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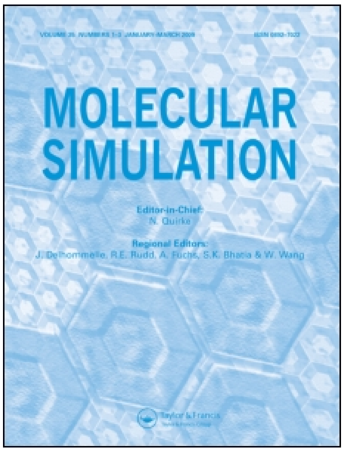

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Association Behavior of PEO–PPO–PEO Block Copolymers in Water or Organic Solvent Observed by FTIR Spectroscopy

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Fourier transform infrared (FTIR) spectroscopy is applied to investigate the association behavior of poly (ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymers in water or organic solvent as a function of temperature. In aqueous solutions, when the temperature approaches the critical micellization temperature, the antisymmetric C—H stretching vibration of methyl groups shifts toward lower wavenumber. It indicates that the methyl groups are experiencing a progressively less polar environment and the interaction of the methyl groups with water molecules is weakened by heat. At higher temperatures, the symmetric deformation vibration of methyl groups is composed of two bands, which are related to hydrated and dehydrated state. The proportion of the dehydrated methyl groups of Pluronic polymers increases with an increase of temperature, which means the exclusion of water from the micelle cores and formation of micelles with a denser PPO core at higher temperatures. A more hydrophobic Pluronic polymer would form a micelle in water with a higher proportion of dehydrated methyl groups. No changes in FTIR spectra correspond to temperature dependent gelation of Pluronic F127 in water. Based on FTIR spectroscopic results of Pluronic P104, the PPO blocks are hydrated only in a condition of lower temperature and lower polymer concentration. In the hydration process, PEO blocks would be hydrated preferentially where H_2O molecules are bound easily to PEO segments. The water-induced reverse micelle formation of Pluronic L92, in *p*-Xylene solution has also been investigated by FTIR spectroscopic technique. The reason of reverse micelle formation is explained by the strengthening of the intermolecular interactions of copolymers, which was originated from the interactions of solubilized water.

Keywords: Fourier transform infrared spectroscopy; PEO–PPO–PEO block copolymers; Critical micellization concentration; Critical micellization temperature

INTRODUCTION

In the past decade, a great deal of effort has been devoted to the study of micellization of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymers, commercially available as Poloxamers or Pluronics, in aqueous solutions [1–3]. The process of self-association can be induced by increasing the block copolymer concentration to be above the critical micellization concentration (CMC) and/or adjusting the temperature to exceed the critical micellization temperature (CMT). The structure of PEO–PPO–PEO block copolymer micelles is well described by the core-corona model in which a spherical core composed of PPO surrounding by a corona composed of the strongly hydrated PEO. At even higher concentrations in water, the block copolymer can form ordered phases, such as cubic, hexagonal and lamellar phases. The formation of the cubic phase can be understood by hard-sphere interaction between the micelles [2]. The self-assembly and phase behaviors of the block copolymers depend on the total molecular weight and the composition of the copolymer.

A variety of experimental methods have been used to measure CMC and CMT, and study the structural and dynamic properties of PEO–PPO–PEO block copolymer micelles in water. The micellization has been modeled with a mean-field lattice theory [4,5]. However, the mechanism of micellization and the structural properties of micelles remain unclear. Fourier transform infrared (FTIR) spectroscopy is

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TABLE I Composition of PEO–PPO–PEO block copolymers

Polymer	M_w	*PPO (%)*	*No. of PO units*	*No. of EO units*
P84	4200	60	43	2 × 19
L92	3650	80	50	2 × 8
P105	6500	50	56	2 × 37
P104	5900	60	61	2 × 27
P103	4950	70	60	2 × 17
P123	5750	70	69	2 × 19
F127	12600	30	65	2 × 100

a quite suitable method for observing changes in the hydration states of individual chemical groups on the polymer chain upon phase transition [6]. Recently, we reported FTIR spectroscopic investigation on the temperature-induced micellization of PEO–PPO–PEO block copolymer in water [7–11], which provides important information concerning the formation of hydrophobic microenvironment in aqueous PEO–PPO–PEO block copolymer solutions. Our aims are to provide fundamental knowledge of the association behavior of PEO–PPO–PEO block copolymers in water or organic solvent.

MATERIALS AND METHODS

Materials

PEO–PPO–PEO block copolymers were obtained from BASF Corporation and used as received. The molecular weight and composition of these Pluronic polymers studied are listed in Table I. Poly(propylene oxide), PPO1000 ($M_W = 1000$), and poly(ethylene oxide), PEO400 ($M_W = 400$), were kindly donated by Shanghai Surfactant Factory (China). Poly(ethylene glycol), PEG4000 ($M_W = 4000$), was purchased from Beijing Chemical Reagent Corporation (China). These homopolymers were also used as received. D_2O (≥99.8%) was purchased from Beijing Chemical Factory (China). Pluronic polymer solutions (15 wt%) were prepared individually by weighing appropriate amounts of the polymer and H_2O or D_2O. The solutions were facilitated mixing with gentle agitation, and then used in 24 h.

Methods

FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with a resolution of $2\,\mathrm{cm}^{-1}$ using a DTGS (deuteriotriglycine sulfate) detector. The temperature of the sample was measured by a thermocouple inserted into a stainless steel block containing the sample cell. FTIR spectra were recorded by scanning 32 times and equilibration time for each measurement was 2 min. Liquid polymers and polymer solutions were sandwiched between two BaF_2 windows of IR cell. For aqueous solutions, a spacer was also nipped to prevent evaporation during the measurement. FTIR spectra of solid polymers were obtained using the KBr pellet method. In the measurement of FTIR spectra as a function of temperature in the range from 0 to 50°C, the samples were first cooled to 0°C by liquid nitrogen and then heated stepwise with 2°C temperature interval. All spectroscopic data was further analyzed using Bruker OPUS software.

RESULTS AND DISCUSSION

Assignments of FTIR Absorption Bands

FTIR spectra of PPO1000, PEO400, PEG4000 and Pluronic polymers were recorded. The frequencies and assignments of the FTIR absorption bands are summarized in Table II. These materials have

TABLE II Assignments of FTIR bands (in cm^{-1}) of PPO1000, PEO400, PEG4000 and Pluronic P103 at 20°C

PPO1000	*PEO400*	*PEG4000*	*Pluronic P103*	*Pluronic F127*	*Assignment*
2970			2971	2971	Antisymmetric C—H stretch of CH_3
2933	2948	2945	2930		Antisymmetric C—H stretch of CH_2
2900					Symmetric C—H stretch of CH_3
2868	2866	2885	2871	2887	Symmetric C—H stretch of CH_2
1374			1373	1374	CH_3 symmetric deformation
		1360		1360	CH_2 wag, C—C stretch
	1350				
1345		1343	1345	1343	CH_2 wag
	1325				
1298	1297		1297		
		1280	1280	1281	CH_2 twist
	1249		1250		
		1242		1242	CH_2 twist
		1149		1149	C—O—C stretch, C—C stretch
1108	1108	1108	1110	1113	C—O—C stretch
		1060		1060	C—O—C stretch, CH_2 rock
1014			1014	1012	
		962		963	CH_2 rock
942	949	946	934	947	CH_2 rock, C—O—C stretch

the same skeleton; PEO400 is liquid at room temperature, but PEG4000 is solid. The profile of FTIR spectrum of Pluronic P103 is similar to that of PEO400, whereas the profile of FTIR spectrum of Pluronic F127 is similar to that of PEG4000. It is deduced that the PEO blocks in Pluronic P103 are amorphous, whereas the PEO blocks in Pluronic F127 are in the crystalline state.

Temperature-dependent Micellization of PEO–PPO–PEO Block Copolymers in Water

An increase of temperature provides the thermodynamic driving force for the transfer of PO groups in PEO–PPO–PEO block copolymer from the aqueous medium into the hydrophobic microenvironment (micellar core). For characterizing the effect of temperature on the properties of PEO–PPO–PEO block copolymer in aqueous solutions, FTIR spectra of aqueous Pluronic polymer solutions at various temperatures were measured. The changes of FTIR absorption intensities, band shapes and band positions reflect directly the influence of temperature on the properties of Pluronic polymers in aqueous solutions. The temperature-induced changes in the spectral regions of the C–H stretching vibration of methyl groups, the C–O–C stretching vibration, and the deformation vibration of methyl groups are discussed, respectively, in the following sections.

C–H Stretching Vibration

The temperature dependence of the wavenumber of the antisymmetric C–H stretching vibration of methyl groups of Pluronic P103 in D_2O and H_2O solutions is showed in Fig. 1. When the temperature is above 14°C, a change occurs leading to a shift of wavenumber abruptly toward lower frequency. The frequency change of methyl groups indicates that the dehydration process accompanies electronic redistribution in the C–H bonds. The red-shift of the antisymmetric C–H stretching vibration of methyl groups with an increase of temperature means that the interaction of the methyl groups in PPO with water molecules is weakened by heat and PPO is experiencing a progressively less polar environment.

At higher temperatures, the antisymmetric C–H stretching band of methyl groups is at $2971\,\mathrm{cm}^{-1}$, whose position approaches that of neat sample, which means that the microenvironment of methyl groups is very similar to that of neat sample. Therefore, a non-polar microenvironment would be created in aqueous solutions. The CMT is defined as the temperature at which the wavenumber deviates from the baseline contributed only by unimers at lower temperatures [7–11]. The CMT of 15 wt% Pluronic P103 in H_2O and D_2O solutions can be determined to be 14°C from Fig. 1.

C–O–C Stretching Vibration

The influence of temperature on the C–O–C stretching vibration of aqueous Pluronic P103 solutions is plotted in Fig. 2. When the temperature is raised from 0 to 50°C, the wavenumber of the band shifts toward higher wavenumber. This band is a combination of the C–O–C stretching vibrations of both PPO blocks and PEO blocks. The ether oxygen of EO and PO of PEO–PPO–PEO block copolymer dissolved in water is considered to form a hydrogen bond with the solvent water. Upon the formation of the hydrogen bond, lone pair electrons on the oxygen atom are withdrawn by the hydrogen atom of water, and therefore, a reduction of electron density on the C–O bond takes place, which induces a red shift of the C–O–C stretching band. The blue shift of the C–O–C stretching band induced by temperature is attributed to the breakdown of hydrogen bonds between the ether oxygen and water.

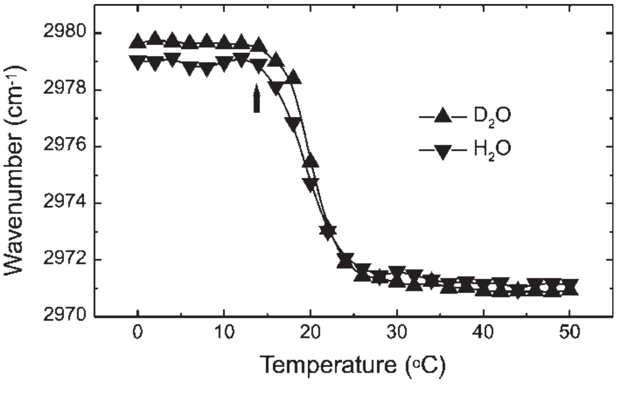

FIGURE 1 Temperature dependence of the wavenumber of the antisymmetric C–H stretching band of methyl groups of 15 wt% Pluronic P103 in D_2O and H_2O solutions, the arrow denotes the CMT.

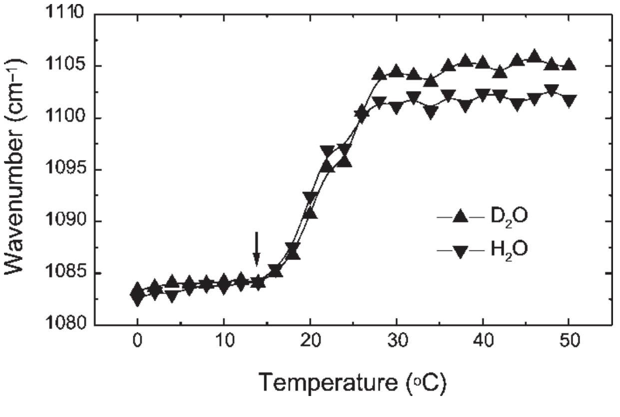

FIGURE 2 Temperature dependence of the wavenumbers of the C–O–C stretching band of 15 wt% Pluronic P103 in D_2O and H_2O solutions, the arrow denotes the CMT.

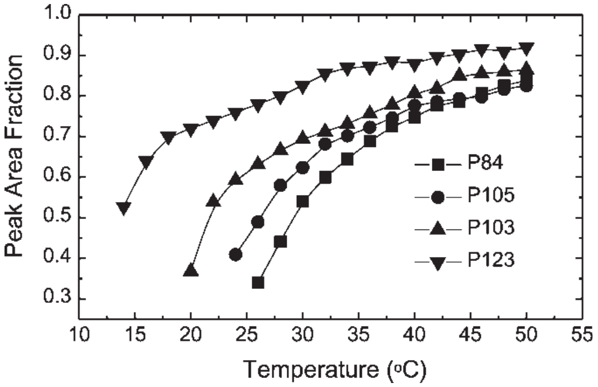

FIGURE 3 Temperature dependence of the relative peak area fractions of the dehydrated methyl groups of 15 wt% Pluronic polymers in D_2O solutions.

Since the methyl groups of PPO constitute a sterical hindrance, an optimal water structure cannot be formed in the PPO hydrous shell. The high-frequency shifts of the C–O–C stretching vibration are mainly attributed to the dehydration of PPO ether backbone.

Deformation Vibration of Methyl Groups

We observed that the symmetric deformation vibration of methyl groups splits into two bands in 15 wt% Pluronic F127 in H_2O, one is a hydrated state around 1381 cm^{-1} (surrounded by water), the other is an anhydrous state near 1373 cm^{-1} [9].

FTIR spectral profiles of 15 wt% Pluronic P84 in D_2O solution at various temperatures are examined carefully: a weak shoulder at 1373 cm^{-1} can be found in the low frequency region of 1378 cm^{-1} peak [10]. The relative peak intensity of 1378 cm^{-1} band decreases while the shoulder at 1373 cm^{-1} increases with an increase of temperature. At higher temperatures, the band at 1373 cm^{-1} dominates over the symmetric deformation band of methyl groups, and the band at 1378 cm^{-1} becomes a weak shoulder. It is deduced that the symmetric deformation vibration of methyl groups is composed of two components, which could be assigned to the hydrated state around 1378 cm^{-1} (surrounded by water), and the other is assigned to the dehydrated state at 1373 cm^{-1}. The similar changes of the symmetric deformation bands of methyl groups with temperature can also be observed in Pluronic P105, P103 and P123 in D_2O solutions.

Effect of Temperature and Polymer Composition on the Structural Properties of Pluronic Micelles

Effect of Temperature

Since the overlap of the absorption bands, the curve-fitting method was used to fit the peaks in the range from 1400 to 1320 cm^{-1}. The integrated peak areas of dehydrated (peak at 1373 cm^{-1}) and hydrated methyl groups (peak at 1378 cm^{-1}) were calculated. The total integrated peak area of dehydrated and hydrated methyl groups was normalized to 1; the normalized integrated peak area of each component corresponds to the fraction of methyl groups in dehydrated and hydrated state [10,11].

Figure 3 shows the plots of the relative peak area fractions of dehydrated methyl groups of 15 wt% Pluronic polymers in D_2O solutions estimated in this way as a function of temperature (the temperature is above CMT). The relative peak area fractions associated with the dehydrated methyl groups of Pluronic polymers increase with an increase of temperature. It illustrates that the proportion of dehydrated methyl groups increases. As the methyl groups are confined to the interior of micelles, water is gradually excluded from micellar core with an increase of temperature. PEO–PPO–PEO block copolymers would form micelles with a denser PPO core at higher temperatures. This result obtained from FTIR studies about the effect of temperature on the structural properties of PEO–PPO–PEO block copolymer micelles is consistent with that obtained by small-angle neutron scattering study [12,13].

Effect of Polymer Composition

The relative peak area fraction of dehydrated methyl groups of Pluronic P123 is higher than those of other polymers at the same temperature. Pluronic P123 is the most hydrophobic among the polymers studied, which would form micelles with a denser PPO core and a smaller amount of solvent in the micellar core than the other polymers. The relative peak area fraction of dehydrated methyl groups of Pluronic P84 is smaller than those of other polymers at the same temperature. Pluronic P84 is a more hydrophilic polymer which would form micelles with a higher concentration of water in the micellar core.

In Fig. 3, at the same temperature, the relative peak area fraction of dehydrated methyl groups in Pluronic P123 is higher than that of Pluronic P103. Pluronic P123 and P103 have the same PPO/PEO ratio; the hydrophobicity of a polymer increases with molecular weight, which increases the tendency for the polymer to aggregate and reduces the water content in the micellar core. The relative peak area fraction of hydrated methyl groups of Pluronic P105 is higher than that of Pluronic P103 at the same temperature. For a series of Pluronic polymers with nearly similar PPO size, the higher the PEO content, the higher the water content that would be contained in the micellar core [4,5].

Gelation and Hydration Process of PEO–PPO–PEO Block Copolymers

At room temperature, it is well known that higher concentration polymer solutions exhibit a dramatic change in viscosity, revealing a "thermoreversible gelation". The 15 wt% aqueous Pluronic F127 solution is liquid at room temperature, but the 20 and 30 wt% aqueous Pluronic F127 solutions are viscous, non-flowing and transparent gels. Small angle neutron scattering and small angle X-ray scattering studies unambiguously showed that the observed change in viscosity is due to a "hard-sphere crystallization"[14]. It is deduced that the effect of gelation on the spectral behavior of Pluronic F127 is too weak to be observed by FTIR spectroscopy. No changes corresponding to temperature dependent gelation can be observed in the FTIR spectra of higher concentration Pluronic F127 in water [9].

At ambient temperature, polymer/water mixture with 80 wt% Pluronic P104 is lamellar phase, 60 wt% Pluronic P104 is hexagonal phase, 40 wt% Pluronic P104 is cubic phase and 22 and 10 wt% Pluronic P104 are isotropic solutions [2]. In Fig. 4, at concentration of 80, 60 and 40 wt%, the wavenumbers of the symmetric deformation bands of methyl groups remain constant and are the same as that observed for neat Pluronic P104, which suggests that the PPO blocks are not hydrated. However, the frequencies of the symmetric deformation bands of methyl groups of aqueous Pluronic P104 solutions at concentration of 22 and 10 wt% change dramatically when the temperature is raised. The changes of the wavenumbers of the C–O–C stretching vibration of polymer/water mixtures with 80, 60, and 40 wt% Pluronic P104 are small with an increase of temperature. However, the wavenumbers of the C–O–C stretching band of 22 and 10 wt% aqueous Pluronic P104 solutions move significantly toward higher wavenumbers with an increase of temperature [11].

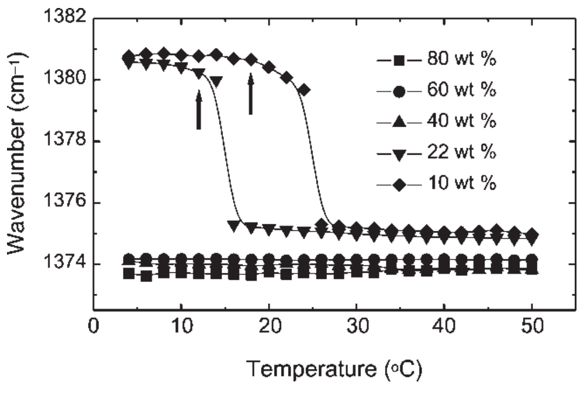

FIGURE 4 Temperature dependence of the wavenumbers of the symmetric deformation band of methyl groups of polymer/water mixtures with various Pluronic P104 content, the arrows indicate the CMT values.

Based on FTIR spectroscopic results, the PEO blocks of Pluronic P104 are hydrated in a large concentration range, while the PPO blocks are hydrated only in a condition of lower temperature and lower polymer concentration. It is suggested that the hydration of PEO–PPO–PEO block copolymer be in the following process. First, water penetrates into the most easily accessible PEO block region where H_2O molecules are bound to PEO segments. Further hydration would swell the disordered PEO blocks. Finally, when the PEO blocks are saturated with water, additional solvent would hydrate the PPO blocks of Pluronic polymer. The swell of the PEO blocks, depending on the degree of hydration, gives an increased interface area per PEO block, which would alter the interface curvature, so that the Pluronic P104 aggregate shapes generally appear in a sequence of lamella–hexagon–sphere.

Water-induced Reverse Micelle Formation in Organic Solvent

PEO–PPO–PEO block copolymers can form reverse micelles in organic solvent. The water-induced reverse micelle formation of PEO–PPO–PEO block copolymer, Pluronic L92, in *p*-Xylene solution has been investigated by FTIR spectroscopic technique. The OH stretching band of water has been resolved by deconvolution and Gaussian curve fitting. The solubilized water can be classified into monomer bound water, dimer bound water, free water and trapped water. Each state of water is sensitive to the amount of water. Therefore, their variations with the water to EO molar ratio (Z) have been employed for the detection of the reverse micelle formation and structural change [15]. It showed that the Pluronic L92 did not form polymolecular micelles when the molar ratio of water to EO (Z) is less than 0.35. For $0.35 < Z < 1.3$, spherical micelles were formed and for $Z > 1.3$, the shape of micelles could be non-spherical. The water–EO interaction dominates at all water content studied. As water was added in the Pluronic L92–*p*-Xylene system, the water–water interaction strengthened during micellization and structural change of micelles. In the meantime, the block copolymer molecules showed stronger intermolecular interactions as compared with those before transition. The mechanism of reverse micelle formation is explained by the strengthening of the intermolecular interactions of copolymers, which was originated from the water–water interaction. The results confirm the leading role of water in the reverse micelle formation of PEO–PPO–PEO block copolymer in organic solvent.

CONCLUSIONS

FTIR spectroscopy is a quite suitable method for exploring the association mechanism of PEO–PPO–PEO block copolymers in water or organic solvent. In aqueous solutions, the temperature-dependent micellization is due to that the interaction of methyl groups with water molecules is weakened by heat and the hydrogen bonding interaction of PPO with water molecules is broken gradually when the temperature is above the CMT. It is deduced from the FTIR spectral data that the proportion of the dehydrated methyl groups increases and water is excluded gradually from micellar interior with an increase of temperature. The more hydrophobic Pluronic polymer would form micelles with lower water content and a higher proportion of dehydrated methyl groups in the micellar core.

In the hydration process, first, water penetrates into the most easily accessible PEO block region where H_2O molecules are bound easily to PEO segments. Further hydration would swell the disordered PEO blocks. Finally, when the PEO blocks are saturated with water, additional solvent would hydrate the PPO blocks of Pluronic polymer.

The mechanism of reverse micelle formation in organic solvent is explained by the strengthening of the intermolecular interactions of Pluronic polymers, which was originated from the water–water interaction.

Acknowledgements

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