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Effects of guest poly(ethyleneglycol) on the order-to-disorder transition of hydrophobically modified poly(ethyleneglycol) (C12E25) micellar solution

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Abstract

Order-to-disorder transition of micellar aqueous solution of hydrophobically modified ethyleneglycol oligomer, poly(ethyleneglycol) monododecylether (C12E25) with addition of poly(ethyleneglycol) (PEG) has been investigated by means of linear-viscoelastic measurements, X-ray scattering, and differential scanning calorimetry. We have revealed the followings. Added PEG having a chain length similar to that of micellar corona PEG can be incorporated into the micellar lattice of C12E25 aqueous solution with maintaining the body-centered-cubic lattice structure. The transition mechanically observed as the sol–gel transition is a thermodynamical first-order transition of disorder-to-order. The transition temperature decreases with increasing concentration of guest PEG. The stability of micellar lattice is discussed in terms of guest chain localization in the lattice.

Keywords: Poly(ethyleneglycol); Micelle; Order–disorder transition

1. Introduction

Hydrophobically modified poly(ethyleneglycol) is widely used as a surfactant, taking advantage of the easiness to control of its hydrophobicity by changing chain lengths of the alkyl group and ethyleneglycol (EG) [1–11]. Especially, modified poly(ethyleneglycol)s' with relatively long EG chains are used for cosmetics and paints to adjust rheological properties. Such a modified poly(ethyleneglycol) aqueous solution forms a gel at higher concentrations [12].

Recently we investigated aqueous solutions of a modified PEG with relatively long EG chains, that is, poly(ethyleneglycol) monododecyl ether (C12E25) with the number of EG units being 25 [13–15]. It has been demonstrated that the micellar solution exhibits a disorder-to-order transition at about 30 wt% with increasing concentration or at 57 °C with decreasing temperature, where mechanical properties dramatically change like those at a sol–gel transition. In the gel region, i.e. in the ordered state, the star-like spherical micelles of C12E25 form a long-range order structure of body-centered cubic lattice. The ordered phase is a cubic phase of lyotropic liquid crystal.

It is interesting to see effects of guest molecules incorporated into the lattice as solvent on the transition behavior since it must give us useful knowledge for the lattice stability and nature of interactions between micellar particles. In particular, addition of chain molecules, which are compatible with the corona units of micelle, may change structure and stability of the lattice by incorporating into the lattice. That is, the ternary system, C12E25–PEG aqueous solution is the case here. If the added PEG's length is so short, the PEG is thought to behave as a component of mixed low-molecular-weight solvent. On the other hand, if the one is longer enough, the PEG chains may not enter into the corona chains but be localized between micellar particles to eventually induce a phase separation. Therefore around certain length of added PEG chains, the transition behavior distinctly changes by the incorporation of PEG chains in the lattice without phase separation.

In this study, we investigate the phase behavior of

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C12E25–PEG1540 aqueous solution, where the chain length of selected PEG 1540 is roughly equal to that of the corona chain of C12E25 micelle. That is, we obtain the phase diagram of sol–gel transition by means of rheological measurements, and see whether the phase separation would occur or not, and how the transition behavior changes with addition of PEG into the lattice. We also make calorimetric and X-ray scattering measurements to confirm the lattice structure of micelles and that the transition is a thermodynamical one. We will discuss the lattice stability in terms of change in interactions between micelles in the ordered structure with the presence of PEG chains between and/or in coronas of micelles.

2. Experiments

2.1. Materials and samples

Poly(ethyleneglycol) monododecyl ether (C12E25) was an extra pure product of Tokyo-Kasei and used without further purification. Poly(ethyleneglycol), PEG1540 with average molecular weight being 1000, was a pure product of Wako Pure Medicine Co. and used as received. Distilled water, a high grade product of Wako Pure Medicine Co., was filtered and de-ionized by an Autostill WG220 (Yamato Scientific Co). The specific resistance of the water was kept at 18.3 MΩ cm. Aqueous solutions were prepared as follows. Solutions with desired concentrations ranging from 25 to 50 wt% for C12E25, and from 1 to 20 wt% for PEG1540, were, respectively, homogenized by stirring at 70 °C for 3 h, and cooled down to room temperature. The prepared solutions were left for 1 day more.

2.2. Measurements

2.2.1. Measurements of dynamic viscoelasticity

The dynamic viscoelasticity was measured with an RFS-II viscoelastic measuring apparatus (Rheometrics) using rotators of cone-plate geometry with the diameter of 25 mm and the angle of 0.04 rad. In order to prevent water from evaporating, a specially designed sample cover was used. No evaporation was detectable for several hours at temperatures up to 60 °C. All the measurements were carried out within the linear viscoelasticity, which was confirmed by no strain dependence of the dynamic storage modulus and loss modulus. The strain γ ranged from 0.001 to 0.2 depending on the composition of solution. The dynamic modulus was measured as a function of frequency, ω ranging 0.1–100 s^{-1} at various temperatures of 25–70 °C for the solutions with different compositions in the ranges of 25–50 wt% for C12E25 and 1–20 wt% for PEG1540.

2.2.2. X-ray scattering measurements

Small angle X-ray scattering (SAXS) measurements were performed with a X-ray generator RINT2500 (RIGAKU Co.) at room temperature (23 °C) and 35 °C. Cu Kα beam (wavelength: $\lambda = 0.15418$ nm; power: 2.7 kW) monochromatized and focused by confocal max flux (CMF) mirrors was radiated to sample solutions sandwiched between thin amorphous polyethylene films for 30 min. The scattered X-ray intensity was integrated on an imaging plate detector. One-dimensional scattering profiles were obtained by circularly integrating the two-dimensional scattering pattern of intensity on the imaging plate.

2.2.3. DSC measurements

Differential scanning calorimetry (DSC) measurement was carried out with a Model 6100 manufactured by Seiko Instrument. Each sample of 20–30 mg was sealed in an aluminum pan for liquid measurements. The sample pan was heated from 5 to 60 °C with the rate of 5 °C min^{-1}, and held at 60 °C for 10 min. After cooling it from 60 to 5 °C with the rate of 5 °C min^{-1}, the pan was held at that temperature for 10 min. Then, a heating run of calorimetric measurement with the rate of 1 °C min^{-1} was subsequently started at 5 °C and carried out up to 70 °C.

3. Experimental results

The C12E25 aqueous solution is transparent, and does not separate into two(or more) phases by an addition of PEG1540 up to 20 wt%. However, by adding more than 20 wt% PEG1540, the solution becomes opaque to show phase-separation under a certain C12E25 concentration and temperature. Therefore, below 20 wt% of PEG, the PEG molecules mix with C12E25 aqueous solution both in the disordered and the ordered phases in the experimental temperature range, and they can penetrate into the lattice of C12E25 micelles. We found no phase separation for any C12E25–PEG aqueous solution in the present experimental ranges of temperature (25–70 °C), and C12E25 concentration (25–50 wt%). In this paper, we investigated C12E25–PEG aqueous solution for the limited condition without phase separation.

3.1. Dynamic viscoelasticity

Fig. 1 shows log–log plots of the storage modulus G' and the loss modulus G'' vs. the frequency ω at 25 °C for C12E25–PEG aqueous solutions with various concentrations of PEG at the fixed C12E25 concentration of 40 wt%. For the solution without PEG (the binary system), G' has a plateau region with lower loss modulus G'' in the range of $1 < \omega < 50\ s^{-1}$, where the solution is elastic in the gel region. For the solution with PEG around 1–2 wt%, where G' is still larger than G'', and the $G'(\omega)$ and $G''(\omega)$ profiles do not change so much. At PEG 5 wt%, although G' is still larger than G'', they decreased by one or two order of magnitude. At 10 wt%

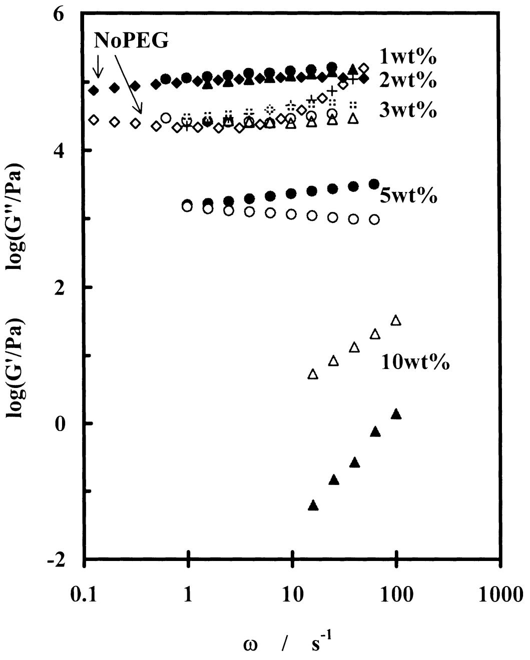

Fig. 1. log–log plots of dynamic moduli G' (filled symbols) and G'' (hollow symbols) against frequency ω for C12E25 (40 wt%)–PEG aqueous solutions of various PEG concentrations indicated at 25 °C.

of PEG, G'' is much larger than G', and the slope of $G''-\omega$ curve is about unity, which indicates the solution behaves as a Newtonian fluid. It is obviously seen that the increasing amount of PEG additive leads to a mechanical change from gel to sol.

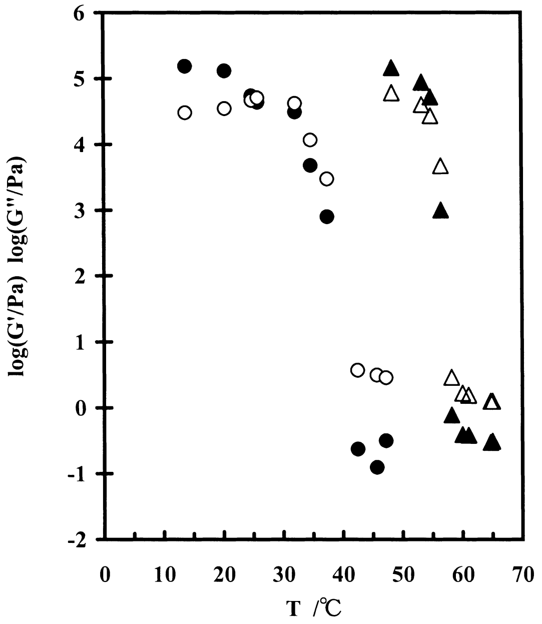

Fig. 2. Temperature dependencies of dynamic moduli G' (filled symbols) and G'' (hollow symbols) at $\omega = 15.8\ \mathrm{s}^{-1}$ for the C12E25 (50 wt%) aqueous solution (triangles) and the C12E25(50 wt%)–PEG(3 wt%) aqueous solution (circles).

Fig. 2 shows temperature dependencies of G' and G'' at the fixed frequency $\omega = 15.8\ \mathrm{s}^{-1}$ for C12E25–PEG ternary solutions as observed through decreasing temperature.

Both of G' and G'' abruptly increase at a certain temperature above a certain concentration as well as in the binary system, C12E25 aqueous solution without PEG. This change in viscoelasticity from viscous liquid to elastic body may indicate the sol–gel transition. The ternary system tends to have a more moderate change than the binary system. To determine the boundary between sol and gel regions, we can define a mechanical sol–gel transition as the point of $G' = G''$ at $\omega = 15.8\ \mathrm{s}^{-1}$, as we did for the binary system in our previous papers [13–15]. Then, we can make the concentration–temperature phase diagram of the sol–gel transition for C12E25–PEG aqueous solution by the dynamic viscoelastic measurements.

Fig. 3(a)–(e) shows the phase diagram thus obtained for the C12E25–PEG solutions with various PEG concentrations. Both sol and gel regions, i.e. the transitions, are observed up to 10 wt% of PEG in the present experimental temperature and C12E25-concentration regions. The sol–gel transition occurs at temperatures lower than those for the binary system. As a result, the gel region becomes narrower with the increase in PEG concentration. The result for the highest PEG concentration suggests that the PEG addition brings about larger transition-temperature shifts at higher C12E25 concentration as well as near the transition concentration, resulting in the peak of the phase boundary of gel at the lowest C12E25 concentration.

Fig. 1 allows us to draw Fig. 4 showing plots of G' and G'' at $\omega = 15.8\ \mathrm{s}^{-1}$ against PEG concentration for the C12E25 concentration of 40 wt% at 25 °C. In the gel region, $G' > G''$, the modulus G' gradually decreases with increasing PEG concentration, and then G' decreases with going into the sol region by further PEG addition.

3.2. Small-angle X-ray scattering

SAXS profiles are shown in Fig. 5 for the ternary solution with 50 wt% of C12E25 and 5 wt% of PEG1540. (The composition is shown in Fig. 3(d) by an arrow.) At 23 °C, which is below the transition temperature, strong sharp diffraction peaks are observed, and the wave-number ratios of peak positions among the peaks are $q_1 : q_2 : q_3 = 1 : 2^{1/2} : 3^{1/2}$, suggesting that the C12E25–PEG gel has a long-range ordered structure with body-centered cubic lattice as well as the binary micellar solution without PEG additive. To the contrary, at 35 °C in the mechanically-determined sol region (see Fig. 3(d)), the peaks clearly disappear, only remaining a little trace. The presence and disappearance of the long-range ordered structure demonstrates that the C12E25–PEG aqueous solution exhibits the sol–gel transition accompanied with disorder-to-order structural transition of micellar lattice as well as found in C12E25 aqueous solution, and furthermore that the mechanically-

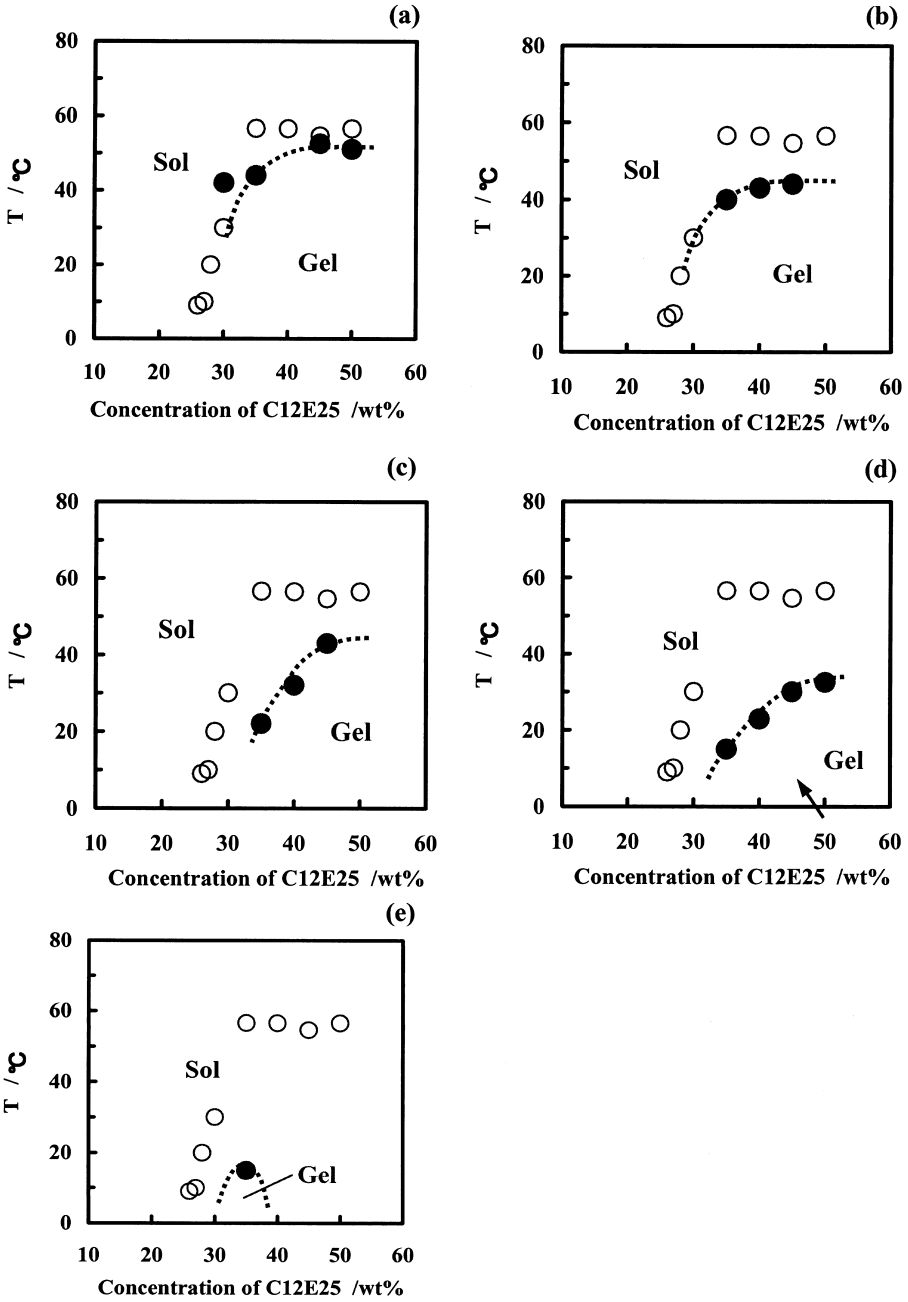

Fig. 3. Concentration of C12E25–temperature (C–T) diagram of sol and gel regions for C12E25–PEG aqueous solutions. The concentrations of PEG are as follows: (a) PEG 1540 = 1 wt%, (b) PEG 1540 = 2 wt%, (c) PEG 1540 = 3 wt%, (d) PEG1540 = 5 wt%, (e) PEG 1540 = 10 wt%. Hollow circles show the boundary between sol and gel regions for C12E25 aqueous solution without PEG.

determined transition point quantitatively corresponds to that of the disorder-to-order transition.

3.3. DSC measurements

DSC thermograms on heating for the binary aqueous solution (C12E25:50 wt%), and the ternary solution (C12E25:50 wt%; PEG1540:1 wt%), are shown in Fig. 6, for examples. Clear endothermic peaks appear for both of the binary and ternary, with the peak temperature corresponding to the mechanical sol–gel transition temperature. For 50 wt%–C12E25 aqueous solutions with various concentration of PEG, are shown in Table 1 the phase transition temperatures obtained by the endothermic peaks, along with those mechanically determined. The differently determined transition temperatures are practically identical with each other, although the mechanically determined transition temperature is slightly higher than the thermally observed one. These results indicates that the transition is of the thermodynamical first-order phase transition due to

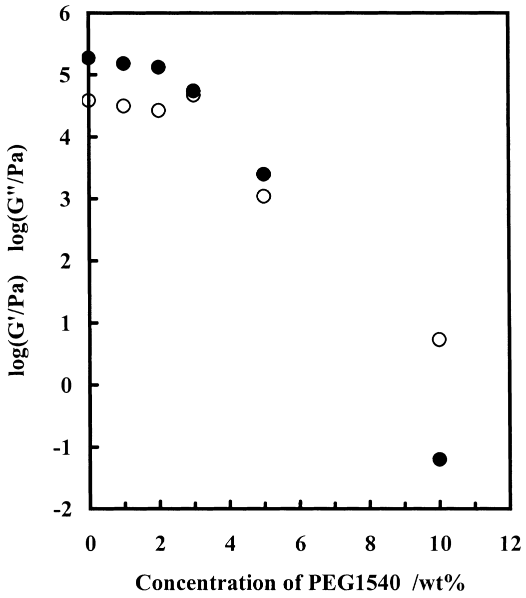

Fig. 4. Plots of dynamic moduli G' (filled symbols), and G'' (hollow symbols) at frequency $\omega = 15.8\ \mathrm{s}^{-1}$ against PEG concentrations for C12E25–PEG aqueous solutions at 25 °C; C12E25 = 40 wt%.

order-to-disorder transition. The endothermal heat on the phase transition is approximately 0.3–0.4 J g^{-1}, which is smaller than that of the micelle–liquid crystal phase transition for didecyldimethylammonium bromide (ca. 3.5 J g^{-1}) [16], by one order of magnitude. Furthermore, the heat of gel–liquid crystal transition for dioctadecyldimethylammonium halide (ca. 70 J g^{-1}) [17], for an example, is two-order of magnitude larger than that of the present transition. Thus it is noteworthy that the transition of order-to-disorder transition of micellar solution has a very small heat of transition, indicating that the transition occurs accompanying with subtle changes in enthalpy and entropy.

4. Discussion

Summarizing the experimental results, we have revealed the followings. Added PEG chains, of which length is similar to that of micellar corona PEG chains, can be incorporated into the micellar lattice of C12E25 aqueous solution, sustaining the body-centered-cubic lattice structure. The transition mechanically observed as the sol–gel transition is the thermodynamical first-order transition of disorder-to-order structural change. The transition temperature decreases with increasing added amount of PEG.

Table 1
Phase transition temperature and the heat of transition ΔH for C12E25–PEG aqueous solution

PEG1540 (wt%)	Phase transition temperature		ΔH (J g^{-1})
	From DSC (°C)	From G' G'' (°C)	
0	56	57	3.4×10^{-1}
1	48	52	3.7×10^{-1}
2	44	46	3.1×10^{-1}
5	32	33	4.1×10^{-1}
10	Disappear	Disappear	–

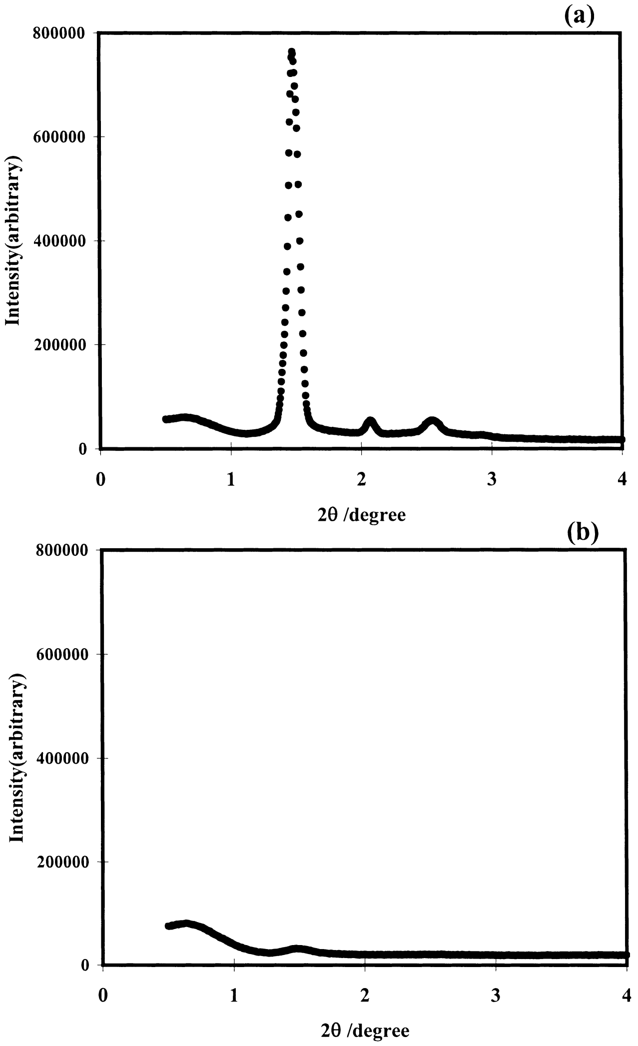

Fig. 5. X-ray scattering profiles for C12E25–PEG aqueous solutions (C12E25:50 wt%, PEG:5 wt%). Horizontal axes show 2ϕ, and vertical axes show intensity; (a) at 23 °C and (b) at 35 °C.

Keys to understand the present experimental findings are obviously roles of PEG chains in the lattice, including their localization in (or their compatibility with) the micellar lattice and their effects on interactions between micellar particles. The present micelle of C12E25 is of star-type with rather long corona chains, so that the corona PEG chains are swollen by solvent water, having a low segment concentration. Therefore the guest chain can penetrate into the swollen corona as well as solvent, as long as the space for penetration is concerned.

The compatibility of linear PEG chains with the corona chains of ordered micelles can be discussed in terms of the localization of guest chains in the micellar lattice. It is basically determined by the chain length (molecular weight) of guest PEG relative to the corona PEG chain length. The PEG of the present case with intermediate chain length, that

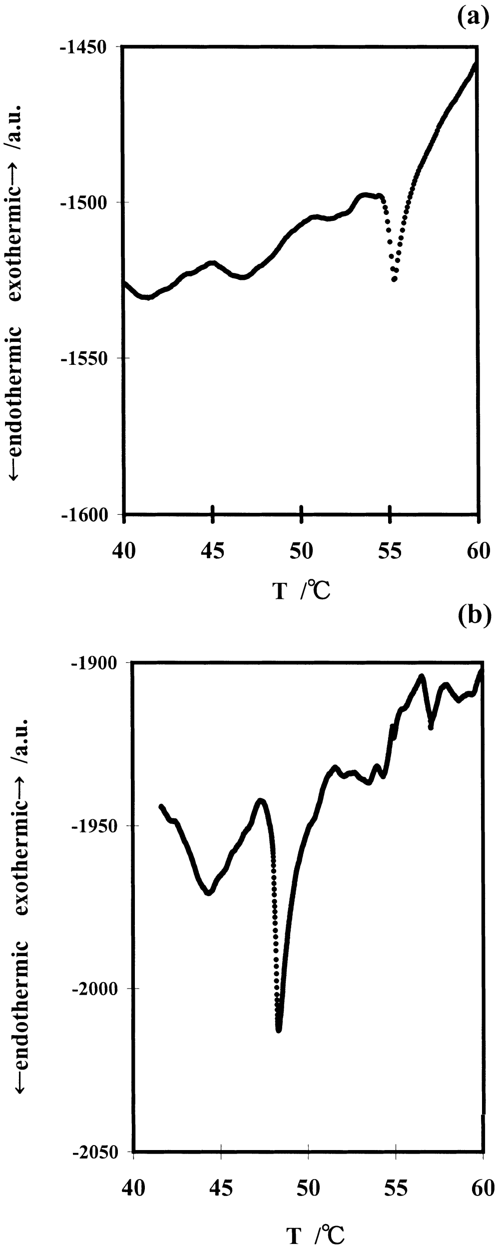

Fig. 6. DSC curves on heating at the rate of 1 °C min^{-1} for C12E25 (50 wt%) aqueous solution(a), and C12E25(50 wt%)–PEG(1 wt%) aqueous solution(b).

is, the similar length to the corona PEG, can penetrate into the bush of corona chains to a certain extent. However, the PEG does not behave as solvent, but more localized, and by exceeding the critical amount, all of the guest PEG chains cannot sit in the bush, but some extra portion will be located between the bushes of corona chains of the nearest neighbor micelles. These excluded chains may weaken the interactions that sustain the lattice structure. Increasing of C12E25 concentration may enhance the exclusion of guest chains, which can explain the larger depression of transition temperature at higher C12E25 concentrations. The present explanation is just based on the simple, intuitive presumption that the presence of excluded guest chains between micellar particles weakens interactions between them to reduce the lattice stability. Strictly speaking, we need to evaluate the difference in free energy between the ordered state and the disordered state to tell the unstabilizing mechanism of the micellar lattice.

The exclusion of the longer linear chains from polymer chain brushes was first proposed by Hashimoto et al. [18] from experimental results for the linear polymers blended in the lamella of microphase-separated block copolymers. The incorporation of linear chains in the bushes of an ordered phase has been studied for the lyotropic liquid crystal of rod-like polymer [19,20]. Inomata et al. reported that rod-like poly(γ-benzyl L-glutamate) (PBLG) and flexible PEG tend to hardly mix with each other. However, if we modify PBLG by introducing PEG as side chains, then the compatibility is improved. That is, linear guest PEG chains can penetrate to the PEG bush to mix with the PBLG in the liquid-crystal phase to some extent [21].

The interplanar spacing calculated by Bragg's law from the first peak of SAXS profile for the (110) plane is 5.97 nm, which is almost the same as that of the binary system without the guest PEG, 6.16 nm. Therefore, in the present case, the lattice size, i.e. distance between the micellar particle, is hardly changed with incorporation of the guest PEG chains, as far as the ordered state is maintained.

The incorporation of PEG chains to the lattice brings about subtle change in viscoelastic properties, i.e. slight decrease in elasticity and slight increase in $\tan \omega$, as far as the guest PEG stably sit in the lattice, i.e. probably most are mixed with the corona part. The departing of the corona chains of neighboring micelles starts to be promoted by incorporation of guest chains excluded from the corona, the interactions between micelles become to fade and cannot keep the lattice structure.

Watanabe et al. [22–26] have extensively studied block copolymer micellar solutions and proposed that the osmotically constrained corona blocks entropically sustain the lattice elasticity. In the present study, we describe and explain the stability of lattice in terms of the effect of localization of guest PEG chains. It should be noted, as is pointed in the previous paper [13,14], that the present micelle has shorter corona chains compared with those in diblock copolymers used usually. Watanabe et al. recently investigated the effect of solvent quality on the viscoelasticity to see roles of corona-chains in swollen and less swollen states [26]. Addition of chain molecules PEG, as is in the present case, makes the solvent quality of water/PEG mixture poor. However, the PEG addition gives rise to the localization of PEG because of macromolecular nature of PEG.

To clarify the present discussion more, we keenly need to study dependencies of the lattice stability and the guest-chain location on the molecular weight of guest PEG chains. These studies by experiments and computer simulations are now under proceeding. The results will be presented in the forthcoming paper.

5. Conclusions

The order-to-disorder transition for aqueous micellar solution of C12E25 with linear PEG additives were investigated to see changes in the stability of the ordered lattice structure with the guest PEG, where the chain length of the PEG is compatible with that of corona chains.

All solutions measured here, with the PEG concentration ranging up to 10 wt%, are transparent even in ordered state, showing no phase separation, but one phase. Incorporation of linear PEG chains into the lattice structure depresses the order-to-disorder transition temperature of thermodynamical first order. Some extra portion of added PEG may be excluded from the corona to be localized between the corona chains of micellar particles. This may weaken the interactions that sustain the ordered lattice structure and make the lattice stability lower, leading to the transition-temperature depression. It may also bring about an appreciable decrease in elastic modulus of the gel right before changing to the sol.

References

[1] Shinoda K, Colloid J. Interf Sci 1970;34:278.
[2] Mitchell DJ, Tiddi DJT, Waring L, Bostock T, McDonald MP. J Chem Soc, Faraday Trans 1 1983;79:975.
[3] Lang LC, Morgan RD. J Chem Phys 1980;73:5849.
[4] Zulauf Z, Rosenbusch JP. J Phys Chem 1983;87:856.
[5] Corti M, Minero C, Cantu L, Piazza R. Colloids Surf 1984;12:34.
[6] Tanfoed C, Nozaki Y, Rohde MF. J Phys Chem 1977;81:1555.
[7] Corkill JM, Walker T. J Colloid Interf Sci 1972;39:621.
[8] Honda C, Kiuchi Y, Nose T. J Chem Soc 1992;11:1301.
[9] Brown W, Rymden R. J Phys Chem 1987;91:3565.
[10] Zana R, Weill C. J Phys (Paris) Lett 1985;46:L-953.
[11] Nilsson PG, Wennerstrom H, Lindman B. J Phys Chem 1983;87:1377.
[12] Suzuki T. J Soc Cosmet Chem Jpn 1991;25:193.
[13] Yamazaki R, Inomata K, Nose T. Kobunshi Ronbunshu 2001;58:286.
[14] Yamazaki R, Inomata K, Nose T. Polymer 2002;43:3647.
[15] Yamazaki R, Inomata K, Nose T. Macromol Chem Phys 2002;203:2322.
[16] Kunieda H, Ito H, Takebayashi S, Kodama M. Colloid Polym Sci 1993;271:952.
[17] Kodama M, Kunitake T, Seki S. J Phys Chem 1990;94:1550.
[18] Hashimoto T, Tanaka H, Hasegawa H. Macromolecules 1990;23:4378.
[19] Ballauff M. Macromolecules 1986;19:1366.
[20] Ballauff M. J Polym Sci, Phys Ed 1987;25:739.
[21] Inomata K, Ohara N, Shimizu H, Nose T. Polymer 1998;39:3379.
[22] Watanabe H. J Soc Rheol Jpn 1994;22:193.
[23] Watanabe H. Acta Polym 1997;48:215.
[24] Watanabe H, Kanaya T, Takahashi Y. Macromolecules 2001;34:662.
[25] Watanabe H. Kobunshi Ronbunshu 2001;58:135.
[26] Tan H, Watanabe H. Polym J 2002;34:775.