FTIR Spectroscopic Investigation of Effects of Temperature and Concentration on PEO−PPO−PEO Block Copolymer Properties in Aqueous Solutions

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ABSTRACT: The effects of temperature and concentration on poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) block copolymer properties in aqueous solutions were studied by Fourier transform infrared (FTIR) spectroscopy. The temperature-dependent changes of some bands were used to denote the critical micellization temperatures (cmt). It was deduced that the appearance of the symmetric deformation band of anhydrous methyl groups in the spectra of aqueous Pluronic F127 solutions at temperature below the cmt means the existence of a hydrophobic microenvironment. The appearance of the symmetric deformation band of hydrated methyl groups at temperature above the transition region indicates that the micellar core must contain a certain amount of water. The proportion of anhydrous methyl groups was increased during the micellization process with the decrease of the proportion of hydrated methyl groups. The cmt values of Pluronic F127 in aqueous solutions were decreased with an increase of concentration. In the meantime, the water content in the micellar core was also decreased. The effect of gelation on the spectral behavior of Pluronic F127 in aqueous solutions is too weak to be observed by the FTIR technique. It was found that a certain part of the PEO segments of Pluronic F127 in aqueous solutions are in the crystalline state, which is not caused by micellization and gelation. The proportion of PEO segments in the crystalline state was increased with an increase of temperature.

Introduction

Poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) triblock copolymers, commercially available as Poloxamers, Pluronics, or Synperonics, are high molecular weight nonionic surfactants. The amphiphilic property of the block copolymers leads to the self-assembly behavior resembling that of the low molecular weight surfactants. In dilute solution and at low temperature, the block copolymers dissolve in aqueous solution as unimers. With an increase of concentration or temperature, the phenomenon of critical micellization concentration (cmc) or critical micellization temperature (cmt) can be observed, while the aggregation of PEO−PPO−PEO block copolymers occurs, leading to the formation of intermolecular micelles. It is generally accepted that micelles are spherical with dense cores consisting mainly of PPO and hydrated PEO swollen coronas.[1−8] This type of structure is attributed to the fact that PPO is lipophilic and PEO is hydrophilic. There is a broad temperature range (transition region) above the cmt where micelles coexist in solution with unimers. When the temperature is above the transition region, most copolymer molecules form micelles. While at still higher temperature, a cloud point is reached, and the copolymer solutions become opaque due to phase separation.

For some PEO−PPO−PEO block copolymers at an appropriate concentration and temperature with the volume fraction of micelles in solution exceeds 0.53, the block copolymer micelles overlap to yield a thermoreversible gel-like medium with supramolecular crystalline structure.[9−15] Aqueous Pluronic F127 solutions at concentrations above 17% show interesting thermoreversible gelation behavior; this gel is attractive for delivery of poorly water-soluble drugs. Pluronic F127 also has the potential to be used as an effective separation medium in capillary electrophoresis for the separation of biomacromolecules, such as DNA fragments and proteins.[11] Recently, Feng reported that at room temperature the synthesis of periodic mesoporous silica by templating with liquid crystal phases prepared from ternary systems consisting of Pluronic F127, cosurfactants, and water.[16]

Though the general micellization and gelation behavior of PEO−PPO−PEO block copolymers has been extensively studied, the “molecular level” mechanism of micellization and gelation remains unclear. Hurter[17,18] and Linse[19,20] have modeled the micellization with a mean-field lattice theory. In this theory the polymer segments are allowed to assume both polar and nonpolar conformations, which are corresponding to the gauche conformer of the C−C skeleton is favored in polar environment and the trans conformer dominates in nonpolar environment. The segment density profiles of the predicted micelles indicate that there is a finite concentration of water in the micellar core.

Vibrational spectroscopy is a very powerful technique which has been extensively used to study the conformation of hydrocarbon chains in the normal low molecular weight surfactant micelles in aqueous solution.[21−26] Many spectral features of the low molecular weight surfactants are sensitive to the conformational changes, the inter- and intramolecular interactions, and the chain mobility. In our previous work, we have reported that FT-Raman and FTIR spectra of PEO−PPO−PEO block copolymers are sensitive to the local polarity and the conformation of block copolymer chains and also their

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Table 1. Assignments of FTIR Bands (in cm^{-1}) of PPO1000, PEO400, PEG4000, and Pluronic F127 at 25 °C

PPO1000	PEO400	PEG4000	F127	assignment[a]
1373			1374	CH_3 symmetry deformation
		1360	1360	CH_2 wag, C−C stretch
1345	1350	1343	1343	CH_2 wag
	1325			
1298	1297	1280	1281	CH_2 twist
	1249	1242	1242	CH_2 twist
		1149	1149	C−O−C stretch, C−C stretch
1108	1108	1108	1113	C−O−C stretch
		1060	1060	C−O−C stretch, CH_2 rock
1014			1012	
	996			
		962	963	CH_2 rock
942	949	946	947	CH_2 rock, C−O−C stretch

[a] Assignment based on refs 31 and 32.

variations with temperature are indicators of micellization.[27,28] The purpose of this work is to explore the temperature-dependent micellization and gelation of PEO−PPO−PEO block copolymer in aqueous solutions using FTIR spectroscopy.

Materials and Methods

PEO−PPO−PEO block copolymer Pluronic F127 was obtained from BASF Corp. and used without further purification. Pluronic F127 has a normal molecular weight of 12 500 and a PEO content of 70%. On the basis of molecular weight and chemical composition, F127 can be represented by the formula $EO_{99}-PO_{69}-EO_{99}$. Poly(propylene oxide), PPO1000 (MW = 1000), and poly(ethylene oxide), PEO400 (MW = 400), were kindly donated by Shanghai Surfactant Factory (China). Poly(ethylene glycol), PEG4000 (MW = 4000), was purchased from Beijing Chemical Reagent Corp. (China). These homopolymers were also used as received. Aqueous solutions of PPO1000, PEO400, PEG4000, and Pluronic F127 were prepared by dissolving the copolymer in distilled water with gentle agitation and then stored in a refrigerator.

FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with a resolution of 2 cm^{-1} using DTGS (deuteriotriglycine sulfate) detector. The temperature of the sample was measured with a thermocouple inserted into a stainless steel block containing the sample cell. This system is comprised of a Graseby-Specac temperature cell (P/N 21525), and the temperature measurement was accurate to 0.1 °C. Equilibration time for each temperature was 2 min. FTIR spectra of PPO1000, PEO400, and aqueous polymer solutions were recorded by scanning 64 times and using a BaF_2 cell. FTIR spectra of PEG4000 and Pluronic F127 were obtained using the KBr pellet method. The OUPS spectroscopic software was used for data handling.

Results and Discussion

Spectrum of Pluronic F127. FTIR spectra of Pluronic F127 and its related compounds, PPO1000, PEO400, and PEG4000, in the 1400−900 cm^{-1} region were recorded; the frequencies of FTIR absorption bands and assignments are summarized in Table 1. These materials have the same skeleton. PPO1000 and PEO400 are liquid at room temperature, while PEG4000 and Pluronic F127 are solid. It is found that band shapes and band positions of Pluronic F127 are similar to those of the PEG4000 spectrum. The band positions of Pluronic F127 are in a very good agreement with those reported in the literature for the PEO crystalline phase.[29−32] It can be concluded that the PEO blocks of Pluronic F127 are in the crystalline state, whereas PEO400 at 25 °C is amorphous. The existence of methyl groups is confirmed by observing the band at 1374 cm^{-1} in the spectrum of Pluronic F127. The weak band at 1014 cm^{-1} of PPO1000 appears in the spectrum of Pluronic F127 with position at 1012 cm^{-1}.

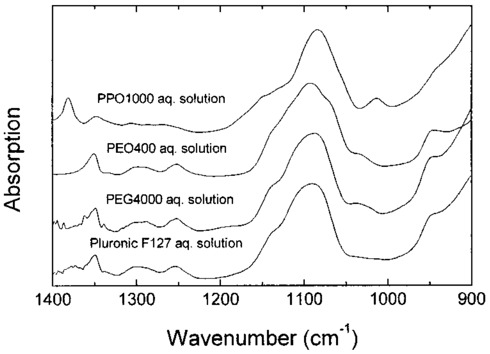

Figure 1. FTIR spectra of 15 wt % aqueous PPO1000, PEO400, PEG4000, and Pluronic F127 solutions at 25 °C in the range from 1400 to 900 cm^{-1}.

Spectrum of Pluronic F127 in Aqueous Solution. FTIR spectra for 15 wt % aqueous PPO1000, PEO400, PEG4000, and Pluronic F127 solutions at 25 °C are shown in Figure 1. The 1360 and 1343 cm^{-1} bands of Pluronic F127 almost disappear in the spectrum of aqueous Pluronic F127 solution. The sharp bands at 1281 and 1242 cm^{-1} of Pluronic F127 become broad and shift toward high frequencies, 1300 and 1254 cm^{-1}, respectively. The bands at 1060 and 963 cm^{-1} of Pluronic F127 disappear in the spectrum of aqueous Pluronic F127 solution. The changes of the characteristic bands for PEO crystalline structure indicate that the PEO blocks of Pluronic F127 in aqueous solution are in the amorphous state. This conclusion is supported by the assignment of the 1349 cm^{-1} band to the amorphous phase.[31] On the whole, the profile of the FTIR spectrum of 15 wt % aqueous Pluronic F127 solution is rather similar to those of PEO400, 15 wt % aqueous PEO400, and PEG4000 solutions.

Another important infrared-active mode is the symmetric deformation vibration of methyl groups, which is sensitive to the local environment and the intermolecular interaction. When PPO1000 is dissolved in water, the 1373 cm^{-1} band shifts toward 1381 cm^{-1}. The symmetric deformation band of methyl groups of 15 wt % aqueous Pluronic F127 solution is at 1377 cm^{-1} (1381 cm^{-1} at low temperature). The weak 1373 cm^{-1} band can also be found in the spectra of aqueous Pluronic F127 solution (see Figures 1 and 2). We deduced that the symmetric deformation vibration of methyl groups splits into two bands: one is the hydrated state around 1381 cm^{-1} (surrounded by water), and the other is the anhydrous state near 1373 cm^{-1}. The band of the symmetric deformation vibration of anhydrous methyl groups does not appear in the spectrum of aqueous PPO1000 solution; the reason may be that the molecular weight of PPO block in Pluronic F127 is higher than that of PPO1000. The microenvironment around hydrated methyl groups is polar while around anhydrous methyl groups is nonpolar.

When Pluronic F127 is dissolved in water, the C−O−C stretching band becomes broad with a shift from 1113 to 1090 cm^{-1} (1085 cm^{-1} at low temperature). The low-

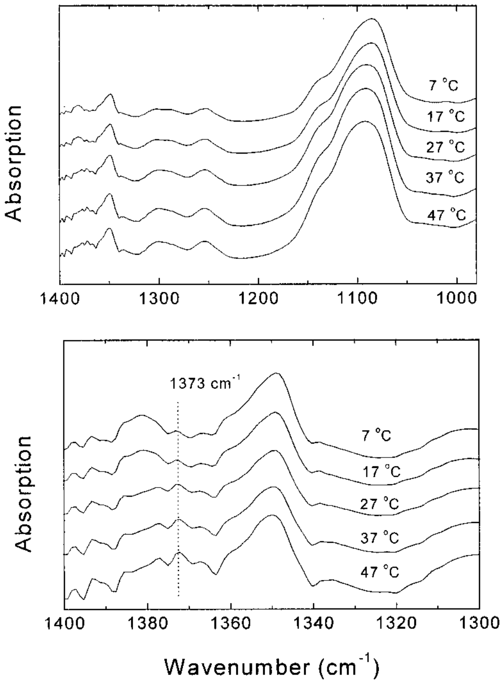

Figure 2. Temperature-dependent FTIR spectra of 15 wt % aqueous Pluronic F127 solution: the top is in the range from 1400 to 950 cm^{-1}, and the bottom is in the range from 1400 to 1300 cm^{-1}.

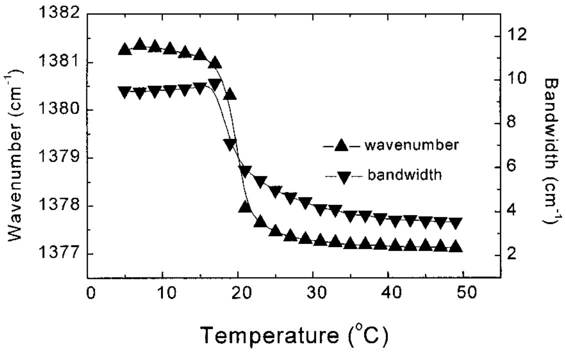

Figure 3. Temperature dependence of the wavenumber and bandwidth of the 1381 cm^{-1} band of 15 wt % aqueous Pluronic F127 solution.

frequency shift of the band is attributed to the formation of hydrogen bonds between oxygen atoms in the ether backbone of Pluronic F127 and water molecules. The broadening of the C—O—C stretching band indicates that the block copolymer in aqueous solution has a higher mobility. The broad background, observed in the region below 1000 cm^{-1}, is due to the bands of water.

Temperature Effect on the Properties of Pluronic F127 in Aqueous Solution. For characterizing PEO—PPO—PEO temperature-dependent properties in aqueous solution, FTIR spectra of 15 wt % aqueous Pluronic F127 solution at various temperatures are shown in Figure 2. The changes of absorption intensities, band shapes, and band positions directly reflect the temperature-dependent properties of Pluronic F127 in aqueous solution as a consequence of changes in the inter- and intramolecular interactions and the molecular conformation.

The changes of frequency and bandwidth of the symmetric deformation band of hydrated methyl groups as a function of temperature are presented in Figure 3. In the temperature range from 5 to 17 °C, the frequency of 1381 cm^{-1} band is decreased slightly with increasing temperature. A change occurs in the temperature interval from 17 to 29 °C; the band shifts abruptly from 1381 toward 1377 cm^{-1}. Since the shift causes the band to be closer to that of neat sample, it indicates a reduction of the interaction between methyl groups and water molecules with a decrease of the polarity of the microenvironment around hydrated methyl groups. It is considered to be related to Pluronic F127 aggregation and formation of micelles. When the temperature is above 29 °C, the frequency of the band was decreased slowly with an increase of temperature. The same tendency of bandwidth change with temperature is observed for the 1381 cm^{-1} band. A decrease in bandwidth means a decrease of the mobility of hydrated methyl groups. When the aggregates are formed, the methyl groups exist in a more fixed position; therefore, there is a dramatic decrease of the mobility of methyl groups. The wavenumber of the symmetric deformation band of anhydrous methyl groups is not changed with increasing temperature from 5 to 50 °C and remains at 1373 cm^{-1} (the 1373 cm^{-1} band is indicated in Figure 2).

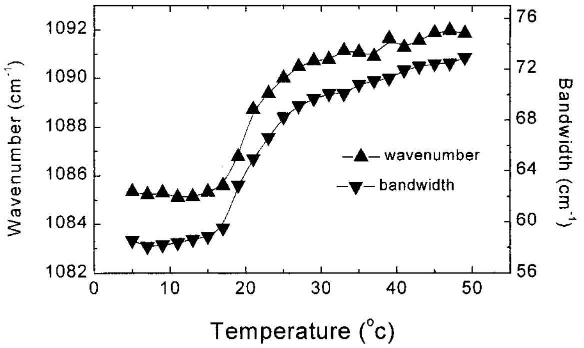

Figure 4. Temperature dependence of the wavenumber and bandwidth of the 1090 cm^{-1} band of 15 wt % aqueous Pluronic F127 solution.

The influence of temperature on the strongest band at 1085 cm^{-1} is presented in Figure 4. This band is a conjugation of the C—O—C stretching vibration of both PPO and PEO blocks. When the temperature was increased from 5 to 50 °C, the frequency of the band shifting toward higher wavenumbers may be related to the dehydration of the ether backbone, and the bandwidth broadening means that further disorder of the conformation of the C—O—C skeletons. It is known that the PEO blocks undergo a small degree of dehydration with an increase of temperature, but the hydrophobic PPO blocks apparently reduce contact with water during the micellization process.[1-8] Because of dehydration, the C—O—C skeletons of the PPO blocks experience a different microenvironment from that of the PEO blocks, which gives rise to a different FTIR frequency of the C—O—C stretching vibration. This distribution of frequency results in a broadening of the C—O—C stretching bandwidth.

A convenient way of using FTIR spectroscopy to detect the temperature-induced micellar formation is to monitor the temperature dependence of infrared key bands. It is evident that a drastic change of the infrared spectrum occurs in a small temperature range, with little change either lower or higher than this temperature range. An increase in temperature of copolymer solution provides the thermodynamic driving force for the transfer of water from the copolymers to bulk water.

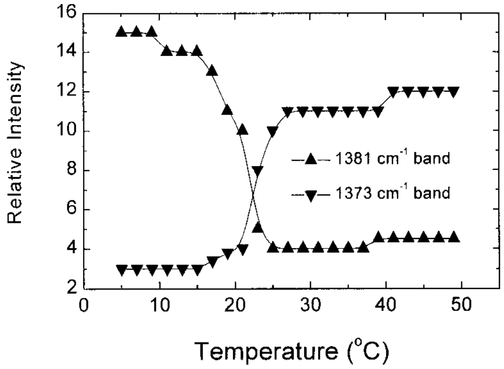

Figure 5. Temperature dependence of the relative peak intensities of the symmetric deformation bands of hydrated and anhydrous methyl groups of 15 wt % aqueous Pluronic F127 solution.

The progressive losses of the PPO hydrous shell will influence the spectral behavior of Pluronic copolymer. The cmt is defined as the temperature at which the wavenumber or bandwidth deviates from baseline contributed only by unimers. In Figure 3, the cmt of 15 wt % aqueous Pluronic F127 solution can be destined at 17 °C. The same result can also be obtained from Figure 4. Above the cmt, there is an equilibrium region referred to as the unimer-to-micelle transition region, where significant amounts of both free and associated copolymer molecules coexist.[33−37] This temperature region for 15 wt % aqueous Pluronic F127 solution can be obtained from Figures 3 and 4 as from 17 to 29 °C, which is a temperature range with spectral data showing dramatic change.

Using the FTIR technique, it was found that methyl groups in hydrous and anhydrous states coexist at temperature below the cmt. The anhydrous methyl groups are hydrophobic and could solubilize hydrophobic compounds. Bohorquez has noted that the solubility of pyrene in Pluronic F127 solution is significantly higher than that in water, even in the absence of micelles (temperature below the cmt).[14] The existence of anhydrous methyl groups in Pluronic F127 aqueous solution at lower temperatures can explain this phenomenon. It can be seen from Figures 2 and 5 that the relative peak intensity associated with anhydrous methyl groups is increased with an increase of temperature, while the relative peak intensity associated with hydrated methyl groups is decreased. It indicates that the proportion of anhydrous methyl groups is increased, while the proportion of hydrated methyl groups is decreased with increasing temperature. Incorporation of unimers into micelles and dehydration of micellar core can be considered as the reason for changes of the relative peak intensities vs temperature. However, the symmetric deformation band of hydrated methyl group does not disappear completely at temperatures above the transition region, and some water may remain in the micellar core even at higher temperature; this is consistent with the results obtained by Goldmints.[36,37]

Concentration Effect on the Properties of Pluronic F127 in Aqueous Solutions. At room temperature, it is well-known that higher concentration Pluronic F127 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, nonflowing, 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" as the micellar concentration approaches the critical volume fraction of 0.53.[10,11] In the gel region the micellar aggregation number is not sensitive to the concentration change.

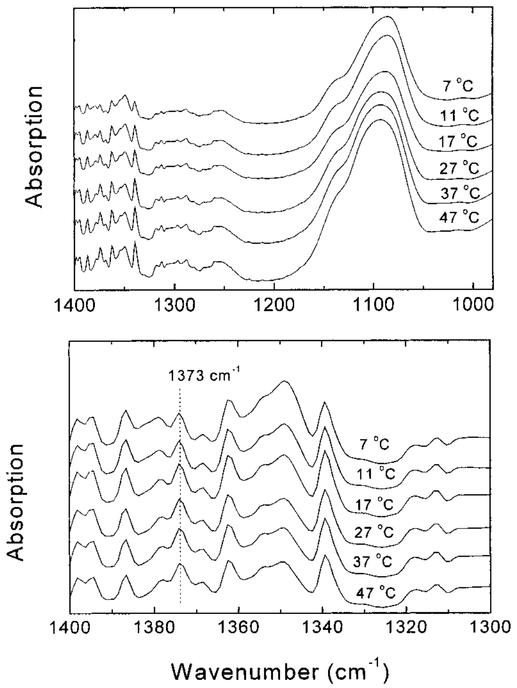

Figure 6. Temperature-dependent FTIR spectra of 20 wt % aqueous Pluronic F127 solution: the top is in the range from 1400 to 950 cm^{-1}, and the bottom is in the range from 1400 to 1300 cm^{-1}.

Figure 6 shows the temperature-dependent spectra of 20 wt % aqueous Pluronic F127 solution. The symmetric deformation band of hydrated methyl groups is at 1378 cm^{-1}, and that of the anhydrous methyl groups is at 1373 cm^{-1}, while both band positions do not change with increasing temperature. The relative peak intensity of the symmetric deformation band of anhydrous methyl groups is increased with an increase of temperature, while the relative peak intensity of the symmetric deformation band of hydrated methyl groups is decreased. There is a very weak peak at 1378 cm^{-1} and a moderately strong and sharp peak at 1373 cm^{-1} when the temperature is above 27 °C.

Figure 7 shows the temperature-dependent spectra of 30 wt % aqueous Pluronic F127 solution. The symmetric deformation band of hydrated methyl groups can only be observed at low temperatures, such as 7 and 11 °C. A very weak shoulder at 1377 cm^{-1} can be found when the temperature is above 17 °C. This indicates that the proportion of hydrated methyl groups is very small at high temperature; almost all methyl groups of Pluronic F127 are in the anhydrous state.

It can be seen from Figures 4, 8, and 9 that the variations of wavenumber and bandwidth of the C−O−C stretching vibration of Pluronic F127 in aqueous solutions at concentrations of 20 and 30 wt % as a function of temperature are similar to those of Pluronic F127 at concentration of 15 wt %. The concentration-dependent cmt can be obtained from Figures 8 and 9. The cmt values of Pluronic F127 in aqueous solutions at concentrations of 20 and 30 wt % are 13 and 9 °C, respectively. The increase of concentration would decreases the cmt

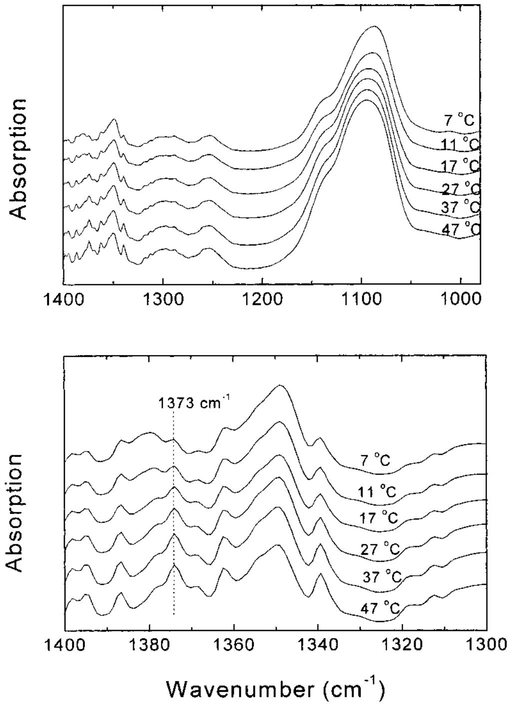

Figure 7. Temperature-dependent FTIR spectra of 30 wt % aqueous Pluronic F127 solution: the top is in the range from 1400 to 950 cm^{-1}, and the bottom is in the range from 1400 to 1300 cm^{-1}.

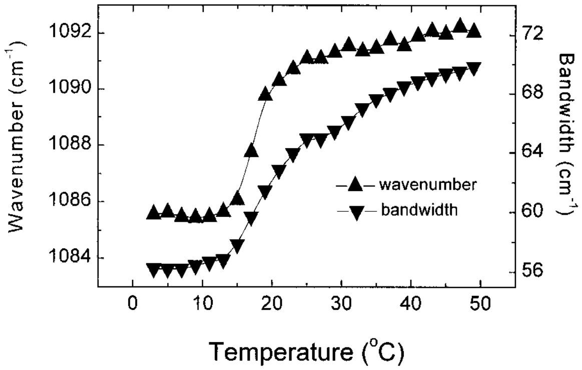

Figure 8. Temperature dependence of the wavenumber and bandwidth of the 1090 cm^{-1} band of 20 wt % aqueous Pluronic F127 solution.

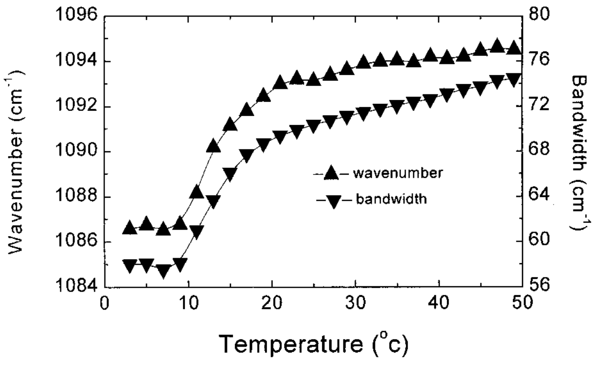

Figure 9. Temperature dependence of the wavenumber and bandwidth of the 1090 cm^{-1} band of 30 wt % aqueous Pluronic F127 solution.

value, which is consistent with dilute aqueous Pluronic F127 solutions.[2,3] The transition region is about from 13 to 25 °C for 20 wt % aqueous Pluronic F127 solution and from 9 to 21 °C for 30 wt % aqueous Pluronic F127 solution. The variation of concentration does not influence the width of transition region.

It is feasible to demonstrate qualitatively the effect of concentration on the properties of PEO−PPO−PEO block copolymer. The symmetric deformation band of hydrated methyl groups appears in the spectra of Pluronic F127 of 15 and 20 wt % aqueous solutions even at higher temperatures (see Figures 2 and 6); this indicates that the micellar core must contain a certain amount of water. But at higher temperatures only the symmetric deformation band of anhydrous methyl groups appears in the spectra of 30 wt % aqueous Pluronic F127 solution; this means that the micellar core contains a very small amount of water (see Figure 7). Comparing the ratio of the relative peak intensities of anhydrous methyl groups to those of hydrated methyl groups, it is deduced that the water content in the micellar core decreased with increasing Pluronic F127 concentration.

Pluronic F127 gelation is due to the close packing of spherical micelles. The gel point can be obtained from rheology and differential scanning calorimetry measurements.[9] The heat values of gelation are about 2 orders of magnitude smaller than the corresponding values for micelle formation.[1,9] However, the effect of gelation on the spectral behavior of Pluronic F127 is too weak to be observed in Figures 6 and 7. No change of FTIR spectral data corresponding to the temperature-dependent gelation can be observed in the spectra of Pluronic F127 solutions at higher concentration.

It should be emphasized that the distinct sharp peaks at 1362 and 1340 cm^{-1} appear in the spectra of aqueous Pluronic F127 solutions at concentrations of 20 and 30 wt %. Sharp peaks at 1360 and 1343 cm^{-1} appear in the spectrum of pure PEG4000, which is assigned to the CH_2 wagging vibration for the PEG4000 crystalline phase. But in the spectrum of 15 wt % aqueous PEG4000 solution weak peaks at 1362 and 1340 cm^{-1} appear at both sides of the moderately strong 1349 cm^{-1} band (see Figure 1). The bands at 1362 and 1340 cm^{-1} are very close to the bands of the PEG4000 crystalline phase at 1360 and 1343 cm^{-1}; the band at 1349 cm^{-1} is assigned to CH_2 wagging vibration of the amorphous state.[31] PEG is completely miscible with water, but the nature and extent of hydration of PEG in aqueous mixtures remain uncertain despite the work have been carried out by numerous investigators.[38−41] It is possible that a few segments of PEG4000 in aqueous solutions are in the crystalline structure. Li and Hsu observed that the intensity of a doublet at 1360 and 1343 cm^{-1} decreased with decreasing crystallinity in a PEO/poly(methyl methacrylate) blend, and this decrease appeared to be correlated with a corresponding intensity increase of a band at 1349 cm^{-1}.[42] They used the relative intensities of these three bands to characterize the crystallization process.

In this work, we deduced that the bands at 1362 and 1340 cm^{-1} are from a part of PEO segments that are in the crystalline structure. Even when the temperature is below the cmt, the peaks at 1362 and 1340 cm^{-1} appear in the spectra of aqueous Pluronic F127 solutions at concentrations of 20 and 30 wt % (see Figures 6 and 7). It is not the micellization and gelation that cause a part of the PEO segments to be in the crystalline structure. The relative peak intensities of 1362 and 1340 cm^{-1} bands are increased with increasing temperature, while the relative peak intensity of the 1349 cm^{-1} band is decreased. This means that the proportion of PEO segments of aqueous Pluronic F127 solutions in the crystalline structure increases with an increase of temperature.

Conclusions

This study has shown that FTIR spectroscopy is an excellent technique for investigation of the effects of temperature and concentration on the properties of PEO−PPO−PEO block copolymer in aqueous solutions at higher concentrations. The relative peak intensity of the symmetric deformation band of anhydrous methyl groups is increased with increasing temperature, while the peak intensity of the symmetric deformation band of hydrated methyl groups is decreased. It indicates that the proportion of anhydrous methyl groups is increased, and the proportion of hydrous methyl groups is decreased during the micellization process. The dehydration of Pluronic F127 ether backbone with increasing temperature could also be inferred by FTIR spectral data from a shift of the frequency of the C−O−C stretching band toward higher wavenumbers and broadening of the bandwidth of the C−O−C stretching vibration.

The cmt values of Pluronic F127 in aqueous solutions are decreased with increasing concentration. In comparison with the ratio of the relative peak intensity of anhydrous methyl groups to that of hydrated methyl groups, it is deduced that the water content in the micellar core is also decreased with increasing concentration. The gelation is due to the close packing of spherical micelles; no change of FTIR spectral data corresponding to the temperature-dependent gelation can be observed in the spectra of Pluronic F127 solutions at high concentrations. It is found that a part of PEO segments of Pluronic F127 in aqueous solutions are in the crystalline state, which is not caused by the micellization and gelation. The degree of PEO segments in the crystalline state for aqueous Pluronic F127 solution with concentration of 20 wt % is higher than those at concentrations of 15 and 30 wt %.

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