

## Temperature Dependent Aggregation Behavior of Polystyrene-Based Amphiphilic Block Copolymers at the Air-water Interface

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We report characteristic spreading behavior of amphiphilic block copolymers, polystyrene-*block*-poly(4-vinyl pyridine) (PS $_m$ -P4VP $_n$ ) at the air-water interface. When the polymers were spread from cyclohexane, a theta solvent for PS and a poor solvent for P4VP, onto the air-water interface, unexpected sharp temperature dependent changes were observed in the surface pressure-area curves. In the cyclohexane solution, the aggregate sizes of the block copolymers strongly depended on the solution temperature as revealed by transmittance measurements. These phenomena observed for cyclohexane should be attributed to the coil-globule conformational transition taking place in the theta solvent. The phase transition temperature in solution and at the air-water interface linearly enhanced with the increase of the molecular weight of PS segments. To our knowledge this work presents the first clear example that the aggregation state of polymers in solution is directly reflected to the two-dimensional spreading behavior at the air-water interface.

Key words : Amphiphilic block copolymers, Polystyrene, Langmuir-films, Polymer micelle, Theta solvent, Coil-globule transition

### 1. INTRODUCTION

Polymer chains in general adopt different conformations in solution and at the air-water interface. The conformations of single polymer chains have a random three-dimensional extended coil at high temperatures and in good solvents, while they have a collapsed globule state or dissolved as an aggregate at low temperatures and in poor solvents [1]. The phase transition between the extended and collapsed state, namely, the coil-globule transition, occurs under the particular temperature [2] or solvent composition [3]. In contrast, polymer chains are stretched upon spreading on water with the repeating units being adsorbed on the air-water interface [4]. On the other hand, the chain conformation of hydrophobic polymers on water is affected by the spreading solvent used. For example, when polystyrene is spread from a highly volatile solvent, it immediately forms aggregates. By selecting the spreading solvents, monomolecular particles [5] or thin films whose thickness is in a few tens of nanometers [6] can be obtained.

When block copolymers are dissolved in a solvent which is good only for one segment, the insoluble blocks associate and form the core of micelle structures, whereas the soluble blocks form a corona [7]. These colloidal aggregates are switched reversibly by solution temperature [8] or

solution compositions [7, 9]. For thin films, morphologies of block copolymers are also altered by solvent conditions. Sohn et al. reported that 2D micelles of polystyrene-*block*-poly(4-vinyl pyridine) (PS-P4VP) switch their nanostructures through core-corona inversion of micelles by selecting solvents of each blocks [10].

Recently, we found the characteristic spreading behavior of amphiphilic block copolymer, (PS $_m$ -P4VP $_n$ , Figure 1) at the air-water interface. An abrupt temperature-dependent change in aggregate size of polymer micelles has been observed when cyclohexane is used as the solvent. The size of the polymer micelle in solution is directly reflected to the two-dimensional spreading behavior at the air-water interface [11]. This paper reports some detailed results of this exploration, focusing on the content of PS in the block copolymer.

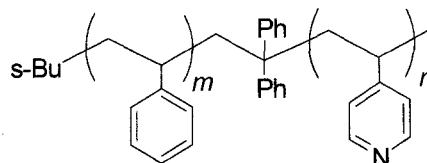


Figure 1. Chemical structure of PS $_m$ -P4VP $_n$ .

## 2. EXPERIMENTAL

The amphiphilic block copolymers, PSm-P4VP $_n$ , were synthesized by living anionic polymerization. Molecular characteristics of block copolymers are listed in Table 1. The PS content of the block copolymers were 76, 83, 88 and 94 wt%, and dubbed as P1 - P4, respectively. The concentration of the spreading solutions was ca.  $1.0 \times 10^{-3}$  mol dm $^{-3}$  per pyridine unit.

The spreading behavior of PSm-P4VP $_n$  was evaluated on pure water (Milli-Q grade, 18 M $\Omega$ cm, pH = 5.8) using a Lauda FW-1 film balance. The temperature of a water subphase was controlled by water circulation in the accuracy of  $\pm 0.1$  °C using a Yamato-Komatsu CTE-22W. After evaporation of the spreading solvent, the film on water was compressed at a speed of 30 cm $^2$  min $^{-1}$ . The surface pressure was recorded versus molecular area per styrene unit.

UV-vis transmittance spectra in solution were taken with an Agilent 8453, and turbidities were measured by monitoring transmittance at 500 nm through 1 cm quartz cell at various temperatures. The solution temperatures were controlled by water circulation at various temperatures in the accuracy of  $\pm 0.2$  °C using a Lauda RE104. The concentration was ca.  $1.0 \times 10^{-3}$  mol (4VP unit) dm $^{-3}$ , respectively.

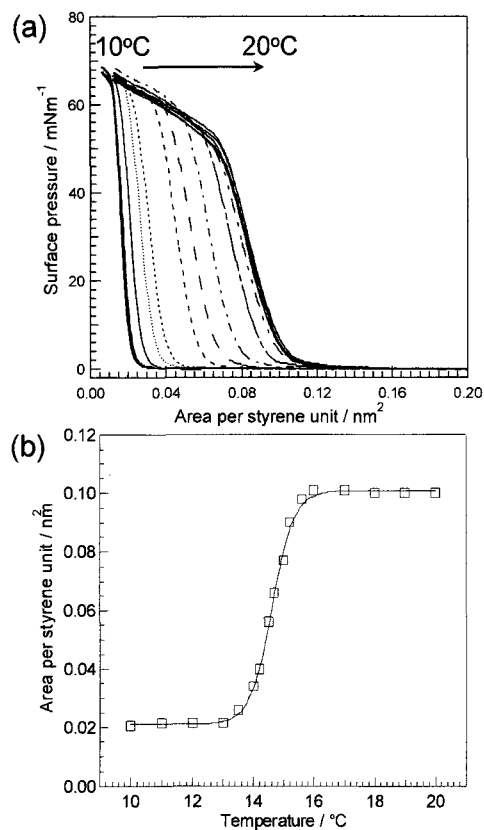
**Table 1.** Characterizations of PSm-P4VP $_n$  used in this study

polymer	m (PS)	n (P4VP)	$M_w/M_n$	PS content (wt%)
P1	88	28	1.14	76
P2	158	32	1.10	83
P3	256	34	1.09	88
P4	555	35	1.09	94

## 3. RESULTS AND DISCUSSION

### 3. 1. Spreading behavior at the air-water interface

Figure 2a depicts the  $\pi$ - $A$  curves of P2 spread from cyclohexane, a theta solvent for PS blocks and poor solvent for P4VP, at subphase temperatures between 10 and 20 °C. The occupying area per styrene unit as a function of the subphase temperature is shown in Figure 2b. This polymer has a large PS content, so the shapes of these curves were similar to PS homopolymer. From 10 to 13.5 °C, polymer chains formed aggregates on water immediately after spreading, their occupying areas staying constant at ca. 0.02 nm $^2$ . Above 16 °C, the area was retained again at a constant area of ca. 0.10 nm $^2$ . A sudden increase of the occupying area by a factor of five was observed between 14 and 16 °C. In contrast, when non-theta solvents for PS such as chloroform and toluene were used, no obvious temperature dependency was observed (data not shown). It is thus concluded that use of the theta solvent on spreading for the block copolymer is essential for the large temperature dependency.

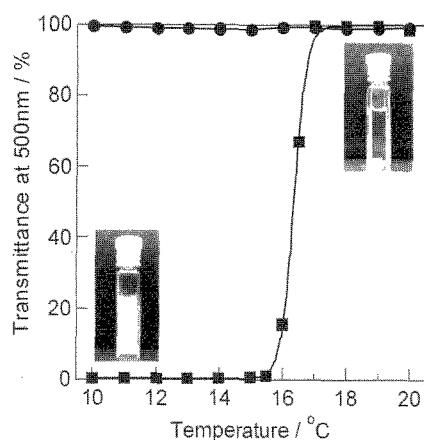


**Figure 2.** Surface pressure ( $\pi$ )-area ( $A$ ) curves of P2 when spread from cyclohexane from 10 to 20 °C (a), and relationship between the area per styrene unit and subphase temperature (b).

### 3. 2. Aggregation behavior in solutions

The aggregates of P2 in cyclohexane solution were also altered by temperature change [11]. Figure 3 exhibits transmittance at 500 nm of P2 in cyclohexane and chloroform solutions at various temperatures. In the figure, photographs of the sample cell are also displayed. The cyclohexane solution was transparent and their transmittance exceeded 95 % between 17 and 20 °C. From 10 to 15.5 °C, in contrast, the solution became highly turbid. A sudden increase of the transmittance was observed in a narrow range between 15.5 and 17 °C. This behavior is closely correlated with the area change at the air-water interface. In contrast, turbidity change and thus transmittance change were not observed in chloroform.

The above observations were explained by assuming the coil-globule phase transition taking place at this temperature (theta temperature). In cyclohexane above the theta temperature, PS chains adopt an extended coil state forming micelles. When solution temperature is lowered down below this temperature, PS chains are transformed from a coil state to a globule one, and polymer micelles become insoluble in cyclohexane. Then, these micelles form larger aggregates. The change in the aggregate size has been already



**Figure 3.** Transmittance of P2 solutions in chloroform (■) and cyclohexane (●) at 500 nm at various temperatures. Photographs display the cyclohexane at 10 and 20 °C.

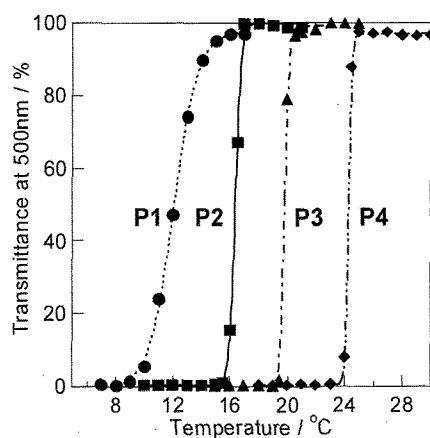
confirmed by the dynamic light scattering measurements [11]. As a result, the turbidity of the polymer micelle solution is suddenly altered by the temperature change.

### 3. 3. Effect of the PS contents of the block copolymers

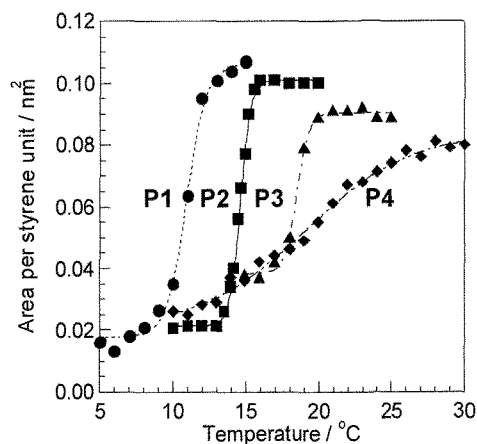
The changes of transmittance in solution and those of surface area per PS unit at the air-water interface examined for the series of  $PS_m-P4VP_n$  are shown in Figures 4 and 5, respectively.

In all polymers, the tendency of the temperature-dependent turbidity change was similar, however, increases in the PS content from 76 to 94 wt%, led to systematic elevations of the transition temperatures. The temperature ranges of the transition were from 9 to 14, 15.5 to 17, 19.5 to 20.5 and 23 to 25.5 °C for P1, P2, P3 and P4, respectively. It is thus indicated that coil-globule transitions of  $PS_m-P4VP_n$  are clearly affected by the PS content. A previous static light scattering study by Tanaka et al. revealed that the radius of gyration of PS in cyclohexane abruptly changes around 32 °C [2, 3]. In the present case, the temperature range was decreased by 10 to 20 °C. The lowered transition temperature should be ascribed to the difference in the molecular weight. Chu and Wang et al. [12] showed that the transition temperature significantly shifts to a lower range when the molecular weight becomes lower. For example, the transition temperature shifts from 39.5 to 12.6 °C as  $M_w$  becomes from  $4.6 \times 10^4$  to  $1.0 \times 10^4$  in methylcyclohexane, also a theta solvent for PS. Tanaka et al. adopted PS with  $M_w = 2.7 \times 10^7$ , and that of the PS block of the copolymer employed in this study ranges  $9.1 \times 10^3$  to  $5.8 \times 10^4$ . Thus, the reduction in the transition temperature seems reasonable.

The temperature range of the transition evaluated by the area change at the air-water interface also indicated systematic changes similar to that in cyclohexane solutions. Their temperature ranges of the area change were from 9 to 12 °C, 14



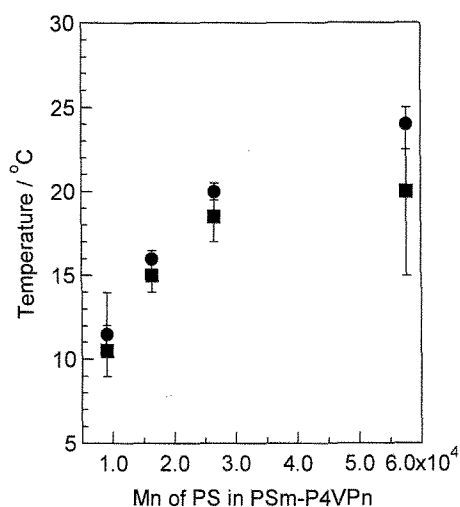
**Figure 4.** Transmittance change at 500 nm in cyclohexane solution of P1 - P4 at various temperatures.



**Figure 5.** Relationship between the area per styrene unit of P1 - P4 at the air-water interface at various temperatures and subphase temperatures.

to 16 °C, 17 to 20 °C and 15 to 25 °C, for P1, P2, P3, and P4, respectively. However, the apparent transition range of P4 obviously became broader. We assume that the broadening of the transition temperature range observed for P4 is related to the large chain length of PS component. Upon spreading on water, the solvent evaporates rapidly and therefore the conformation and aggregate state is quickly frozen. When the longer chains are quickly frozen, various states of micelle size will be produced due to possible chain entanglements. In other words, the transition broadening should occur for the kinetic reason. In contrast, the chain conformation and aggregate states in solution are always in an equilibrium state, indicating the sharp transition independent of the chain length (Figure 4). For a precise understanding, further investigation will be required.

The coil-globule phase transition temperatures estimated in solution and at the air-water interface for P1 - P4 are summarized in Figure 6. From both evaluations, the transition temperatures were increased with the increase in PS segments of



**Figure 6.** The phase transition temperature estimated by the turbidity change in cyclohexane solution (●) and change at the air-water interface when spread from cyclohexane (■).

PSm-P4VPn.

The relationship strongly suggests that the polymer micelle structure is commonly formed in these four polymers. In the process of spreading onto the water surface from the cyclohexane solution, the state of micelle aggregate is memorized and retained during the rapid evaporation of the solvent. The close correlation between the aggregation state in the solvent and the film area on water can be explained by such assumption.

#### 4. CONCLUSIONS

In this study, we have found the obvious relationship between the aggregates in theta solution and the spreading behavior at the air-water interface when a theta solvent for PS segments (cyclohexane) is used for spreading. An unexpectedly large (5-folds) area change on water and transmittance change in solution are observed at a very narrow temperature range by 2 °C. Such behavior is most probably attributed to the thermally induced coil-globule transition. Thus, the aggregation state in solution is memorized and retained during the spreading process on water. With the increase in the molecular weight of PS led to elevation of the transition temperature. We expect that this new knowledge should be of help in fundamental understandings in polymer chain conformations and in polymer thin film technology.

#### ACKNOWLEDGEMENT

We thank Drs. T. Nakanishi and Y. Masuda at Nagoya University for dynamic light scattering measurements. This work was supported by Grant-In-Aid Scientific Research (No. 16205019 to TS) from MEXT, Japan.

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(Received December 10, 2005; Accepted March 13, 2006)