NOTE

A study on emulsion stabilization induced with linear and cyclized polystyrene-poly(ethylene oxide) block copolymer surfactants

Eisuke Baba, Toshiaki Yatsunami, Takuya Yamamoto and Yasuyuki Tezuka

INTRODUCTION

Cyclic polymers have been drawing increasing attention because they differ from their linear or branched counterparts in the absence of chain ends and because their unique topologies are expected to reveal unprecedented properties and functions.[1] In particular, cyclic block copolymers composed of hydrophobic–hydrophilic segments, as well as their linear counterparts, tend to produce self-assemblies such as micelles in aqueous media.[2] In such self-assembly states, the distinction between a single linear molecule and a cyclic molecule could be amplified, even if they share the relevant chain lengths and chemical compositions.[1]

Indeed, we have recently shown that a micelle formed by cyclic block copolymer amphiphiles, that is, a series of poly(alkyl acrylate)-b-poly(ethylene oxide)s, exhibits significantly improved thermal and salt stabilities in comparison with the corresponding micelles formed by the linear counterpart.[3,4] Furthermore, the micelle stability can be modulated using the blend of cyclic and linear polymer surfactants with various compositions. The relevant amphiphilic cyclic and multicyclic block copolymers have been studied by others as well, and unique *topology effects* have been demonstrated for their self-assemblies in aqueous medium or at the interfaces.[5–9]

To gain further insights in the topology effect of the linear and cyclized polymer amphiphiles, we examined the emulsion formation and subsequent phase-separation of water/toluene mixtures. Emulsion stabilization using polymer surfactants is critical in diverse applications such as coating formation, pharmaceutics/cosmetic formulation, food processing, detergent preparation and dyes/pigment production.[10] Hence, a class of cyclic polymer surfactants can be applied as a potentially attractive emulsion modifier because both cyclic and linear polymer surfactants are chemically identical and considered inherently compatible with each other.

In the present work, we used a block copolymer surfactant composed of polystyrene (PS) and poly(ethylene oxide) (PEO) as hydrophobic and hydrophilic segment components, respectively, because a variety of linear PS-PEO block copolymers have been studied extensively for their use in various self-assemblies, such as micelles, vesicles and other complex aggregates.[2,11,12] In particular, the formation of simple to complex emulsion structures using toluene/water mixtures has been reported in the presence of the A-B type linear PS-PEO block copolymer.[13] In addition, we recently developed an effective means to produce cyclic PS-PEO block copolymers using a ring-closing metathesis of a linear symmetric PS-PEO-PS block copolymer precursor having olefinic end groups (Scheme 1).[14] Thus, to reveal the topology effects of polymer surfactants by using a simple and convenient experimental setup, we examined the macroscopic emulsion stability of toluene/water mixtures using a pair of linear PS-PEO-PS and its cyclized PS-PEO amphiphilic block copolymer with unaltered chemical composition.

MATERIALS AND METHODS

Materials

A linear block copolymer surfactant and its cyclized counterpart (**1** and **2**, respectively) with hydrophobic PS and hydrophilic PEO segments were prepared according to a procedure described previously.[14] The detailed synthetic procedures and product characterization using nuclear magnetic resonance (Supplementary Figure S1) and SEC (Supplementary Figure S2) techniques are shown in Supplementary Information.

Emulsion-stabilization measurements

As a typical example,[15,16] a $1 \, mg \, ml^{-1}$ toluene solution of either a linear or a cyclized block copolymer (**1** or **2**, respectively) was prepared by dissolving the weighed amount of either block copolymer (9.4 mg of **1** in 9.4 ml toluene or 9.5 mg of **2** in 9.5 ml of toluene, respectively). Then, an aliquot of the toluene solution (1.0 ml each) was transferred into a 30 ml graduated glass cylinder (inner diameter of 1.77 cm), and a 10 ml toluene solution of the surfactant concentration of $0.1 \, g \, l^{-1}$ was prepared by further dilution. Next, a measured volume of distilled water (5, 10 or 15 ml) was added slowly to form the two-layer solution (Figure 1). After the glass cylinder was immersed for more than 10 min in a water bath, which was thermostated at 25, 50 or 75 °C, the capped glass cylinder was taken from the bath and manually shaken vertically (200 times within ~1 min) to form a homogenous emulsion (Figure 1). The glass

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan
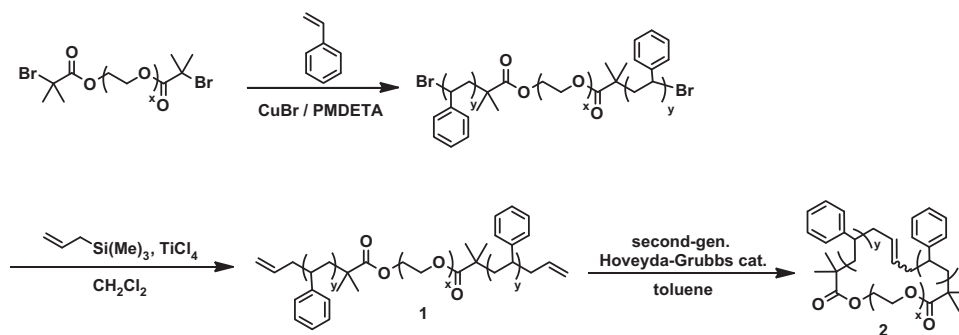
Scheme 1 Preparation of a linear PS-PEO-PS block copolymer with allyl end groups (1) and a cyclized PS-PEO block copolymer (2).
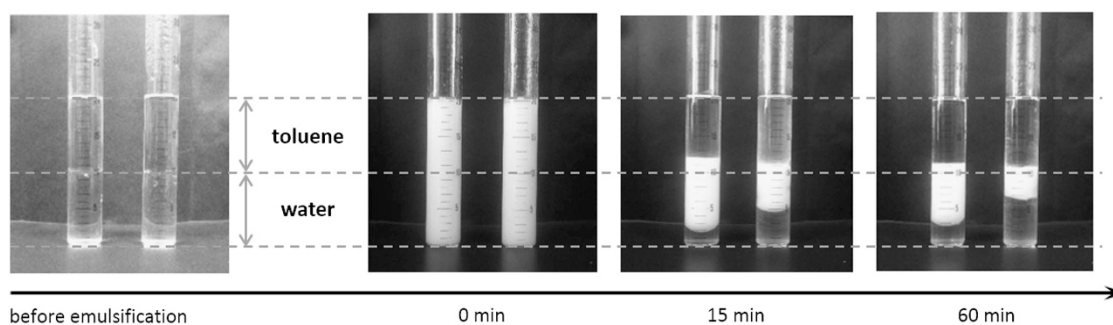

Figure 1 Photographs of a typical time course of the phase separation from the toluene/water emulsion in the presence of (left in each photo) a linear PS-PEO-PS block copolymer (1) and (right in each photo) a cyclized PS-PEO block copolymer (2) (10 ml/10 ml of toluene/water, initial surfactant concentration of $0.1\,g\,l^{-1}$ in toluene, at 50 °C). A full color version of this figure is available at *Polymer Journal* online.

cylinder containing the emulsion mixture was placed again in a thermostated water bath to monitor over time the volume of the transparent layers regenerated in water and in toluene phases. The high reproducibility of the applied emulsification/shaking procedure was confirmed by monitoring the time course of the phase separation from the emulsion (Supplementary Figure S3). A set of five experiments was conducted by using separately prepared samples (Supplementary Figure S4), and the average of the three medium values for the phase-separation profile was used to represent the results in Figures 2 and 3.

RESULTS AND DISCUSSION

A set of a linear and a cyclized block copolymer surfactants (1 and 2, respectively) with hydrophobic PS and hydrophilic PEO segments were prepared and used in the present study. An allyl-terminated linear PS-PEO-PS block copolymer, 1, with the molecular weight of 4100-2100-4100, was prepared by using an atom transfer radical polymerization (ATRP) technique with a bifunctional PEO initiator of the molecular weight of 2000 and the subsequent end-capping reaction with allyltrimethylsilane. The subsequent intramolecular metathesis reaction in the presence of the second-generation Hoveyda–Grubbs catalyst under dilution afforded a cyclized PS-PEO block copolymer, 2, with the molecular weight of 8900-2100.[14] Thus, we obtained 1 and 2 with highly similar segment compositions, which would form vesicle-type self-assemblies in aqueous medium,[12] for the subsequent experiments. We used the linear A-B-A block copolymer surfactant 1 instead of the A-B counterpart because we assumed that the linear/cyclized topology effect with the former, which could specifically undergo the folding/extending motion with the A segments, should be more eminent than that of the latter, as observed in their micelles.[3,4]

The emulsified solution was prepared using toluene/water mixtures of different compositions in the presence of either surfactant 1 or 2, and the subsequent macroscopic phase separation was monitored at various temperatures.[15,16] As shown in Figure 1, a homogeneous toluene solution (10 ml) containing a weighed amount of the polymer surfactant was first prepared in a 30 ml graduated glass cylinder (inner diameter of 1.77 cm) because both PS and PEO components are soluble in toluene. Next, a measured volume of distilled water (5, 10 or 15 ml) was added slowly to form the two-phase solution, and the cylinder was shaken vigorously to form a homogeneously emulsified solution. The subsequent phase separation was confirmed to proceed in a reproduced manner using the manual shaking procedure (Supplementary Figure S3). A set of five emulsified solutions was prepared separately and subjected to the phase-separation experiments (Supplementary Figure S4).

Then, the emulsified solution was placed in a water bath, which was thermostated at 25, 50 or 75 °C, to monitor the macroscopic phase-separation process (Figure 1). It was consistently observed that the transparent toluene layer recovered rapidly to the original volume (Supplementary Figure S5), presumably because the emulsion in the toluene phase tends to destabilize kinetically owing to the toluene-soluble nature of both PS and PEO components in 1 and 2. By contrast, the phase separation from the emulsified layer in the water phase was noticeably slower. Accordingly, the time course of the phase separation to form the transparent layer in the water phase, which corresponds to the emulsion stabilization caused by either 1 or 2, was quantitatively monitored.

The results obtained in the presence of either surfactant 1 or 2 at the concentration of $0.1\,g\,l^{-1}$, with different toluene/water volume ratios (10/5, 10/10 and 10/15 in ml/ml) and at various temperatures
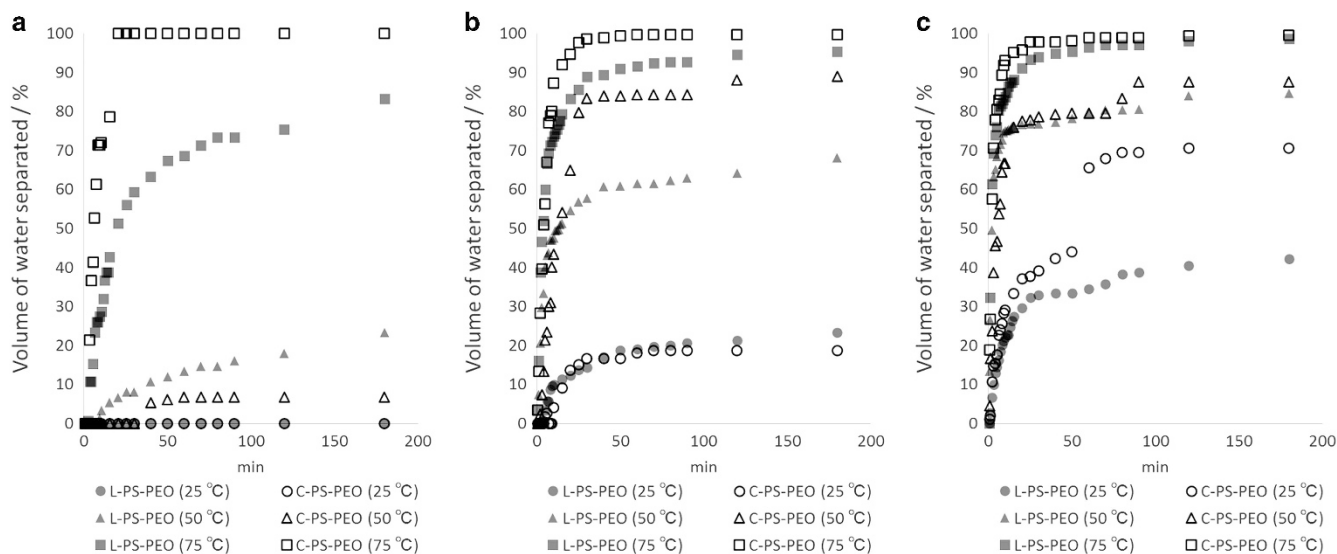
Figure 2 Time dependence of the volume ratio of the separated water layer from the water phase emulsion, in the presence of a linear PS-PEO-PS block copolymer (**1**) and a cyclized PS-PEO block copolymer (**2**) (initial surfactant concentration of $0.1\,g\,l^{-1}$ in toluene) at different toluene/water ratios of (**a**) 10/5 in ml/ml, (**b**) 10/10 in ml/ml and (**c**) 10/15 in ml/ml, and at ($\bigcirc$,●) 25 °C, (△,▲) 50 °C and (□,■) 75 °C.
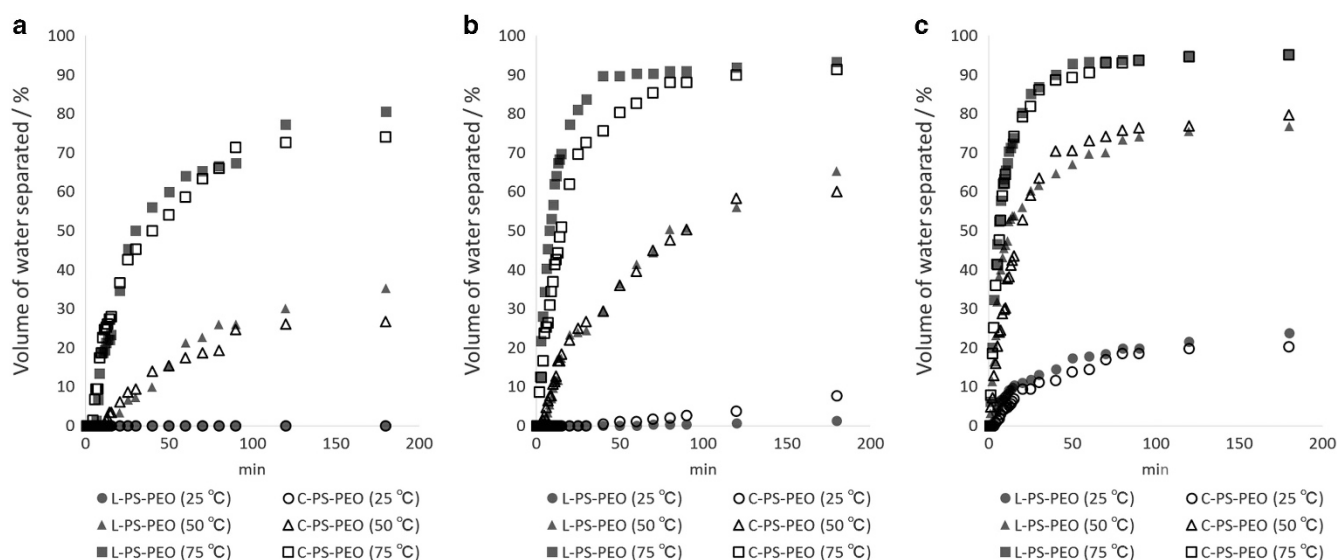

Figure 3 Time dependence of the volume ratio of the separated water layer from the water phase emulsion, in the presence of a linear PS-PEO-PS block copolymer (**1**) and a cyclized PS-PEO block copolymer (**2**) (initial surfactant concentration of $0.2\,g\,l^{-1}$ in toluene) at different toluene/water ratios of (**a**) 10/5 in ml/ml, (**b**) 10/10 in ml/ml and (**c**) 10/15 in ml/ml and at ($\bigcirc$,●) 25 °C, (△,▲) 50 °C and (□,■) 75 °C.

(25, 50 and 75 °C), are collected in Figure 2. It was confirmed that either block copolymer surfactant **1** or **2** could suppress the macroscopic phase separation from the emulsion in the water phase under the applied conditions. In addition, as expected, the phase separation was observed to proceed more rapidly at higher temperatures at any toluene/water composition, as shown in the profiles of □/■ compared with △/▲ and $\bigcirc$/● in the A, B and C graphs in Figure 2. Furthermore, the phase separation was promoted by adding an increasing amount of water (from 5 to 15 ml) to the constant volume (10 ml) of toluene, as can be seen by comparing the profiles of □/■ in **a** with □/■ in **b** and □/■ in **c** in Figure 2 and comparing the profiles of △/▲ and $\bigcirc$/● in the same manner. This observation is accounted for by the decrease in the

effective concentration of the surfactant in the water phase, since the increase in water corresponds to the increase of the total solution volume.

Moreover, it is particularly remarkable that the significant deviation was observed between the phase-separation profiles by **1** and **2** under relevant conditions, that is, at 75 °C in a toluene/water volume ratio of 10/5 in ml/ml (□ vs ■ in Figure 2**a**), at 50 °C in a toluene/water volume ratio of 10/10 in ml/ml (△ vs ▲ in Figure 2**b**), and at 25 °C in a toluene/water volume ratio of 10/15 in ml/ml ($\bigcirc$ vs ● in Figure 2**c**), respectively. The observed contrast in the phase-separation kinetics is attributable to the distinctive structure of either the linear or the cyclized surfactants because they direct the phase-separation process from the emulsions.

By contrast, no notable or systematic difference between **1** and **2** was observed under other phase-separation conditions (Figure 2). Thus, we carried out additional experiments with the increased surfactant concentration of $0.2\,g\,l^{-1}$ as compared with the $0.1\,g\,l^{-1}$ so far discussed. As shown in Figure 3, the phase separation was constantly slowed at the higher surfactant concentration. In addition, the phase separation was faster at the higher temperature and slower with larger amounts of added water, as in the experiments with lower surfactant concentrations described above. Furthermore, no appreciable difference was observed in the phase-separation profiles of **1** or **2** under applied conditions.

These findings, together with the previous results for micelle stabilization by the linear or cyclized block copolymer surfactants, enabled us to elucidate, in particular, the topology effect of the linear and the cyclized surfactants in the present emulsion stabilization. In the previous studies,[3,4] we showed that the micelles formed with the cyclized block copolymer surfactants are significantly stabilized in comparison with those with the linear counterparts. This was attributed to the folding/extending motion of the hydrophobic A segments in the linear A-B-A surfactants, which is inherently prohibited with the cyclized counterpart because of the linking of the free chain ends. The extended A-B-A surfactant could cause the bridging between neighboring micelles and eventually destabilize the

micelles via their agglomeration through the bridging to form a macroscopically turbid solution.

In addition, as shown in a study on emulsion formation/stability using toluene/water mixtures in the presence of the linear PS-PEO block copolymer,[13] the present emulsion system in the water phase is reasonably assumed to be an O/W, that is, toluene (oil) in water, type (Figure 4). The phase separation from the emulsified solution was shown to involve such complex processes as creaming/sedimentation, flocculation and coalescence. Nevertheless, the coalescing of oil (toluene) droplets is considered a crucial step, and the coalescence is promoted by the mass transfer of the block copolymer surfactant, initially placed at the interface area of water/toluene phase into the oil (toluene) droplets phase because the components of both PS and PEO are soluble in toluene. In addition, the mass transfer of the permanently folded, cyclic block copolymer surfactant **2** into oil droplets tends to proceed after the dehydration of the PEO segments at the interface.

By contrast, the linear A-B-A block copolymer surfactant **1** can assume the extended segment conformation and cause the bridging between the oil droplets dispersed near the coalescing in the water phase. The subsequent mass transfer process of **1** into oil droplets (toluene phase) should be circumvented because the translocation of the hydrophobic PS segment should involve the passing across the
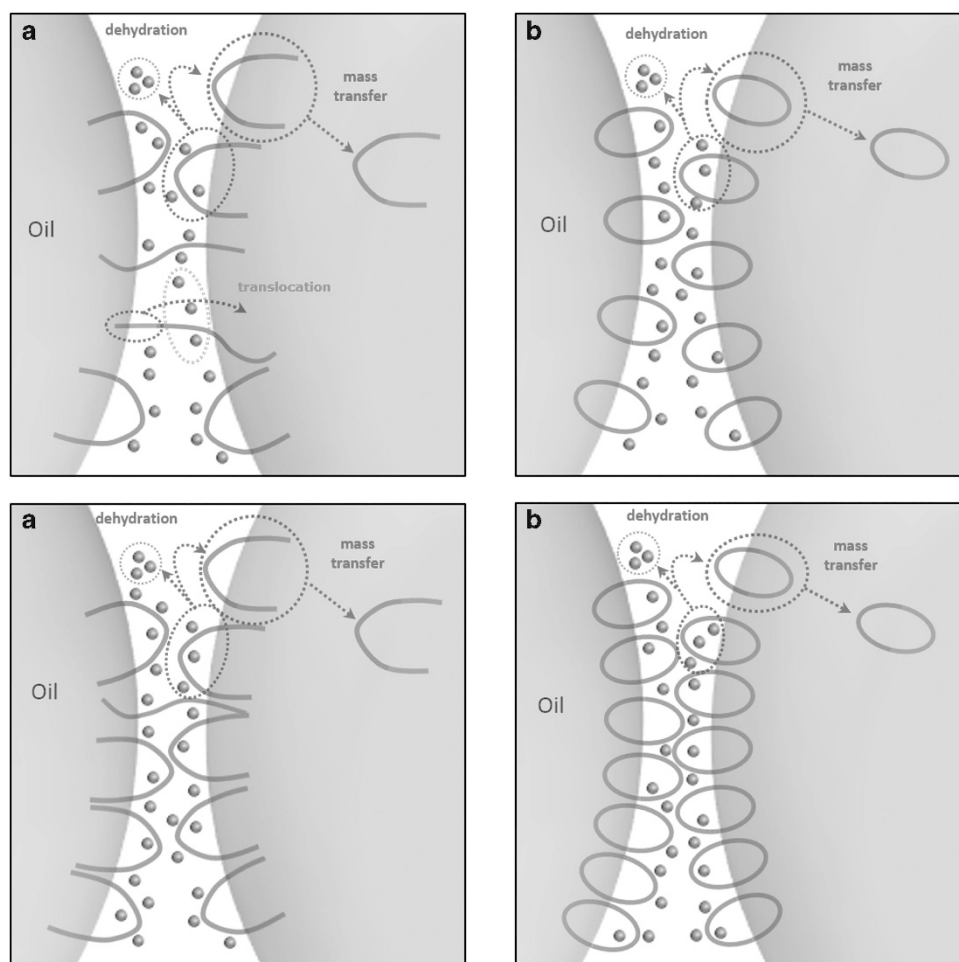

Figure 4 Schematics of the emulsion-stabilization effects of (**a**) a linear PS-PEO-PS block copolymer (**1**) and (**b**) a cyclized PS-PEO block copolymer (**2**) surfactants at (top) low and (bottom) high surfactant concentrations. Note that at the high surfactant concentration (bottom, **a** and **b**), **2** is accumulated in denser arrangements than **1** at the interface. A full color version of this figure is available at *Polymer Journal* online.

water phase maintained with the hydrated PEO segment. Consequently, the bridging of the PS segments of the linear surfactants can suppress the phase-separation process but is not applicable to the cyclized counterpart (Figure 4 (top), **a** and **b**).

At the same time, X-ray structural analysis[17] showed that the cyclized block copolymer surfactants, **2**, are more densely ordered to form a compact micelle in comparison with that by the linear counterparts, **1**. Therefore, it is speculated that, at the higher surfactant concentration, **2** at the toluene–water interface area can be accommodated in a denser arrangement in comparison with **1**, having free chain ends (Figure 4 (bottom), a and b). Consequently, the mass transfer of **2** could be suppressed and the bridging effect by **1** could eventually be canceled out. Thus, the topology effect by **1** and **2** has been observed under the selected conditions, whereas the overall emulsion stabilization is directed primarily by the surfactant concentration and by the temperature.

CONCLUSION

Using a simple and convenient experimental setup, we have shown the distinction in the phase-separation process of the toluene/water emulsion formed by either the linear or the cyclized PS-PEO block copolymer surfactant under selected conditions of the surfactant concentration, temperature and toluene/water ratio. Thus, a class of cyclic polymer surfactants can become a potentially attractive emulsion modifier because cyclic and linear polymer surfactants are chemically identical and considered inherently compatible with each other. Further microscopic and physicochemical studies on emulsion formation/stability using the linear/cyclized polymer surfactants are in progress and will be reported separately.

ACKNOWLEDGEMENTS

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