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SHORT COMMUNICATION

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A Fourier transform infrared study of the phase transition in aqueous solutions of Ethylene oxide–propylene oxide triblock copolymer

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Abstract The phase transition between unimer and micellar phases of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer Pluronic P105 in aqueous solution has been investigated as a function of temperature using Fourier transform infrared spectroscopy. The transition of 8 wt% Pluronic P105 in aqueous solution was found to occur at 25 °C. As temperature increases, PO blocks appear to be stretched conformers with strong interchain interaction, and the formation of a hydrophobic core in the micellar phase. The EO chains are found to change to a more disordered structure with low-chain packing density from the unimer phase to the micellar phase. Both the EO and PO blocks exhibit dehydration during the phase transition.

Key words Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) – triblock copolymer, Fourier transform infrared spectroscopy, Micelle

Introduction

Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymers are high-molecular-weight nonionic surfactants commercially known as Poloxamers and Pluronics. The hydrophilic-lipophilic property of these copolymers can be readily altered by varying their molecular weight and chemical composition. Thus, the PEO–PPO–PEO block copolymers can meet the specific requirements of different applications such as detergency, dispersion stabilization, foaming, emulsification, and lubrication [1, 2]. In the past decade, considerable efforts [3–7] have been made to understand the properties of PEO–PPO–PEO block copolymers.

The most characteristic property of PEO–PPO–PEO block copolymers is the inverse temperature dependence of micellization and gelation. In dilute solutions and at low temperatures, the block copolymers dissolve in aqueous solution as unimers (molecular copolymers) [8]. With increasing block copolymer concentration or temperature, the critical micelle concentration (cmc) or critical micelle temperature (cmt) can be observed where the aggregation of PEO–PPO–PEO block copolymers occurs and leads to the formation of intermolecular micelles. Within a certain concentration and temperature range, the block copolymers form spherical micelles consisting of a relatively compact core of hydrophobic PO blocks surrounded by a corona or shell of EO segments with strong hydration. The micellization of PEO–PPO–PEO block copolymers is very similar to the behavior of conventional surfactants, which follow a closed association mechanism with equilibrium between unimers and micelles. A theoretical model based on mean-field lattice theory has been developed for aqueous solutions of block copolymers. This model can be used to predict the regions for the unimer solution, spherical micelles, and elongated rods as well as the two-phase region as a function of temperature and concentration [9, 10]. The effects of temperature on the properties of PEO–PPO–PEO block copolymer solutions have been studied extensively; however, there are only a few reports of studies on PEO–PPO–PEO block copolymers by Fourier transform infrared (FTIR) spectroscopy [4, 11].

In the present work, the effects of temperature on structural features of the unimer-to-micelle phase transition in the PEO–PPO–PEO block copolymer-water system have been investigated by FTIR spectroscopy.

Experimental

Materials

The Pluronic P105 PEO–PPO–PEO triblock copolymer is manufactured by BASF, and was used as received. The P105 polymer has a nominal molecular weight of 6500, and a PEO content of 50 wt%. On the basis of molecular weight and chemical composition, P105 can be represented by the formula $(EO)_{37}(PO)_{58}(EO)_{37}$. The Pluronic P105 aqueous solutions were prepared by dissolving the copolymer in distilled water with gentle agitation.

FTIR measurements

FTIR spectra with a resolution of 2 cm^{-1} were recorded on a Bruker Vecter 22 FTIR spectrometer; deuterotriglycine sulfate detector was used. The temperature study of the anhydrous PEO–PPO–PEO block copolymer samples was carried out in the range 5–70 °C, and that of the aqueous samples was in the range 2–50 °C. The temperature of the sample was measured by a thermocouple inserted into a stainless steel block containing the sample cell. The system comprised a Graseby-Specac temperature cell (P/N 21525). The temperature measurement was accurate to ± 0.1 °C. The equilibration time for each temperature was 2 min. A BaF_2 cell was used for the liquid samples and a KBr cell was employed for the anhydrous samples. The OPUS spectroscopic software was used for data handling. The frequency and half linewidth of the bands were determined using the OPUS peak pick function. For the 1200–1000 cm^{-1} region, the deconvolution of spectra was performed using the OPUS deconvolution function; then the deconvoluted spectra were curve-fitted with Gaussian bands, and the frequency and half linewidth of the subbands were obtained.

Results and discussion

Characteristic infrared spectral features

The IR spectra of the anhydrous PEO–PPO–PEO block copolymer Pluronic P105 and the 8 wt% Pluronic P105 in aqueous solution were recorded at various temperatures. Large differences among the infrared spectra of the Pluronic P105 PEO–PPO–PEO block copolymer can be observed in Fig. 1 when the copolymer is in a crystalline (5 °C) or in a molten state (70 °C) as an anhydrous sample, and in aqueous solution at 2 °C (unimer phase) and at 50 °C (micelle phase). The band intensity of the block copolymer in aqueous solution is much weaker than that of the anhydrous sample. In order to compare the spectra of samples in aqueous solution with those of anhydrous samples, the spectra were normalized to have the same intensity scale. The spectra were shifted so that the minimum y-value is set to zero and they are expanded in the y-direction so that the maximum y-value is placed at 2 absorbance units. The important bands appearing in the C—H stretching region contain symmetrical and asymmetrical C—H stretching of methyl groups and methylene groups. The bending motion of hydrogen in a C—H bond gives bands in the region 1300–1500 cm^{-1} [12, 13]. The methyl group exhibits two types of bending vibrations while the methylene groups produce four types of bending vibrations, viz., scissoring, rocking, wagging, and twisting. The band due to the C—O stretching mode for aliphatic ethers has been observed in the region 1200–1000 cm^{-1} [14]. The infrared spectra of the anhydrous sample and the sample in aqueous solution underwent dramatic changes in the region of C—H stretching, C—H bending and C—O stretching modes not only in the frequencies but also in the intensities and widths of the infrared bands.

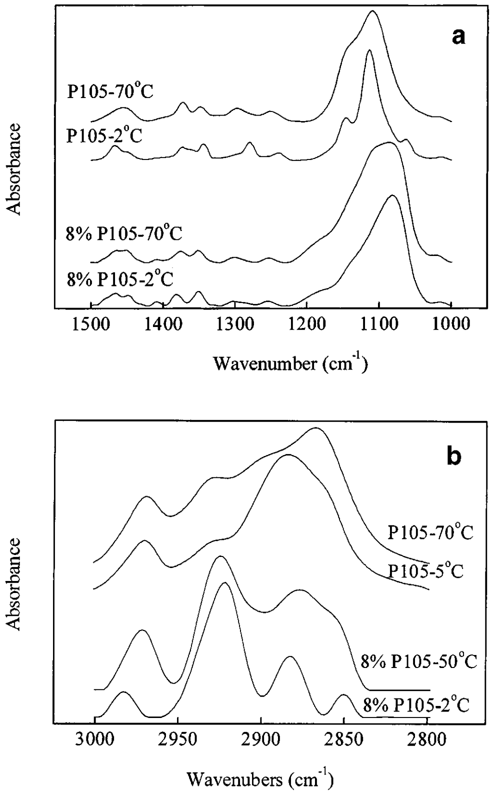

Fig. 1a,b Infrared spectra of the poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymer Pluronic P105 in crystalline and molten states as an anhydrous sample, and in aqueous solution at a concentration of 8 wt% at 2 °C and 50 °C. 1500–1000 cm^{-1}, 3000–2800 cm^{-1}

In the crystalline state, there are three coupled C—O stretching and C—C stretching bands. The strongest band in this spectral region is at 1114 cm^{-1}, and the other two bands are at 1146 and 1063 cm^{-1}, respectively. It should be emphasized that there are only small shifts in wavenumber between the crystalline and the molten states; however, for the molten state, the 1063 cm^{-1} band is weak and all the bands are in general broader than the corresponding bands for the crystalline state. When Pluronic P105 dissolves in water, the 1063 cm^{-1} band disappears, and the other two bands are much broader and are accompanied by a shift of wavenumber (1114 cm^{-1}) to lower frequencies. The unique feature of the 1063 cm^{-1} band for the crystalline state is the characteristic band of the helical structure of PEO [15]. The disappearance of the 1063 cm^{-1} band and the broadening of the bandwidth for the molten state or in aqueous solution indicate that, as expected, the PEO–PPO–PEO block copolymer molecules under these two conditions have higher mobility and are more disordered in packing. The 1114 cm^{-1} band is sensitive to hydrogen bonding between the oxygens of the Pluronic polymer and the hydrogens of water molecules [16]. When Pluronic P105 dissolves in aqueous solution, the low-frequency shift of the 1114 cm^{-1} band is attributed to hydrogen bonding between the block copolymer and water.

The strongest band for the crystalline state in the C—H stretching region is the CH_3 symmetric stretching band at 2884 cm^{-1}. The CH_2 symmetric and asymmetric bands are two weak shoulders at each side of the 2884 cm^{-1} band around 2860 and 2929 cm^{-1}. In the disordering process caused by heating the samples, the 2860 and 2884 cm^{-1} bands shift to higher frequencies, and the strongest band for the molten state is the CH_2 symmetric mode at 2868 cm^{-1}. The infrared spectra of Pluronic P105 in aqueous solution show different spectral features in the C—H stretching region. The CH_2 symmetric and asymmetric bands shift to higher frequencies with increase of temperature, while the CH_3 symmetric and asymmetric bands shift to lower frequencies.

The spectrum of crystalline Pluronic P105 shows two bands in the CH_2 twisting region: they are assigned to the helix structure at 1238 cm^{-1} and to the trans structure at 1280 cm^{-1}. In the CH_2 wagging region, the crystalline Pluronic P105 exhibits two bands at 1344 and 1358 cm^{-1}, which are assigned to the trans structure and the helix structure, respectively [15]. When heating the anhydrous sample or when dissolving Pluronic P105 in water, the broadening of bandwidth, decreasing of band intensity, and shifting of wavenumber to high frequency are shown in the CH_2 twisting and wagging region. This indicates that a more disordered structure and higher mobility are observed for the PEO–PPO–PEO block copolymer at high temperature and when dissolved in aqueous solution.

Temperature-dependent phase transition

It is well documented that temperature can induce the phase transition for copolymers in aqueous solution from an unimer phase to a micellar phase [6]. As shown in Fig. 1, the infrared spectra of the unimer and the temperature-induced micellar phases of Pluronic P105 are considerably different. It is therefore expected that drastic changes in the infrared spectra of the Pluronic P105 aqueous solution occur at the cmt with the unimer phase transforming into a micellar solution. Such changes in the infrared spectra of Pluronic P105 in aqueous solution with a concentration of 8 wt% are indeed observed at 25 °C. Abrupt changes at the cmt can be visualized from the spectra shown in Fig. 2 which illustrate infrared spectra as a function of temperature for Pluronic P105 in the 1500–1200 cm^{-1} region. The spectra in the 3000–2800 cm^{-1}, 1500–1200 cm^{-1}, and 1200–1000 cm^{-1} regions are discussed in the following sections.

3000–2800 cm^{-1} region

The infrared spectral parameters normally used to characterize the lipid transition are frequencies and bandwidths of the C—H stretching mode. Each of these parameters is sensitive to various aspects of lipid conformation and mobility [17, 18]. Because the CH_2 and CH_3 symmetric stretching bands are more sensitive to the conformational change of the anhydrous sample (Fig. 1), these two bands are naturally chosen to study the thermal transition of the PEO–PPO–PEO block copolymer Pluronic P105. The changes in the CH_3 symmetric stretching band are quantitatively monitored by determining the temperature dependencies of frequency and bandwidth. (Fig. 3). In the temperature range 2–25 °C, a slight increase in bandwidth and a slight decrease in wavenumber are observed. It is found that there are drastic decreases in wavenumber and bandwidth centered at about 25 °C. These changes may correspond to the unimer-to-micelle transition for the concentration of 8 wt% copolymer in aqueous solution. The decrease in wavenumber of the symmetric CH_3 stretching band is quite possibly due to the decrease in

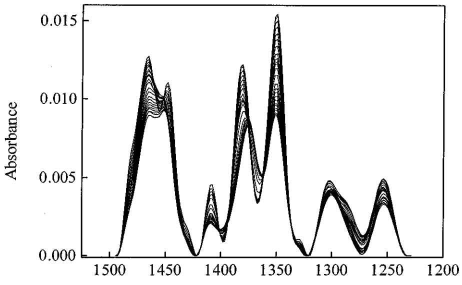

Fig. 2 Infrared spectra of the 1500–1200 cm^{-1} region of the PEO–PPO–PEO block copolymer Pluronic P105 in aqueous solution at a concentration of 8 wt% in the temperature range 2–50 °C

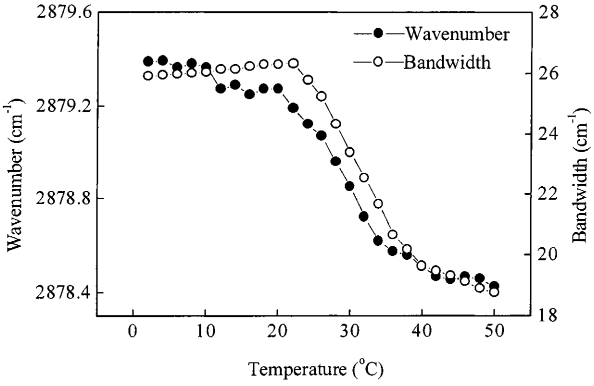

Fig. 3 The temperature dependence of the frequency and the width of the CH_3 symmetric stretching band in the infrared spectra of the PEO–PPO–PEO block copolymer Pluronic P105 in aqueous solution at a concentration of 8 wt%

the gauche conformer of the PO chains (which contain CH_3 group) from the unimer phase to the micellar phase. The bandwidth indicates that at higher temperature in the unimer phase, the PO block has higher mobility. When micelles are formed, the methyl groups exist in a more fixed position; therefore, there is an abrupt decrease in bandwidth with increase of temperature above 25 °C. The CH_2 symmetric and asymmetric modes show different temperature-dependent changes compared with the CH_3 stretching modes of the PO blocks. As Pluronic P105 has more EO fragments than PO fragments and EO fragments have more methylene groups than PO fragments, the different temperature-dependent changes of methylene symmetric and asymmetric modes may reflect the conformation and mobility of EO blocks. The temperature dependence of the frequency and width of the CH_2 symmetric stretching band at 2850 cm^{-1} is illustrated in Fig. 4. The effects at the transition temperature result in a sharp increase in frequency and an abrupt broadening of this band. Similar effects on the frequency and the bandwidth are observed on the melting of *n*-alkanes and can be correlated with a higher population of gauche conformers in the liquid hydrocarbon phase [13]. The same results can also be found in disorder processes of Pluronic P105 by heating the anhydrous sample (Fig. 1). Thus, the CH_2 stretching vibrations shift to higher frequencies, suggesting that the molecular thermal motion increases the population of gauche conformers in the EO chains, which results in a decrease in chain packing density and leads to weaker screening and stabilization of the hydrophobic PO blocks from water. Therefore the unimers aggregate to micelles to stabilize the block copolymer-water system.

1200–1000 cm^{-1} region

To probe the temperature effect on the hydration of PO and EO blocks, the deconvolution method was used to obtain independent information about the possible components under a complex band profile in the C—O stretching region. In the deconvoluted spectra, the strong band in the 1200–1000 cm^{-1} region can be separated into two components, one around 1071 cm^{-1} and the other around 1091 cm^{-1}. The frequencies of the two bands are plotted in Fig. 5 versus temperature. From an inspection of Fig. 5, it is clear that an increase in temperature leads to drastic changes in the frequencies of the 1071 and 1091 cm^{-1} bands in C—O stretching region, but the 1091 cm^{-1} band exhibits a big change, while the 1071 cm^{-1} band shows a small change. The two bands broaden, and shift to higher frequencies at the cmt, which can be identified to be at 25 °C.

The PO block is the hydrophobic part of the block copolymer, while the EO block is the hydrophilic one.

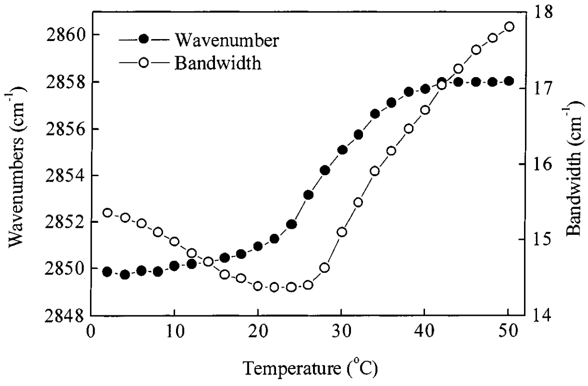

Fig. 4 The temperature dependence of the frequency and the width of the CH_2 symmetric stretching band in the infrared spectra of the PEO–PPO–PEO block copolymer Pluronic P105 in aqueous solution at a concentration of 8 wt%

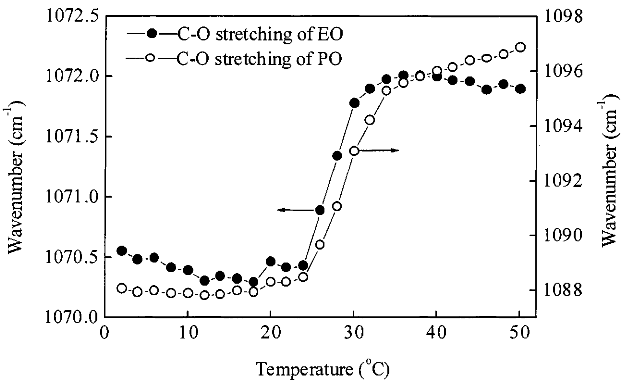

Fig. 5 The temperature dependence of the frequency of the C—O stretching mode of the PO and EO blocks in the infrared spectra of the PEO–PPO–PEO block copolymer Pluronic P105 in aqueous solution at a concentration of 8 wt%

The C—O stretching band shifts to lower frequency when the water molecules bind to the block copolymer. The band around 1071 cm^{-1} is assigned to the C—O stretching mode of the EO block, and the band around 1091 cm^{-1} to that of the PO block. By probing the frequency shift of the C—O stretching modes of the EO and PO blocks given in Fig. 5, we could deduce the dehydration of the EO and PO chains associated with the transition from the unimer phase to the micellar phase. In the unimer phase, the copolymer dissolves in water as a molecular copolymer, which forms a PPO hydrophobic core surrounded by the hydrophilic PEO blocks [8]. The water molecules could bind to the hydrophilic EO blocks and could also penetrate into the hydrophobic PPO core. Therefore, at low temperature, the wavenumbers of the C—O stretching modes of the PO and EO blocks are both low. The result that the core contains water was also found by Goldmints et al. [19] using small-angle neutron scattering. When the temperature increases to the cmt, the PO block undergoes a large degree of dehydration, as is evident from Fig. 5. The water molecules are removed from the C—O groups of the PO block, so the repulsion between PO blocks is minimized. This creates a proper nonpolar environment in the micellar core region for the PO blocks in the micellar phase. With increasing temperature, the EO blocks undergo a small degree of dehydration. The EO block-water interaction is somewhat decreased while the interaction between EO blocks is increased, so the EO blocks aggregate to form a hydrophilic micellar corona.

1500–1200 cm^{-1} region

The bending modes of CH_2 and CH_3 in the 1500–1200 cm^{-1} region are shown in Fig. 2. The most important signals belonging to this region are the bands near 1350 cm^{-1} assigned to the out-of-phase CH_2 wagging mode in a gauche conformation, the bands near 1300 cm^{-1} assigned to the out-of-phase CH_2 bending motions of gauche conformers, and the bands near 1284 cm^{-1} assigned to out-of-phase CH_2 bending motions of trans conformers.

As shown in Fig. 2, the out-of-phase CH_2 bending modes show a band at 1300 cm^{-1} and a shoulder at 1284 cm^{-1} at low temperature, which suggests the existence of trans defects in disordered EO chains. The two bands merge to a single band at 1300 cm^{-1} with increasing temperature. The disappearance of the 1284 cm^{-1} band is an indication of the disappearance of trans conformers in EO blocks in the micellar phase. Another important infrared-active mode, in the 1500–1200 cm^{-1} region, is the CH_3 umbrella deformation mode near 1376 cm^{-1}, which is sensitive to the environment and to the intermolecular interaction [20]. The temperature dependency of frequency and bandwidth exhibits a similar trend as for CH_3 asymmetric stretching modes versus temperature. In the temperature range 2–25 °C, the bandwidth of the 1376 cm^{-1} band increases and the wavenumber decreases slightly with increase of temperature. There are drastic changes centered at about 25 °C: the band shifts abruptly to lower frequencies accompanied by a decrease of the bandwidth. This means an increase in the intermolecular interaction and a decrease in the rotational motion of the PO chains in the micellar phase. The increase of the bandwidth with the increase of temperature below 25 °C is due to the increase in mobility of the PO blocks in the unimer phase.

Conclusions

The conformational changes and dehydration of both EO and PO blocks in Pluronic P105 from the unimer phase to the micellar phase can be seen by FTIR spectroscopy. The deconvoluted spectra can be used satisfactorily to provide microenvironmental information on PEO and PPO blocks in triblock copolymers. Both PEO and PPO chains undergo dehydration with increasing temperature; however, the degree of dehydration of PEO chains is lower than that of PPO chains.

In the unimer phase, the PPO blocks exhibit disordered structure and the intermolecular interaction is weak. The rotation of the methyl groups increases with increasing temperature. The PEO blocks shows trans defects in polymer chains. The presence of bound water is evident in both the PO block and the EO block.

In the micellar phase, PPO blocks show extended structure and strong intermolecular interaction. The methyl groups are restricted. The trans defects disappear and the gauche conformers increase in the PEO blocks with low-chain packing density. With increasing temperature, water is gradually replaced by polymer. Above the transition region the PO core is nearly anhydrous. Although the EO blocks undergo a little dehydration as the temperature is increased, there is water in the corona.

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References

1. Schmolka IR (1977) J Am Oil Chem Soc 54:110–116
2. Bahadur P, Riess G (1991) Tenside Surf Det 28:173–179
3. Alexandridis P, Hatton TA (1995) Colloids Surf A 96:1–46
4. Chu B, Zhou Z (1997) In: Nace VM (ed) Nonionic surfactants: polyoxyalkylene block copolymers. Dekker, New York, pp 67–143
5. Almgren M, Brown W, Hvidt S (1995) Colloid Polym Sci 273:2–15
6. Zhou Z, Chu B (1988) J Colloid Interface Sci 126:171–180
7. Alexandridis P, Holzwarth JF, Hatton TA (1994) Macromolecules 27:2414–2425
8. Al-Saden AA, Whateley TL, Florence AT (1982) J Colloid Interface Sci 90:303–309
9. Linse P (1993) J Phys Chem 97:13896–13902
10. Hurter PN, Scheutjens JMHM, Hatton TA (1993) Macromolecules 26:5030–5040
11. Guo C, Liu H-Z, Wang J, Chen J-Y (1999) J Colloid Interface Sci 209:368–373
12. Yang PW, Mantsch HH (1986) J Colloid Interface Sci 113:218–224
13. Casal HL, Mantsch HH (1984) Biochim Biophys Acta 779:381–401
14. Kimura N, Umemura J, Hayashi S (1996) J Colloid Interface Sci 182:356–364
15. Marcos JI, Oriandi E, Zerbi G (1990) Polymer 31:1899–1903
16. Cabana A, Aït-Kadi A, Juhász J (1997) J Colloid Interface Sci 190:307–312
17. Casal HL, Cameron DG, Smith ICP, Mantsch HH (1980) Biochemistry 19:444–451
18. Cameron DG, Casal HL, Mantsch HH (1979) J Biochem Biophys Methods 1:21–36
19. Goldmints I, von Gottberg FK, Smith KA, Hatton TA (1997) Langmuir 13:3659–3664
20. Zerbi G, Magni R, Gussoni M, Moritz KH, Bigotto A, Dirlikov S (1981) J Chem Phys 75:3175–3182