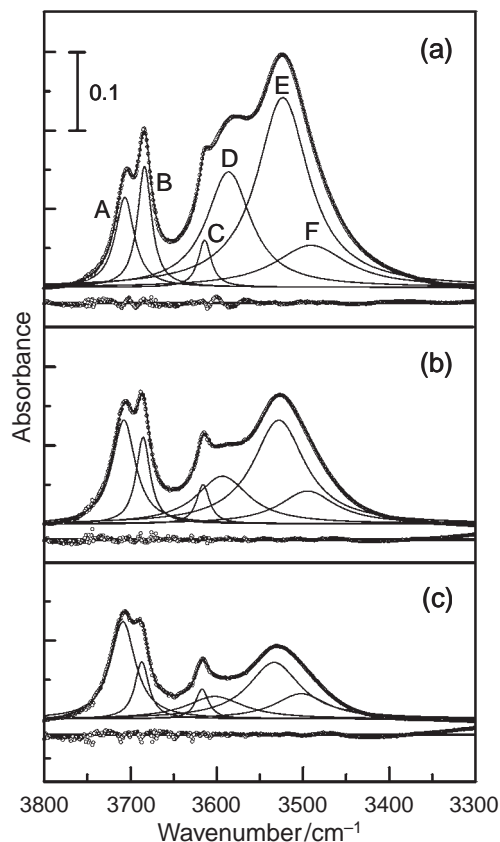
The temperature-dependent infrared spectra of water dissolved in carbon tetrachloride containing varying amounts of short-chain poly(oxyethylene) (POE) have demonstrated that an increase of temperature destabilizes bidentate hydrogen bonds between water and POE, and changes them to monodentate hydrogen bonds, which are eventually disrupted at higher temperatures. This process of hydrogen bond breakdown is a possible mechanism, among others, of the phase separation in the POE–water system.

Poly(oxyethylene) (POE) or poly(ethylene glycol) is a polymer of wide applications in biotechnology and biomedical sciences.<sup>1,2</sup> A large number of studies have in fact been performed on peculiar properties of POE in water such as the practically unlimited solubility at moderate temperatures and the occurrence of phase separation at elevated temperatures.<sup>3–5</sup> These studies have indicated that hydration is one of the key factors responsible for the emergence of hydrophilicity of this polymer. The previous spectroscopic studies<sup>6–8</sup> have yielded significant results on the hydration of short-chain POEs in aqueous solutions in moderate to high concentration regions. In a situation where the hydrogen bond is formed exclusively between a water molecule and a single POE chain, there is a possibility of observing incipient primitive hydration structure of POE. In spite of its essential importance, no relevant studies have been reported possibly because of experimental difficulties. Recently, we have succeeded in an observation of the hydrogen bond under such conditions by studying infrared spectra of POE in carbon tetrachloride with a very small amount of dissolved water.<sup>9</sup> The results showed that there exist two types of hydrogen bonds, monodentate and bidentate, and the water molecule in the latter hydrogen bond bridges oxygen atoms of POE separated by two or more monomer units. These experimental findings encouraged us to investigate thermal stability of the hydration structure of POE in carbon tetrachloride, with an aim to elucidate the mechanism of phase separation in the POE–water system.

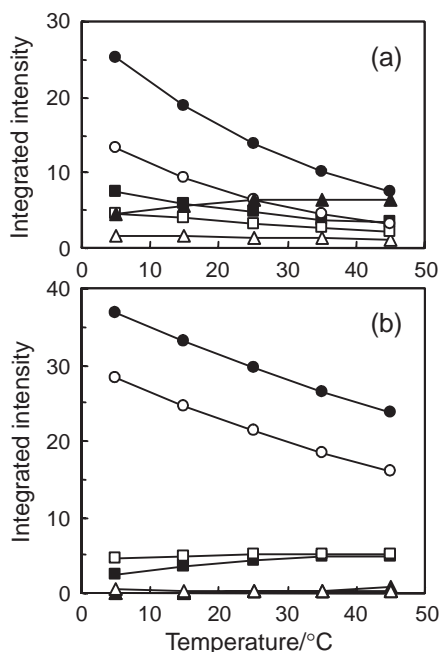
We studied temperature-dependent infrared spectra of solutions of a series of short-chain POE compounds,  $\text{CH}_3(\text{OCH}_2\text{-CH}_2)_m\text{OCH}_3$  (abbreviated as  $\text{C}_1\text{E}_m\text{C}_1$ ), in carbon tetrachloride with dissolved water. In this letter, we report the results for  $\text{C}_1\text{E}_3\text{C}_1$ , since this compound is the shortest POE that preserves the intrinsic structural properties of long-chain POEs.<sup>7</sup> The spectra were measured at 5, 15, 25, 35, and 45 °C by using a Peltier device for temperature regulation. The samples for infrared measurements were contained in a quartz cell of 2-cm path length. The mole ratio of water to carbon tetrachloride was held constant in all experiments at 0.00042:1, which is equivalent to

half the saturated concentration of water in carbon tetrachloride.<sup>10</sup> The precise adjustment of the solution concentration to this mole ratio was carried out by diluting water-saturated carbon tetrachloride prepared at 25 °C with the same amount of water-free carbon tetrachloride. The mole ratio  $\text{H}_2\text{O}:\text{C}_1\text{E}_3\text{C}_1:\text{CCl}_4$  was varied from 0.00042:0.005:0.995 to 0.00040:0.06:0.94, where the ratio of the first to the third substance was constrained as mentioned. The infrared spectra were recorded on a Bruker IFS66V vacuum spectrometer with a spectral resolution of  $2\text{ cm}^{-1}$ .

The hydrogen bonding between water and  $\text{C}_1\text{E}_3\text{C}_1$  was studied by examining the O–H stretching vibrations of water in the  $3300\text{--}3800\text{ cm}^{-1}$  region. The absorptions of  $\text{C}_1\text{E}_3\text{C}_1$  in this region (the combinations and the overtones), which may disturb



**Figure 1.** Infrared spectra of water in a solution of  $\text{H}_2\text{O}:\text{C}_1\text{E}_3\text{C}_1:\text{CCl}_4 = 0.00042:0.005:0.995$  at (a) 5, (b) 25, and (c) 45 °C. The resolved components, A–F, and the residuals of curve fitting (2.0 times enlarged) are also shown.



**Figure 2.** Integrated intensities of bands A–F plotted against temperature for solutions of (a)  $\text{H}_2\text{O}:\text{C}_1\text{E}_3\text{C}_1:\text{CCl}_4 = 0.00042:0.005:0.995$  and (b)  $0.00040:0.06:0.94$ .  $\blacktriangle$ : band A,  $\square$ : band B,  $\triangle$ : band C,  $\circ$ : band D,  $\bullet$ : band E, and  $\blacksquare$ : band F. Integrated intensities are given in arbitrary units on a scale common to (a) and (b).

analysis of the water bands, were eliminated by spectral subtraction as described previously.<sup>9</sup> The infrared spectra of water in a solution of  $\text{H}_2\text{O}:\text{C}_1\text{E}_3\text{C}_1:\text{CCl}_4 = 0.00042:0.005:0.995$  at three selected temperatures are shown in Figure 1. The spectral profiles of the O–H stretching bands were fitted with six Lorentzian components with the use of a program for curve fitting.<sup>12</sup> The six resolved bands, A–F, have been assigned on a purely experimental basis to the O–H stretching modes of free and mono- and bidentate hydrogen-bonded water;<sup>9</sup> band A ( $3707\text{ cm}^{-1}$ ): antisymmetric stretching of free water, B ( $3684\text{--}3686\text{ cm}^{-1}$ ): unbonded O–H stretching of monodentate water, C ( $3615\text{ cm}^{-1}$ ): symmetric stretching of free water, D ( $3588\text{--}3600\text{ cm}^{-1}$ ): antisymmetric stretching of bidentate water, E ( $3523\text{--}3530\text{ cm}^{-1}$ ): symmetric stretching of bidentate water, and F ( $3485\text{--}3498\text{ cm}^{-1}$ ): bonded O–H stretching of monodentate water.

Figure 1 shows remarkable dependence of the spectra on temperature. The integrated intensities of bands A–F plotted against temperature are given in Figure 2(a). The intensities of bands D and E due to the O–H stretching vibrations of bidentate hydrogen-bonded water decrease noticeably with increasing temperature. The intensities of bands B and F, associated with monodentate hydrogen-bonded water, also decrease, but their rate of decrease with temperature is smaller than that of bands D and E. Band A for free water, on the other hand, increases in intensity with increasing temperature. The weakest band C, which is another band for free water, exhibits intensity behavior different from band A, possibly because of incomplete cancellation of the absorption of  $\text{C}_1\text{E}_3\text{C}_1$ .

The integrated intensities of bands A–F for a solution of  $\text{H}_2\text{O}:\text{C}_1\text{E}_3\text{C}_1:\text{CCl}_4 = 0.00040:0.06:0.94$  are shown in Figure 2(b). The intensities of bands A and C (free water) are much

weaker than the intensities of the same bands at a mole ratio  $0.00042:0.005:0.995$  (Figure 2(a)), because the number of water molecules per  $\text{C}_1\text{E}_3\text{C}_1$  molecule, approximately 0.007, is significantly smaller than the number, approximately 0.08, for the mole ratio  $0.00042:0.005:0.995$ . When the temperature is raised, the intensities of bands D and E (bidentate hydrogen-bonded water) decrease, while those of bands B and F (monodentate hydrogen-bonded water) increase to a small extent. The experimental results for other mole ratios of  $\text{H}_2\text{O}:\text{C}_1\text{E}_3\text{C}_1:\text{CCl}_4$  studied are consistent with the results for the two mole ratio extremes,  $0.00042:0.005:0.995$  and  $0.00040:0.06:0.94$ , described above.

The results in Figure 2 demonstrate that an increase of temperature destabilizes the bidentate hydrogen bonds and alters them, as a result of the breaking of one of the two hydrogen bonds, to the monodentate hydrogen bonds, which are eventually disrupted at higher temperatures. A relevant note is that the formation of bidentate hydrogen bonds is possible only when the POE chain assumes conformations favorable for them, e.g., *trans-gauche-trans-trans-gauche'-trans* for the  $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$  segment. The formation of monodentate hydrogen bonds, on the other hand, is possible in most cases with the POE chain in any conformational state.

A possibility that more than one water molecule is hydrogen-bonded to the same  $\text{C}_1\text{E}_3\text{C}_1$  molecule may not be ruled out, when the number of water molecules per  $\text{C}_1\text{E}_3\text{C}_1$  molecule becomes large. However, the discrimination between a 1:1  $\text{C}_1\text{E}_3\text{C}_1$ -water adduct and a 1:2 adduct (or adducts with more water molecules) is substantially not possible, because the O–H stretching bands of water we can discern are only those associated with different types of hydrogen bonds.

The phase separation of aqueous solutions of POE at elevated temperatures can be explained by the destabilization of the hydration structure. The result of the present study indicates that, with increasing temperature, the dominant bidentate hydrogen bonds between water and POE are changed to the monodentate, and the phase separation will occur when the monodentate hydrogen bonds are largely destructed. This process of hydrogen bond breakdown is a possible mechanism, among others, of the phase separation in the POE–water system.

#### References and Notes

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