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Thermoreversible micellization and gelation of a blend of pluronic polymers

Lin Li*, Lee Hoon Lim, Qiqiang Wang, San Ping Jiang

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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Abstract

Aqueous solutions of a blend consisting of a PEO–PPO–PEO triblock copolymer, Pluronic F127 (EO_{100}–PO_{65}–EO_{100}) and a PPO–PEO–PPO triblock copolymer, Pluronic-R 25R4 (PO_{19}–EO_{33}–PO_{19}) were studied. Thermoreversible micellization and gelation properties of the blend were examined as a function of temperature and molar ratio of 25R4 to F127 by means of micro DSC and rheology. The completely thermoreversible behaviors of micellization and gelation were observed for all the blend solutions with two F127 concentrations (10 and 15 wt%) and various 25R4/F127 molar ratios (0–4) even though the pure 25R4 solution itself was not thermoreversible. At a given concentration of F127, three effects of 25R4 on F127 were found as follows. (a) The micellization temperature of F127 shifts to a lower temperature with increasing 25R4 content, implying a "salt-out like" effect of 25R4. (b) Beyond the primary peak for micellization a secondary peak appears due to the effect of 25R4. (c) At the molar ratio of 25R4/F127 = 3:1, the gelation of the 15 wt% F127 solution occurs twice at low and high temperatures, respectively. When the ratio > 3:1, the gelation occurs only at high temperatures. The possible mechanisms involved in these unique behaviors of micellization and gelation have been proposed and discussed. The effect of 25R4 on F127 was compared with another Pluronic polymer F108 (EO_{133}–PO_{50}–EO_{133}).

Keywords: Pluronic; Micellization; Gelation

1. Introduction

Water-soluble triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) are well known as nonionic polymeric surfactants [1,2]. A great number of research works on the triblock copolymers of PEO and PPO have been available in the literature [1–30]. In general, there are two types of triblock copolymers of PEO and PPO. One with the sequence of PEO–PPO–PEO is commercially known as Pluronics (manufactured by BASF) or Poloxamers (manufactured by ICI) while another with the reverse sequence (PPO–PEO–PPO) is named Pluronics-R (BASF). Variation of PPO/PEO ratio and molecular weight (length of PEO and PPO blocks) leads to the production of triblock copolymers with various compositions and properties that meet the specific requirements in numerous applications such as detergents, dispersion stabilizers, foaming agents, emulsifiers, lubricants, drug solubilizers, drug carriers for controlled delivery and release, burn wound covering, etc. [1,2].

At low temperatures such as room temperature, both the PEO and the PPO blocks are hydrophilic and hence soluble in water to form a transparent solution. At this stage, the triblock copolymers remain as unimers surrounded by water molecules with hydrogen bonds formed between them. Upon heating, the PPO blocks in an aqueous solution gradually become hydrophobic and insoluble at high temperatures while the PEO blocks are still hydrophilic and remain soluble in water. Thus, at high temperatures, molecular aggregation of hydrophobic PPO blocks takes place. The aggregation of the PPO blocks leads to the formation of micelles when the critical micellization concentration (CMC) or the critical micellization temperature (CMT) is reached [1,2,16]. The micellization process of PEO–PPO–PEO copolymers in water is endothermic and driven by a decrease in the polarity of ethylene oxide (EO) and propylene oxide (PO) segments as temperature increases and by the entropy increase in water when unimers aggregate to form micelles [2]. In addition,

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* Corresponding author. Tel.: +65 6790 6285; fax: +65 6791 1859.
E-mail address: mlli@ntu.edu.sg (L. Li).

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since micellization of a Pluronic polymer is a temperature-dependent physical process, it is thermally reversible when precipitation does not occur.

When the copolymer concentrations are high, the micelles formed may further develop into structured systems, such as micellar crystals or gels [1,2,4,5,23,25]. The onset temperature of gelation and the thermal stability range of the gel increase with increasing PEO block length [2].

Pluronic F127 ($EO_{100}-PO_{65}-EO_{100}$) is one of the well-known typical Pluronics because of its high ratio of EO/PO (70 wt% EO) and big molar mass (3780) of PPO as compared to other members of Pluronics. The micellization behavior, micellar structures, and gelation properties of F127 have been extensively studied by many researchers [1,2,5,12,13,15–18,20,23,24]. The phase diagram of F127 is also available in the literature [2,13]. The critical micellization concentration (CMC) of F127 decreases remarkably with temperature [6]. For example, the critical micellization temperature (CMC) of F127 is 1 wt% at 25 °C but decreases to 0.03 wt% at 35 °C [6]. This temperature-dependence of CMC is due to the increased hydrophobicity of PO blocks by temperature.

While a number of research works have been available in the literature for Pluronics copolymers, few studies can be found for Pluronics-R [26–29]. 25R4 ($PO_{19}-EO_{33}-PO_{19}$) was studied by SAXS and NMR, and found not to form spherical micelles in dilute solutions [29]. For Pluronics-R copolymers to form micelles, looping of the polymer chains is important. Since the molecular looping for the Pluronics-R chains with short EO blocks will require a great reduction in entropy, it will not be favorable thermodynamically. In concentrated solutions (18–40 wt%), it is possible to form interconnected micelles in which the two outer PPO blocks of a chain participate in two different micelles or aggregates [26].

In our previous study [30], we found that an aqueous solution (13.2 wt%) of 25R4 itself was not thermoreversible. The dehydration of 25R4 occurred, as indicated by a broad endothermic peak, in a heating process but the precipitation occurred as evidenced by the fact that there were no exothermic peaks detectable in the subsequent cooling process [30].

While individual Pluronics or Pluronics-R have been studied, it is interesting to study a blend of a Pluronic copolymer and a Pluronic-R copolymer. Since the PO blocks in both Pluronics and Pluronics-R are of the same chemical structure, it is reasonably expected that the PO blocks of PPO–PEO–PPO molecules would participate in the micellization of PEO–PPO–PEO molecules and vice versa. At high concentrations, gelation of the blend would be affected too. However, we have not found any studies for such a blend. Since 2004, we have been working on the Pluronics/Pluronics-R blends. The first piece of our work was the study on the effects of 25R4 on the thermoreversible micellization and gelation properties of a Pluronic F108 ($EO_{133}-PO_{50}-EO_{133}$) [30]. It was observed that 25R4 did not affect the thermoreversibility of F108 but it caused the significant salt-out like effect on the micellization of F108. Furthermore, a secondary endothermic peak occurred beyond the primary micellization peak of F108, indicating the strong interaction between the two polymers.

In the present work, another Pluronic polymer, F127, is chosen as the base polymer because of its highest PPO content within the Pluronic family [2], well-known micellization properties and micellar structures [1,2,5,12,13,15–18,20,23,24]. 25R4 is used as an "additive" in order for us to investigate its effects on the thermoreversible micellation, gelation, and formation of micellar and network structure of F127 in aqueous solutions. Micro DSC is used for the micro-thermal analysis while fluid rheology is employed for the rheological observation. The effects of 25R4 on F127 are analyzed as functions of temperature, blend composition, and polymer concentration. The possible driving mechanisms and microstructures formed during micellization and gelation will be proposed and discussed.

2. Experimental

2.1. Materials

Pluronic F127 and Pluronic-R 25R4 were kindly provided by BASF Corp. The molecular structures of F127 and 25R4 are $EO_{100}-PO_{65}-EO_{100}$ and $PO_{19}-EO_{33}-PO_{19}$ with molecular weights of 12,600 and 3,600, respectively. F127 has a form of flakes at room temperature, and its melting point is 56 °C, while 25R4 is a wax-like material at room temperature. The materials were used as received. Before use, the materials were vacuum-dried at 50 °C and kept in a desiccator to avoid the absorption of moisture. Two concentrations of 10 wt% and 15 wt% of F127 were prepared. To each concentration of F127, 25R4 was added to achieve the molar ratio of 25R4/F127 = 0.5:1, 1:1, 2:1, 3:1 and 4:1, respectively.

In addition, a 17.1 wt% 25R4 solution was also prepared. 17.1 wt% is the highest concentration of 25R4 used in this study. The sample solutions were placed into a refrigerator and kept for 24 h before use.

2.2. Micro-thermal analysis

A micro-differential scanning calorimeter (VP-DSC Microcalorimeter, Microcal Inc.) was used to determine the thermal properties of the solutions through a thermal cycle of heating-to-cooling. The reference cell was always filled with deionized water. The sample was injected to the sample cell of a volume 0.516 mL. The slow heating and cooling rates of 0.5 °C/min were employed in order to fully explore the details of the thermal behavior of the F127/25R4 blends in water. After each cycle was completed for the sample, the sample cell was cleaned by a continuous flow of deionized water. A water–water baseline DSC test was followed to insure the condition of no-contamination of the sample cell by the last sample.

2.3. Rheological measurements

The rheometer (ARES 100FRTN1, Rheometric Scientific) with a geometry of parallel plates was used. The parallel plates of 25 and 50 mm in diameter were used for the relatively high and low viscosity solutions, respectively. The dynamic viscoelastic functions such as shear storage modulus G' and loss modulus G'' were measured as a function of temperature. To prevent dehydration during the rheological measurements, a thin layer of low viscosity silicone oil was placed on the periphery surface of the solution held between the plates.

All the dynamic viscoelastic measurements (e.g. temperature ramp) were carried out at an angular frequency of 1 rad/s. The samples in the liquid state were first loaded to the bottom plate of the rheometer at room temperature and tested through a temperature ramp mode, in which G' and G'' were measured during a heating process from about 25 to about 75 °C. Large strains (>5%) were applied before the vicinity of the sharp increase of G' and G'' to meet the minimum torque requirement that the transducer could detect, while from the sharp increase of G' and G'' (i.e. the sol–gel transition), the strains applied were adjusted to be below 1% gradually to ensure the gel like sample was tested in the linear region of viscoelasticity.

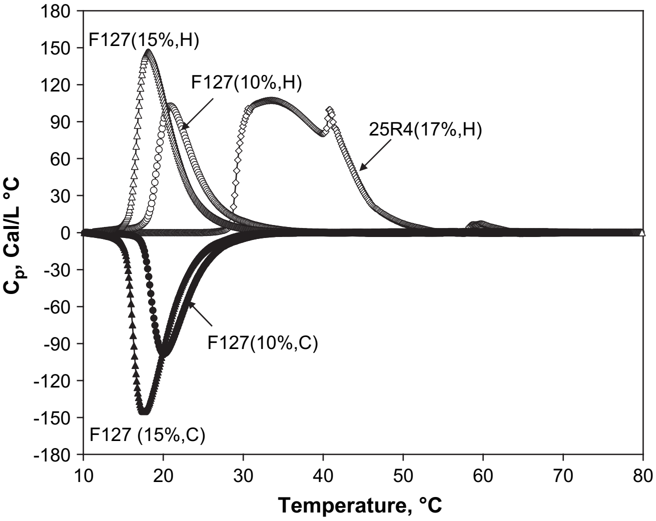

Fig. 1. Thermal capacity, C_p, as a function of temperature for two F127 aqueous solutions (10 and 15 wt%) and a 17.1 wt% 25R4 solution during a thermal cycle from 10 to 80 °C at a scanning rate of 0.5 °C/min. The letters "H" and "C" mean "heating" and "cooling", respectively. The cooling curve is not shown for the 25R4 solution.

3. Results and discussion

3.1. Thermal reversibility of 25R4 and F127

Before studying the thermal behavior of a blend of F127 and 25R4, it is important to know the thermal property of each component polymer. In our previous study on a blend of F108 and 25R4 [30], 25R4 was not found to exhibit the thermal reversibility that is often observed for most Pluronic polymers. The fact that 25R4 doesn't show the thermoreversible behavior is because of the precipitation that occurs at high temperatures. 25R4 exhibits a broad endothermic peak of micellization, but does not show any detectable exothermic peak(s) in the subsequent cooling process. In this work, for a purpose of confirmation, a 17.1 wt% of pure 25R4 was scanned using micro DSC at a slow scanning rate of 0.5 °C/min for two cycles of heating-to-cooling. The concentration of 17.1 wt% was the highest of 25R4 used in this study for the blends of F127 and 25R4. In addition, in order to investigate the effect of temperature range on precipitation, two sets of temperature range were used: 10 °C–80 °C and 10 °C–70 °C. The similar results were obtained as observed for 13.2 wt% of 25R4 [30], indicating that the precipitation of 25R4 could occur below 70 °C. Fig. 1 shows the heating curve for the 17.1 wt% 25R4 solution. A broad endothermic peak is observed in the temperature range from 28 °C to about 50 °C, implying that 25R4 dehydrates to form aggregates. There is also a sharp peak occurring in the vicinity of 40 °C, which could indicate a structural transition from a relatively simple micelle-like structure to a more complicated and packed structure. For example, the aggregation number could be increased with temperature, resulting in the increase in the size of aggregates and eventually leading to precipitation.

Two aqueous solutions of pure F127 with two concentrations (i.e. 10 and 15 wt%) were scanned at a scanning rate of 0.5 °C/min for a thermal cycle from 10 to 80 °C, and the results are also shown in Fig. 1. From Fig. 1, a complete thermoreversibility is verified for both concentrations of F127 by observing the mirror images of the endothermic and exothermic curves along the baseline. The concentration dependence is indicated by two factors: the shift of the peak to the lower temperature and the increase of the peak height, with increasing polymer concentration. In other words, the micellization of F127 occurs at a lower temperature when the concentration is higher, which has been reported in the literature [25]. From Fig. 1, the micellization peak for each solution of F127 is present separately with the broad endothermic peak of 25R4, which provides us with a boundary condition for the preparation of an ideal blend from a F127 solution (≥10 wt%) and a 25R4 solution (≤17.4 wt%). In other words, the micellization peak of 10 wt% F127 or 15 wt% F127 does not overlap with that of 25R4 along the temperature axis, and F127 and 25R4 form micelles in the different temperature ranges. When they are mixed in water together, however, it is interesting to know if they will still form micelles independently.

3.2. Thermal reversible micellization of F127/25R4 solutions

Being the same as a pure F127 solution but different from a pure 25R4 solution, the complete thermoreversibility has been verified for all of the F127/25R4 solutions studied in this work. Fig. 2 gives an example for the 10 wt% F127 aqueous solutions with various ratios of 25R4/F127. Fig. 2(a) shows the thermal capacity C_p (endothermic), which has been normalized for 1 L of solution from the DSC sample cell volume of 0.516 mL, as a function of temperature in the heating process, while Fig. 2(b) gives the C_p curves (exothermic) in the cooling process. From Fig. 2, it is observed that the endothermic and exothermic curves for each ratio of F127/25R4 still form the mirror image along the baseline. This means that the thermoreversibility property of pure F127 is

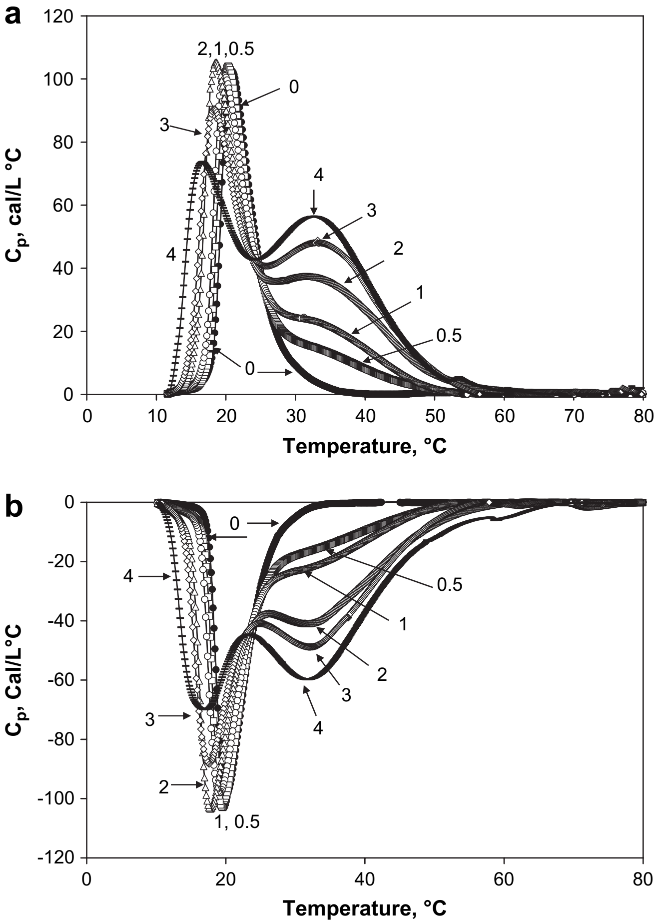

Fig. 2. Thermal capacity, C_p, as a function of temperature for aqueous solution of F127 and solutions of 10 wt% F127 with various molar ratios (0, 0.5, 1, 2, 3, 4) of F127/25R4, as indicated, during a thermal cycle at a scanning rate of 0.5 °C/min: (a) heating and (b) cooling.

not affected by adding 25R4. This also implies that 25R4 does not precipitate in the heating process due to the presence of F127 and F127 prevents 25R4 from precipitating. The complete thermoreversibility property of the blend of F127 and 25R4 is considered to be attributed to the constructive interaction between F127 and 25R4. The similar results have been obtained for the 15 wt% F127 solutions with the same molar ratios of 25R4/F127.

Since the endothermic and exothermic curves are symmetrical, we like to focus our discussion on the endothermic curves obtained from the heating process. By adding 25R4 into an F127 solution, besides the thermoreversibility, two other significant effects are clearly observed from the thermal capacity curves. The first effect is that at a given concentration of F127 the endothermic peak temperature shifts to the left, the lower temperature side. This is a significant effect of 25R4 on the micellization of F127, which is known as a "salt-out like" effect. The "salt-out like" agent, in this case 25R4, increases the hydrophobicity of water. When 25R4 dissolves in the aqueous solution, the water molecules available in the solution for F127 molecules become less than those in pure water because some of the water molecules are used to interact with 25R4 molecules. In this sense, one may consider that the water becomes more "hydrophobic" due to the presence of 25R4 than before adding 25R4. As a result, the PPO blocks of F127 may associate more easily to form micelles at a lower temperature and the endothermic peak shifts to a lower temperature with increasing concentration of 25R4 in the blend.

Another similar explanation for the salt-out like effect of 25R4 is that as 25R4 molecules "consume" water molecules for its hydration or solubilization, the effective volume of water available for F127 is reduced, causing F127 to micellize early. On the other hand, F127 may act as a supporting medium for 25R4 not to precipitate.

The primary peak temperatures are listed in Table 1 and plotted against the molar ratio of 25R4/F127 in Fig. 3(a). It is found that the peak temperature at each concentration of F127 is approximately a linear function of the molar ratio of 25R4/F127. The higher the F127 concentration is, the stronger the dependence of the peak temperature on the molar ratio of 25R4/F127 is.

The second effect of 25R4 is that the primary peak of micellization decreases with increasing concentration of 25R4 and a shoulder or even a secondary peak appears just after the primary micellization peak. The secondary peak grows in height with increasing 25R4 present in the blend. As a result, a valley is formed between the primary and secondary peaks. Since the temperature range for the secondary peaks is of the similar range for that of pure 25R4 as shown in Fig. 1, we consider that 25R4 predominantly contributes to the appearance of the shoulder or secondary peak while F127 mainly contributes to the primary peak. It is also possible that the mixed micelles of F127 and 25R4 are formed.

However, the observations from Fig. 2 are not the same as observed for the F108/25R4 system where the primary peak becomes higher and broader with increasing 25R4 when F108 < 15 wt% [30]. The different effects of 25R4 on F108 and F127 are considered to be due to the different miscibilities of 25R4 with the Pluronics. We will discuss the difference between F127 and F108 later.

The endothermic enthalpy changes of micellization were calculated by integrating the C_p curves and then converted to the values per liter of solution. The results are shown in Table 1 and Fig. 3(b). If one plots the enthalpy changes against the molar ratio of 25R4/F127, an approximately linear

Table 1
Enthalpy changes and primary peak temperatures in the heating process. The values ΔH^* are the enthalpy changes calculated using Eq. (1)

Molar Ratio of 25R4/F127	10 wt% F127			15 wt% F127		
	Peak Temp., °C	ΔH, kcal/L	ΔH^*, kcal/L	Peak Temp., °C	ΔH, kcal/L	ΔH^*, kcal/L
0	20.9	0.64	0.64	18.1	0.81	0.81
0.5	20.4	0.83	0.79	17.4	1.04	1.02
1	19.8	0.97	0.94	15.1	1.42	1.26
2	18.6	1.36	1.24	13.2	1.63	1.71
3	18.3	1.52	1.54	9.5	2.28	2.16
4	16.6	1.66	1.84	6.0	2.85	2.60

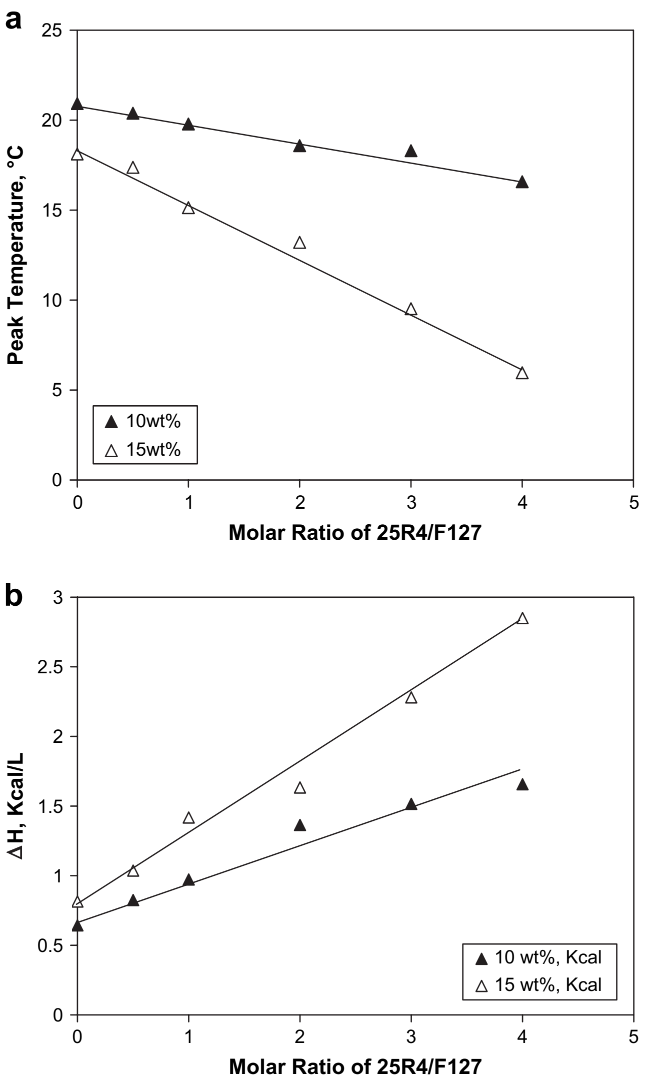

Fig. 3. (a) Endothermic peak temperature and (b) endothermic enthalpy changes as a function of molar ratio of 25R4/F127 for 10 wt% and 15 wt% F127 aqueous solutions.

relationship can be obtained at each F127 concentration. From the enthalpy curves, it is known that the enthalpy change for the 15 wt% F127 solution has a higher sensitivity to the molar ratio of 25R4/F127 than that of 10 wt% F127 solution. Furthermore, since the temperature range for 25R4 to dehydrate is different from that for F127, we may reasonably make an assumption that F127 and 25R4 contribute to the total enthalpy change independently. Under this assumption, we can estimate the total enthalpy change ΔH for a blend of F127 and 25R4 in terms of their respective enthalpy changes of micellization (or dehydration), ΔH_{F127} and ΔH_{25R4}:

$$\Delta H = \Delta H_{\mathrm{F127}} + \omega \Delta H_{\mathrm{25R4}} \tag{1}$$

where w is the wt% of 25R4 in the blend solution. ΔH_{25R4} is determined from Fig. 1 by integrating the C_{p} curve against temperature and then converted to a value per wt% of 25R4 ($\Delta H_{\mathrm{25R4}} = 0.104$ kcal/L/wt%). The calculated ΔH values are compared with the experimental ones in Table 1. The results in Table 1 show that the enthalpy for a blend of F127 and 25R4 can be approximately expressed by Eq. (1), suggesting that the total energy used for the dehydration of F127 in the presence of 25R4 is almost independent of 25R4.

3.3. Effect of 25R4 on gelation of F127

The further interest is to know how 25R4 affects the gelation of F127. For convenience, we plotted the thermal capacity C_{p}, storage modulus G' and loss modulus G'' against temperature in Fig. 4 for the 15 wt% F127 solutions with 6 molar ratios [i.e. 0:1 to 4:1 from (a) to (f)] of 25R4/F127. The pure F127 solution shown in Fig. 4(a) represents the typical micellization–gelation behavior of a Pluronic polymer in aqueous solution. The sharp C_{p} peak is for the endothermic energy used for dehydration of F127 molecules for micellization. From the G' and G'' curves, it is known that during the micellization the solution is a liquid. In the vicinity (about 30 °C) of the endothermic peak offset, both G' and G'' suddenly and sharply increase and then crossover to result in a G' plateau that is higher than G''. The crossover of G' and G'' occurs at about 32.2 °C beyond which a solid gel is formed. It is noted that there is no detectable endothermic heat during the gelation, implying that the gelation of F127 is approximately an athermal process. This observation is consistent with that for F108 [25]. The reason for the athermal gelation is that the gelation mainly involves the structural arrangement of micelles and does not require further dehydration of F127 molecules.

At the lowest concentration of 25R4 [Fig. 4(b)], although a weak shoulder appears at the high temperature side of the endothermic peak, which is caused by 25R4, the gelation of F127 is not actually affected. The sol–gel transition ($G' = G''$) occurs at about 30.4 °C and the high plateaus of G' and G'' are shown. The slight shift of the sol–gel transition temperature to the lower temperature is due to the "salt-out like effect" of 25R4. The similar results are observed for the molar ratios of 1:1 and 2:1 [Fig. 4(c) and (d)] while the shoulder or secondary peak increases with the molar ratio. The sol–gel transition still takes place in the vicinity of 31 °C, indicating that F127 dominates the gelation.

An interesting phenomenon is observed when the molar ratio of 25R4/F127 is increased to 3:1, as shown in Fig. 4(e). The rheological measurements were repeated for three times for the same sample and the same results were obtained. In this figure, it is observed that there are two sol–gel transitions: the first one at about 31 °C and the second one at about 58 °C. As the temperature range for the first sol–gel transition is consistent with that for the F127 solutions with the low ratios (<3) of 25R4/F127, the first transition is considered to be primarily dominated by F127, which is similar to the gelation of a pure F127. The gel structure formed by the first gelation could contribute to the G' value that is as high as 10,000 Pa. However, the gel formed from the first sol–gel transition is unstable and collapses quickly with increasing temperature. After the collapse, the solid gel returns to a liquid state by showing $G'' > G'$. At high temperatures, the solution gels again form

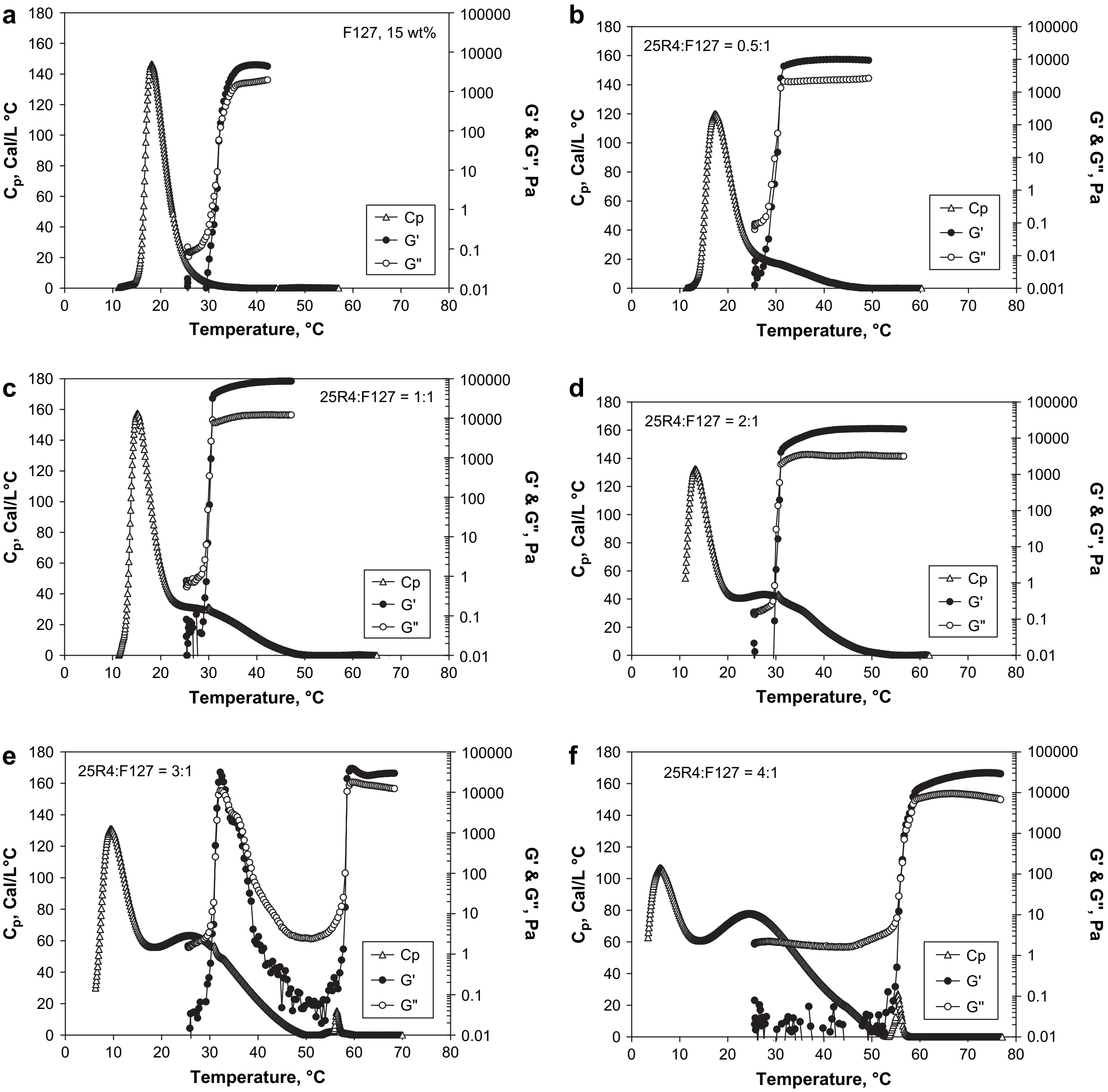

Fig. 4. Thermal capacity C_p, storage modulus G', and loss modulus G'' as a function of temperature for aqueous solutions of 15 wt% F127 with various molar ratios of 25R4/F127 at a heating rate of 0.5 °C/min: (a) pure F127; (b) 25R4/F127 = 0.5:1; (c) 1:1; (d) 2:1; (e) 3:1; and (f) 4:1. An angular frequency of 1 rad/s was used for the measurement of G' and G''.

a solid gel with the high storage modulus (>10,000 Pa). The second sol–gel transition occurs at about 58 °C defined by the crossover of G' and G''. The difference between the first and the second sol–gel transition temperatures is 27 °C, which is very big.

Here we propose a mechanism for explanation of the unique phenomenon. During the first gelation, the micelles of F127 formed through the primary peak of endotherm are packed into a crystal-like ordered structure, which is similar to that formed from a pure F127 solution [e.g. Fig. 4(a)]. At the same time, 25R4 molecules dehydrate inside the gel network of the F127 micelles to expose their PPO blocks. These PPO blocks of 25R4 may not form their own micelles but interrupt the gel network structure of F127 through the affinity between the PPO blocks of 25R4 and the cores of F127 micelles. One may also consider the formation of mixed micelles of F127 and 25R4. As a result, the gel network structure of F127 is weakened by the interaction between 25R4 and F127 and eventually collapses when the interaction is sufficiently strong at the high ratio of 25R4/F127. Thermodynamically, this degelation can be considered to be caused by an entropy-driven solubilization of the F127 micellar gel. However, the F127 micelles do not demicellize during the gel's collapse because no exothermic heats are detected.

As temperature increases, the F127 micelles become more densely packed due to the increased hydrophobicity of PPO blocks. For the dispersed micelles of F127 to be connected to form a gel network again, the intermicellar bridges are considered to be necessary. Now, the role of 25R4 has to be taken into account. As the PPO blocks of 25R4 are short, however, it would be impossible for a single chain of 25R4 to bridge two micelles of F127 by inserting each PPO block into the core of a F127 micelle. A possible way for 25R4 chains to form intermicellar bridges is that at least two 25R4 chain blocks may form a bridge between two micelles of F127: one PPO block of each 25R4 chain joins one F127 micelle while other PPO block of the 25R4 chain is dangling but it combines with the same dangling PPO block of the second 25R4 chain to form a junction. Two factors are important for considering the possibility of forming the intermicellar bridges from 25R4 chains at high temperatures. The first factor is that the intermicellar distance between the neighboring F127 micelles should become shorter due to the increased sizes of F127 micelles at high temperatures. Mortensen and Talmon reported that the core radius of F127 increased from 50–70 Å at low temperatures to 70–80 Å at high temperatures as determined using SANS [15]. The second factor is that the dehydrated 25R4 molecules should not form their own micelles in the sea of F127 micelles and they may like to exist as individual chains, dimers or trimers in the micellar dispersion and/or partially join the F127 micelles.

In the vicinity of the second sol–gel transition, it is noted that there is a small but sharp peak of endotherm. The peak temperature is 56.4 °C, which is slightly lower than the crossover temperature (58.2 °C) of G' and G''. The small endothermic peak is considered to be caused by excluding some water molecules that surrounded the F127 micelles in order for the F127 micelles to be well and densely packed into a crystal-like gel network structure.

At the highest ratio of 25R4/F127 [=4:1, Fig. 4(f)] used in this study, although the two peaks of endotherm appear before 50 °C, the gelation of F127 is not observed until 55 °C. This is a further confirmation of the above proposed mechanism for the effect of 25R4 on the gelation of F127. The increased amount of 25R4 in the solution strongly interrupted the F127 micelles so that the latter could not be packed into an ordered gel structure. Thus, the gelation of F127 has to take place at the high temperatures. For the gelation of F127, 25R4 might form the intermicellar bridges connecting the F127 micelles. Similar to Fig. 4(e), an endothermic peak with a peak temperature of 55.4 °C is also observed in the vicinity of the sol–gel transition for the 4:1 ratio of 25R4/F127. The peak is still sharp but higher in height than the peak in Fig. 4(e). The higher peak for the higher ratio of 25R4/F127 could be due to the stronger interruption by more 25R4 molecules, which requires more energy to exclude extra water molecules to connect F127 micelles.

Fig. 5 shows the sol–gel transition temperature, which is defined by the crossover temperature of G' and G'' for the 15 wt% F127 solution, as a function of molar ratio 25R4/F127. The sol–gel transition temperature slightly decreases with the molar ratio before the ratio reaches 3:1, which shows a weak salt-out like effect of 25R4. At the critical ratio of 3:1, two sol–gel transitions are observed: the first one is consistent with that observed at the low ratios of 25R4/F127, which is the F127-dominated gelation, while the second one jumps to a very high temperature by 27.4 °C. Since the second gelation is a result of the 25R4 effect, it is known as "25R4-affected gelation". Beyond the critical ratio, only a single sol–gel transition is possible, which is called "F127-dominated gelation".

3.4. Difference between F127/25R4 and F108/25R4

We previously reported the thermal and rheological properties for a blend of F108 and 25R4 [30]. The results for the F127/25R4 system look similar to those for the F108/25R4 system. However, the main differences between two polymers (F127 and F108) and their interaction with 25R4 can be understood as discussed below.

F127 is similar to F108 in molecular structure, but they are not the same in micellization and interaction with 25R4. For the EO content, F127 contains 70% while F108 has 80%, which makes F127 to be less hydrophilic than F108. F127 has a lower molecular weight (12,600 g/mol) than F108 (14,600 g/mol). As a result of these differences in molecular structure and composition, the critical micellization temperature (CMT) of F127 is lower than F108 at a given concentration [12]. For example, at 0.1 wt% concentration, CMT of F127 is 31 °C while CMT of F108 is 36 °C. On the other hand, the critical micellization concentration (CMC) of F127 at room temperature (25 °C) is 0.56 mM while CMC of

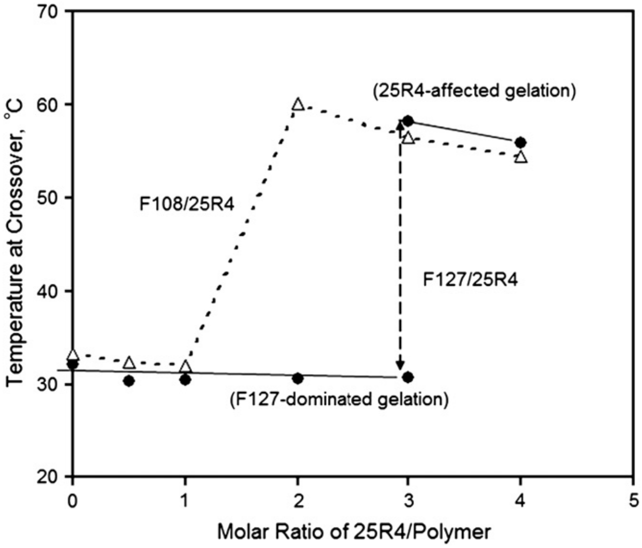

Fig. 5. Temperature (filled circles) at the crossover point of G' and G'' as a function of molar ratio of 25R4/F127 for 15 wt% F127 aqueous solution. For comparison, the crossover temperatures (triangles) of G' and G'' for a F108/25R4 aqueous system is shown [30].

F108 is 3.08 mM that is nearly 6 times higher than F127 [12]. In summary, F127 seems to be more hydrophobic and easily forms micelles than F108. Therefore, it is expected that there should be a significant difference in the interaction with 25R4 between F127 and F108.

From the previous [30] and current results for F108 and F127, respectively, the following differences between F127 and F108 are observed. For micellization, as plotted in Fig. 6, the endothermic peak temperature of micellization for the F127 system is always lower than the F108 system and the effect of 25R4 on the decrease in the micellization temperature is stronger for F127 than F108. The comparison in Fig. 6 indicates that (i) F127 is easier to form micelles in water than F108 and (ii) 25R4 has a stronger ‘‘salt-out like’’ effect on F127 than F108. At a given ratio of 25R4/polymer, the endothermic enthalpy changes for F127 are greater than F108 because the micellization of F127 takes place at a lower temperature than F108.

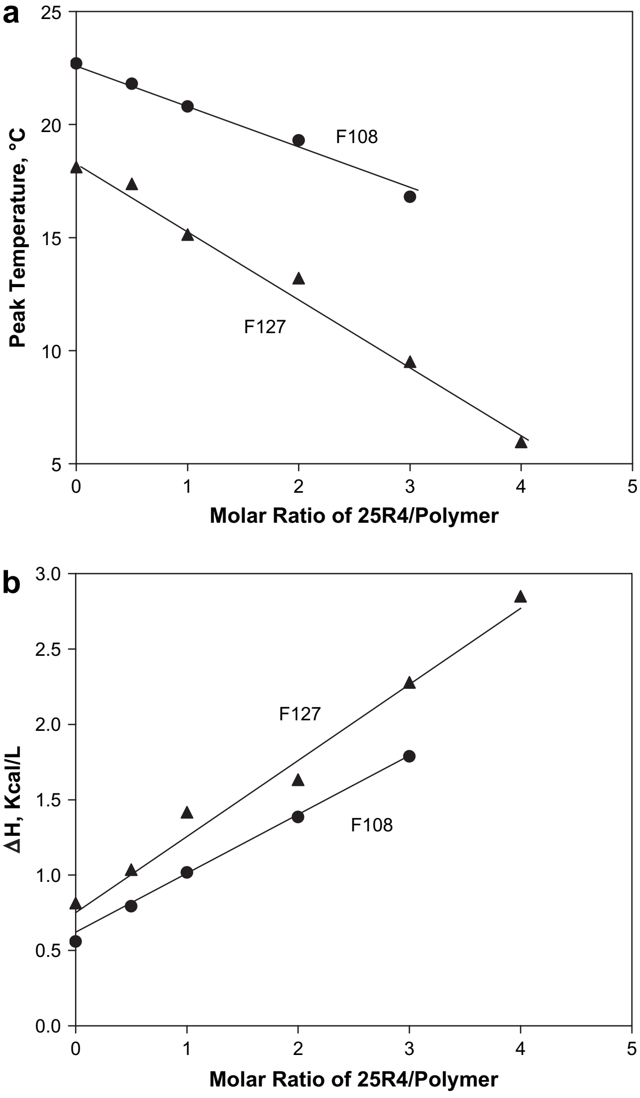

Fig. 6. Comparison between F127 and F108 at a fixed concentration of 15 wt%: (a) endothermic peak temperature and (b) endothermic enthalpy changes as a function of molar ratio of 25R4/polymer, where polymer is F127 or F108.

For gelation, 25R4 causes the degelation–gelation transition to occur at a higher content for F127 than for F108. As shown in Fig. 5, the transition from the F127-dominated gelation to the 25R4-affected gelation is observed at the ratio of 25R4/F127 = 3:1 for the solution of 15 wt% F127 (Fig. 5) while the similar transition occurred at a ratio of 25R4/F108 between 1:1 and 2:1 for a solution of 18 wt% F108 [30]. This difference between F127 and F108 proves that there is a weaker interaction between F127 and 25R4 than that between F108 and 25R4, which causes the transition to occur later at a higher ratio of 25R4/F127. In other words, F127 needs more 25R4 to exhibit the similar ‘‘25R4-affected gelation’’ as compared to F108. Interestingly, the polymer-dominated gelation and the 25R4-affected gelation occur at similar levels of temperature for both F127 and F108.

4. Conclusions

The aqueous solutions consisting of a blend of F127 and 25R4 were prepared by varying the F127 concentration and the molar ratio of 25R4/F127. The micro-thermal and rheological properties of these solutions have been studied by focusing on the effects of 25R4 on the thermoreversible micellization and gelation of F127. In the temperature range studied, F127 is thermally reversible while 25R4 is not. The addition of 25R4 from low to the highest molar ratio of 25R4/F127 = 4 does not alter the thermoreversibilty of F127, due to the constructive interaction between F127 and 25R4. But a ‘‘salt-out like’’ effect is obtained from 25R4, which is the shift of F127 micellization to a lower temperature. The salt-out like effect of 25R4 is found to be approximately a linear function of 25R4 concentration. At the same time, the appearance of a secondary peak of micellization, which overlaps with the primary peak, is an indication of a strong interaction of F127 with 25R4. However, the total energy used for the dehydration of F127 in the presence of 25R4 is almost independent of 25R4 as described by Eq. (1). The effect of 25R4 on the gelation of F127 is dependent on the molar ratio of 25R4/F127. When 25R4/F127 < 3:1, 25R4 does not affect the gelation of F127 significantly, which is similar to a pure F127 solution, and there is only a weak salt-out effect of 25R4. When 25R4/F127 > 3:1, however, the gelation of F127 jumps to a high temperature by more than 27 °C, indicating a strong effect of 25R4. The critical ratio of 25R4/F127 for the above change is found to be 3:1 at which two sol–gel transitions are shown. The increased interaction of 25R4 with F127 by increasing the molar ratio to 25R4/F127 is the driving force to cause the unique changes in the gelation and micellization properties of F127. Finally, F127 was compared with F108 for the effect of 25R4. It was found that 25R4 has a stronger effect on micellization but a weaker effect on gelation for F127 than F108.

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