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ORIGINAL CONTRIBUTION

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# Micelle formation of a diblock copolymer having pyridine as pendant groups by carboxylic acids in nonselective solvents

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**Abstract** The micelle formation of a poly(4-pyridinemethoxymethylstyrene)-*block*-polystyrene diblock copolymer (PPySt-*b*-PSt) was investigated in nonselective solvents using bifunctional and trifunctional carboxylic acids. The copolymer showed no self-assembly in 1,4-dioxane and tetrahydrofuran (THF) because the PPySt and PSt blocks were solvophilic to the solvents. Dynamic light scattering studies demonstrated that the copolymer formed micelles in the nonselective solvents in the presence of bifunctional carboxylic acids. Oxalic acid, maleic acid, citric acid, and phospholic acid promoted the micellization, while malonic acid, succinic acid, and glutalic acid had no effect on the micellization. The micellar size, aggregation number, and critical micelle concentration were dependent not only on the acid strength but also on the type of acid and the functionality. The micellization was also affected by the solvent quality. The micellization proceeded more effectively in 1,4-dioxane than in THF. It was found that the micellization occurred by hydrogen bonding between the pyridine moiety and the carboxylic acid and by the interaction among the carboxylic acids. This is because the copolymer needed over an equivalent of the acid to the PySt unit to complete the micellization. Furthermore, monofunctional carboxylic acid such as trichloroacetic acid and trifluoroacetic acid promoted the micellization, although dichloroacetic acid had no effect on the micellization.

**Keywords** Poly{4-(pyridinemethoxymethyl)styrene}-*b*-polystyrene (PPySt-*b*-PSt) · Micellization · Nonselective solvents · Carboxylic acids · Acid strength

## Introduction

Pyridine and its derivatives are widely used as proton acceptors. They serve as acid-trapping agents in many organic syntheses to drive the objective reactions [1–3]. Pyridine supported on polymers manipulates the association of the polymers by absorbing and desorbing protons. The control of the self-assembly of the pyridine-containing polymers by the proton transfer was found in pH-induced micellization. Examples include the pH-dependent micellization of poly(2-vinylpyridine)-*block*-poly(ethylene oxide) [4] and the size control of micelles for a metallo-supramolecular ABC triblock copolymer of polystyrene-*block*-poly(2-vinylpyridine)-*block*-poly(ethylene oxide) [5]. The interaction between pyridine attached to polymers and carboxylic acids is also effective for promoting the micellization of the polymers. Wangqing et al. and Zhang et al. prepared micelles of poly(acrylic acid)-containing block copolymers through the formation of hydrogen bonding with poly(vinyl pyridine) [6, 7], while Gohy et al. found micellization induced by interpolyelectrolyte complexes between poly(vinyl pyridine)-*block*-poly(ethylene oxide) and poly(methacrylic acid)-*block*-poly(ethylene oxide) [8]. Yao et al. reported micellization by the formation of the interelectrolyte complexes of poly(vinyl pyridine)-*block*-polystyrene with formic acid [9]. The micellization of poly(vinyl pyridine)

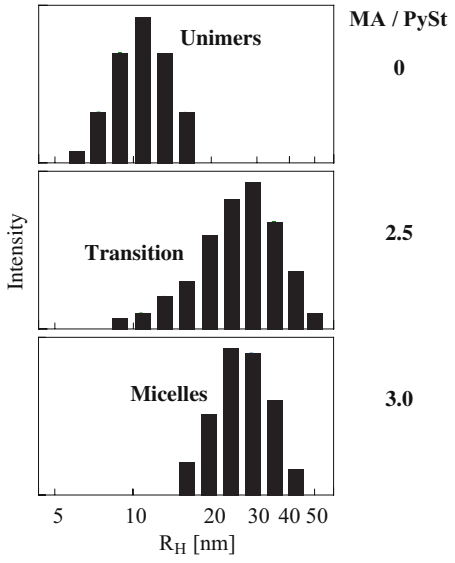


**Fig. 1** Variation in the intensity distribution of the hydrodynamic radius of the PPySt-*b*-PSt diblock copolymer through the micellization by maleic acid. [copolymer]=$3.33\times10^{-3}$ g/ml; solvent, 1,4-dioxane; and temperature, 20°C

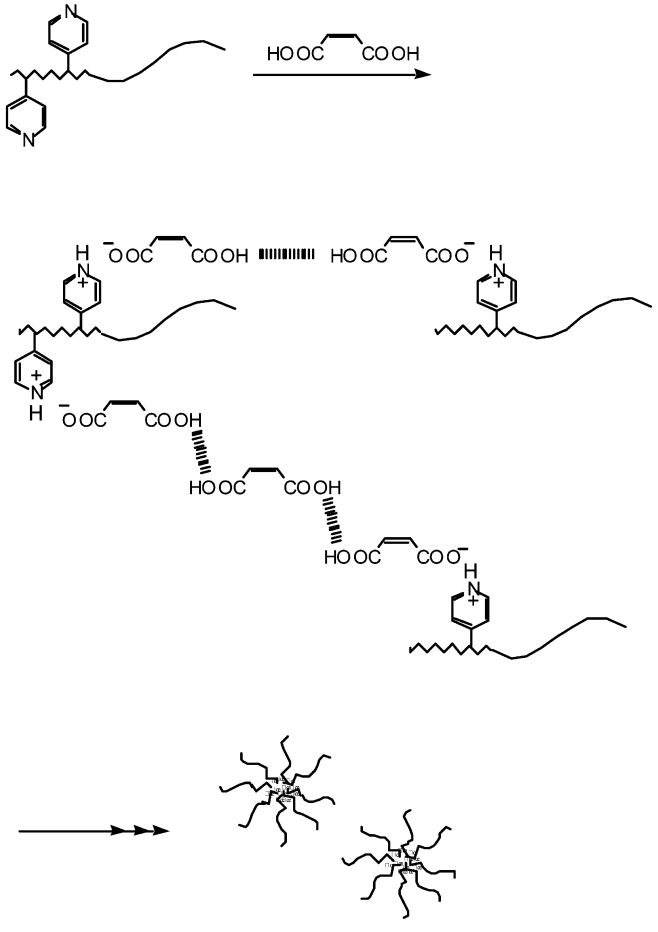


**Fig. 2** The micellization of the PPySt-*b*-PSt diblock copolymer by maleic acid

itself has been found by Liu et al. and Duan et al. using carboxy-terminated polystyrene [10] and polyimide [11], respectively.

We have recently reported the micelle formation of a poly(4-pyridinemethoxymethylstyrene)-*block*-polystyrene diblock copolymer (PPySt-*b*-PSt) in a nonselective solvent using perfluoroalkylcarboxylic acids [12, 13]. The micellization was induced by the interaction between both the pyridine moieties and the carboxylic acids and between the perfluoroalkyl groups. The critical micelle concentration (CMC), micellar size, and aggregation numbers were dependent on the length of the perfluoroalkyl chains of the carboxylic acids. Furthermore, the thermostability of the micelles was determined by the functionality of the acids.

We found that the PPySt-*b*-PSt diblock copolymer produced micelles in nonselective solvents in the presence of bifunctional or trifunctional carboxylic acids with a comparatively high acidity. This paper describes the effects of the acid strength and functionality of the carboxylic acids on the micellization of PPySt-*b*-PSt.

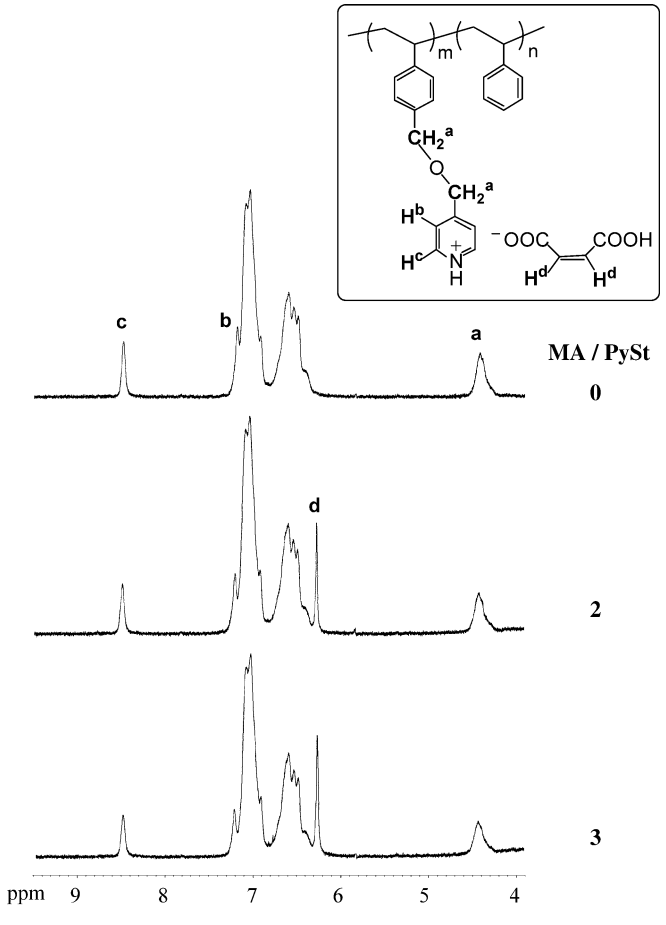


**Fig. 3** $^1$H NMR spectra of the PPySt-*b*-PSt copolymer in the absence and presence of maleic acid. [copolymer]=$3.33\times10^{-3}$ g/ml; solvent, 1,4-dioxane-$d_8$; temperature, 20°C

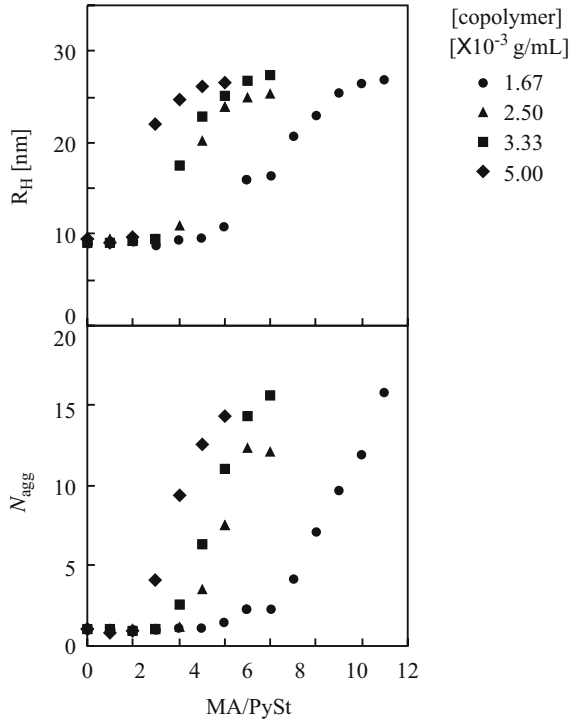


**Fig. 4** Variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization in 1,4-dioxane by maleic acid at four copolymer concentrations. Temperature, 20°C

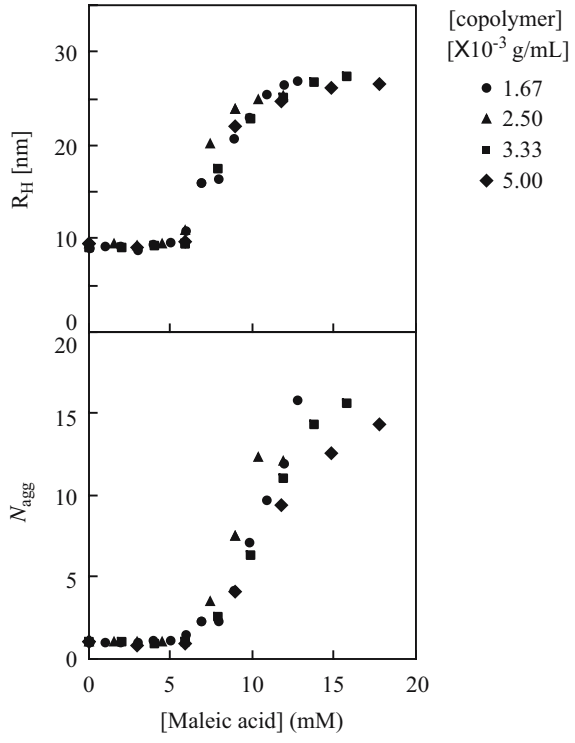


**Fig. 5** Plots of the hydrodynamic radius and the aggregation number of the copolymer vs the concentration of maleic acid for four copolymer concentrations. Temperature, 20°C

## Experimental

### Instrumentation

$^1$H nuclear magnetic resonance (NMR) spectra were obtained with a Bruker ARX-500 NMR spectrometer. Light scattering experiments were performed at 20°C with a Photal Otsuka Electronics DLS-7000 super dynamic light scattering spectrometer equipped with LS-71 control unit, an LS-72 pump controller, and an argon ion laser operating at λ=488 nm.

### Materials

PPySt-*b*-PSt was prepared as reported previously [12]. The molecular weight of the copolymer was estimated as Mn (PPySt-*b*-PSt)=12,000-*b*-33,000 by $^1$H NMR on the basis of the signal intensity of the methoxy protons of 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy (4-methoxy-TEMPO). 1,4-Dioxane and tetrahydrofuran (THF) were refluxed over sodium and distilled. Extra-pure maleic acid, oxalic acid, malonic acid, succinic acid, glutalic acid, phosphoric acid, dichloroacetic acid, trichloroacetic acid, and trifluoroacetic acid were used without further purification.

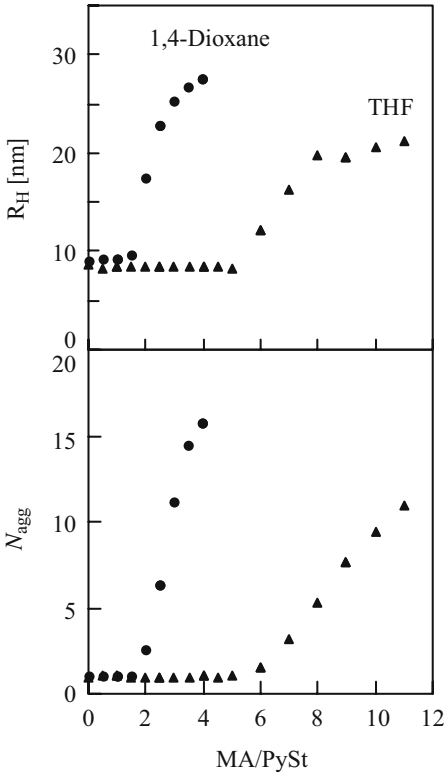


**Fig. 6** Variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization in 1,4-dioxane and THF by maleic acid. [copolymer]=3.33×10$^{-3}$ g/ml; temperature, 20°C

Light scattering measurements: general procedure

PPySt-*b*-PSt (10 mg) was dissolved in 1,4-dioxane (3 ml), and, using a syringe, the resulting solution was injected through a microporous filter into a cell. The solution was subjected to light scattering measurement at 20°C. After the measurement, 4 μl of maleic acid solution (maleic acid, 172 mg, 1.48 mmol) in 1,4-dioxane (1 ml) was added to the copolymer solution in the cell, and the mixture was shaken vigorously. The solution was allowed to stand at 20°C for 5 min and then subjected to light scattering again. This procedure was repeated until distribution due to the unimers disappeared completely in nonnegatively constrained least-squares (NNLS) analysis [14].

## Results and discussion

The PPySt-*b*-PSt diblock copolymer showed no self-assembly in 1,4-dioxane because the PPySt and PSt blocks are solvophilic to this solvent. Dynamic light scattering studies demonstrated that PPySt-*b*-PSt formed micelles in non-selective solvents in the presence of maleic acid. Figure 1 shows the variability in the intensity distribution of the hydrodynamic radius of the copolymer through the micellization by maleic acid. The distributions were obtained by the NNLS analysis. The copolymer shows no micellization in the absence of maleic acid, so that the distribution observed around 10 nm is attributed to the isolated copolymers, i.e., unimers. As maleic acid was added to a copolymer solution at 2.5 as the molar ratio of maleic acid to the PySt unit (MA/PySt), the distribution was shifted to the higher side of the hydrodynamic radius. However, the distribution of the unimers was still observed at this molar ratio. At the MA/PySt of 3.0, no observation was made of the unimer distribution, indicating that the micellization was completed at this ratio. The copolymer required the acid over an equivalent to the PySt unit to complete the micellization, suggesting that the micellization proceeded through hydrogen bonding between the pyridine moiety and the carboxylic acid and through the interaction among the carboxylic acids (Fig. 2).

Figure 3 shows $^{1}$H NMR spectra of the PySt moieties of the copolymer in 1,4-dioxane-$d_8$ throughout the micellization by maleic acid. Signals originating from the two different methylene protons attached to the styrene and pyridine moieties were observed at 4.40 ppm. Signals of the protons located at the 2 and 3 positions on the pyridine rings were discerned at 7.20 and 8.50 ppm, respectively. The intensities

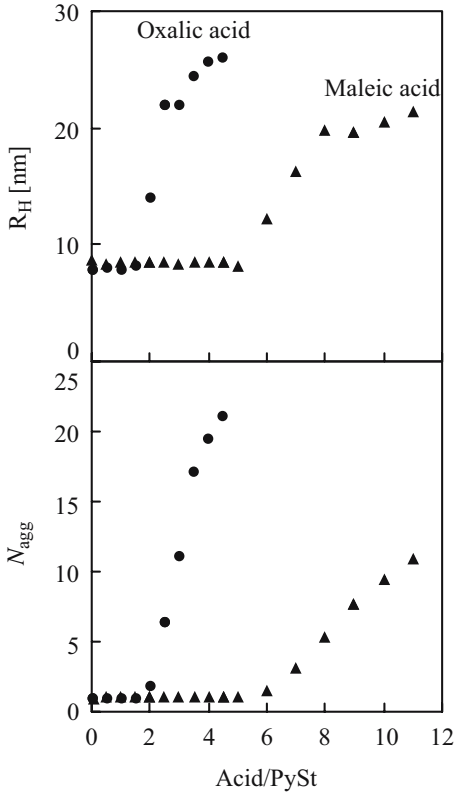


**Fig. 7** Variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by oxalic acid and maleic acid. Solvent, THF; [copolymer]=3.33×10$^{-3}$ g/ml; temperature, 20°C

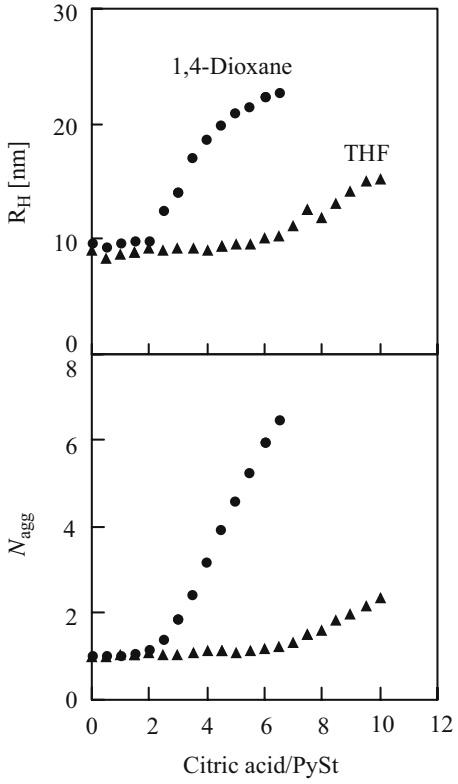


**Fig. 8** Variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by citric acid in 1,4-dioxane and THF. [copolymer]=3.33×10$^{-3}$ g/ml; temperature, 20°C

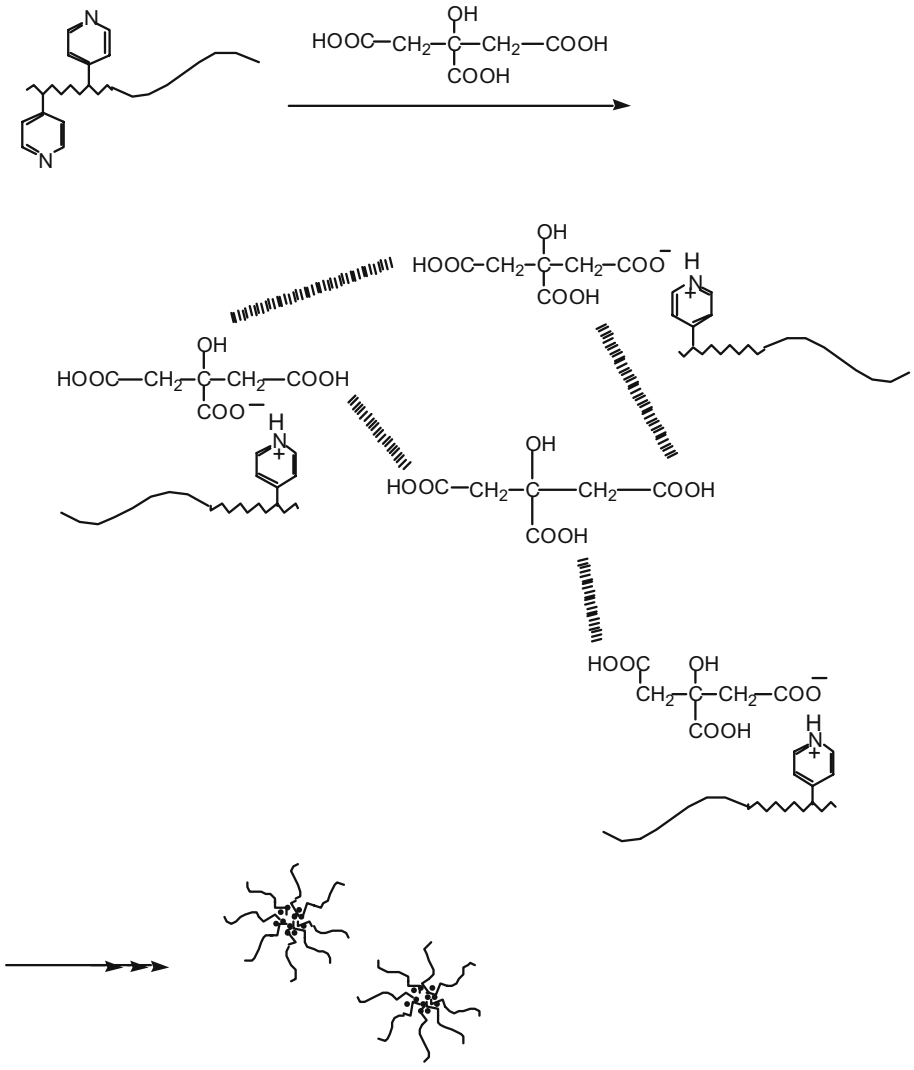

**Fig. 9** The micellization of the PPySt-*b*-Pst copolymer by citric acid

of the three different signals decreased by the addition of maleic acid. This decrease in the signal intensity of the pyridine moieties implies that the PPySt blocks forming the cores of the micelles were protected from the magnetic field. In addition, the sharp signal at 6.25 ppm originated from the olefin protons of maleic acid.

Figure 4 shows the variation in the hydrodynamic radius and aggregation number of the copolymer vs the MA/PySt ratio for four different copolymer concentrations. The aggregation numbers were estimated as relative aggregation numbers using the relative scattering intensity. This estimation is based on the fact that the pyridinium salt formation accompanying no aggregation makes no changes in the scattering intensity. As the copolymer concentration increased, the transition from the unimers to the micelles was shifted to the lower side of MA/PySt. This shift of the transition to the lower side of MA/PySt indicates that the CMC decreased with an increase in the copolymer concentration. The copolymer at a higher copolymer concentration needs less maleic acid to form micelles. The micellar size and aggregation number for the complete micellization were almost independent of the copolymer concentration. By plotting the hydrodynamic radius and aggregation number of the copolymer vs the concentration of maleic acid instead of the MA/PySt ratio, a slight difference was observed in the transition among the four copolymer concentrations (Fig. 5). It was found that the CMC was determined by the concentration of maleic acid rather than by the copolymer concentration.

The formation of hydrogen bonding is affected by the solvent quality. THF is a nonselective solvent for the copolymer, as is 1,4-dioxane. Figure 6 shows the variation in the hydrodynamic radius and aggregation number of the copolymer during the micellization in THF by maleic acid. The copolymer formed smaller micelles with a lower aggregation number in THF compared with those in 1,4-dioxane. The CMC in THF was also higher than that in 1,4-dioxane. These results are accounted for by the fact that the formation of the

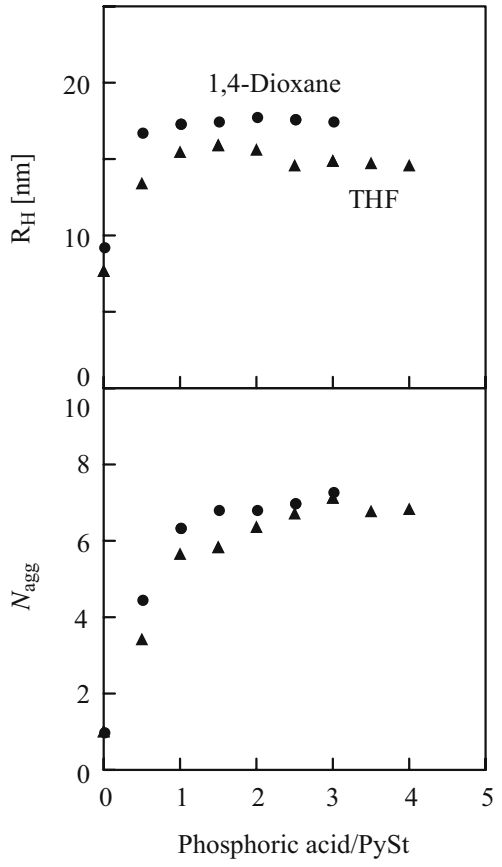


**Fig. 10** Variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by phospholic acid in 1,4-dioxane and THF. [copolymer]=3.33×10$^{-3}$ g/mL. Temperature: 20°C

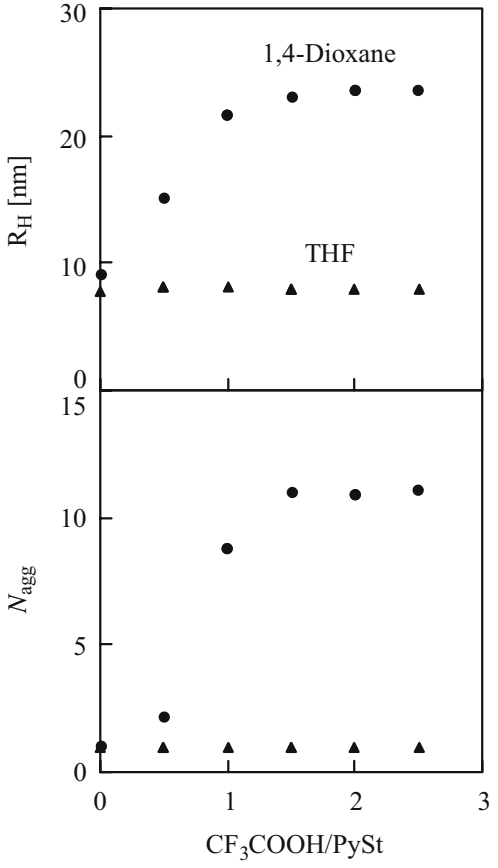


**Fig. 11** Variation in the hydrodynamic radius and the aggregation number of the copolymer through the micellization by trifluoroacetic acid in 1,4-dioxane and THF. [copolymer]=3.33×10$^{-3}$ g/mL. Temperature: 20°C

hydrogen bonding is more difficult in THF than in 1,4-dioxane due to the higher polarity.

The micellization should be dependent on the acid strength. Oxalic acid has a higher acidity than maleic acid. The $pK_1$ of oxalic acid and maleic acid are 1.23 and 1.83, respectively [15]. Oxalic acid is soluble in THF but insoluble in 1,4-dioxane. Figure 7 shows the variation in the hydrodynamic radius and aggregation number of the copolymer through the micellization by oxalic acid. The copolymer needed a lower amount of oxalic acid to form the micelles compared with maleic acid, indicating that oxalic acid more effectively promoted the micellization. This is reflected in the larger hydrodynamic radius and higher aggregation number of the micelles prepared by oxalic acid. Malonic acid, succinic acid, and glutalic acid promoted no micellization in 1,4-dioxane and in THF because of their low acidity: $pK_1$=2.83 (malonic acid), 4.16 (succinic acid), and 4.31 (glutalic acid) [15]. The aromatic carboxylic acid, phthalic acid, also provided no micelles because of the weak acidity ($pK_1$=2.98) [15].

Citric acid has a lower acidity ($pK_1$=3.14 [15]) than maleic acid and malonic acid; however, it is a trifunctional carbox-

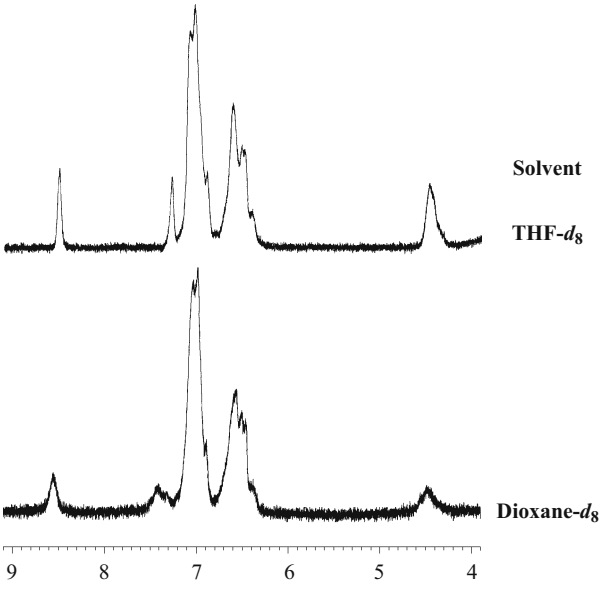


**Fig. 12** $^1$H NMR spectra of the PPySt-*b*-PSt copolymer in the presence of trifluoroacetic acid in THF-$d_8$ and 1, 4-dioxane-$d_8$. [copolymer] = 3.33X10$^{-3}$ g/mL. Temperature: 20°C

ylic acid. Citric acid also promoted the micellization, which occurred more effectively in 1,4-dioxane than in THF (Fig. 8). The micellization should proceed through hydrogen bond cross-linking via the carboxylic groups and the hydroxyl (Fig. 9). The micellization by citric acid showed a higher CMC than that by maleic acid due to the lower acidity. Phosphoric acid is also trifunctional, although it is not carboxylic acid. The acid strength is $pK_1$=2.16 [15]. As can be seen in Fig. 10, phosphoric acid made a slight difference in the micellization when in 1,4-dioxane or in THF. Regarding the micellization in 1,4-dioxane, the size of the micelles prepared by phosphoric acid was still smaller than that by citric acid, while the aggregation number was almost equal to that by citric acid. Compared with the micellization by maleic acid, the CMC for phosphoric acid was lower than that for maleic acid in spite of the fact that phosphoric acid has the lower acid strength than maleic acid. It can be deduced that the micellar size, aggregation number, and CMC are dependent not only on the acid strength but also on the type of acid and the functionality.

The bifunctional and trifunctional acids used in this study precipitated a PySt homopolymer in THF, with the exception of succinic acid and glutalic acid. Dichloroacetic acid, which has a similar acidity to oxalic acid (pK=1.29 [16]), also precipitated the homopolymer in THF. However, no micelles were obtained by dichloroacetic acid both in 1,4-dioxane and in THF. On the other hand, trichloroacetic acid and trifluoroacetic acid promoted the micellization in 1,4-dioxane. The acids have pK values of 0.65 [15] and 0.23 [17], respectively, and precipitated the PySt homopolymer in THF. Figure 11 shows the variation in the hydrodynamic radius and aggregation number of the copolymer through the micellization by trifluoroacetic acid in 1,4-dioxane and THF. The micellization occurred with trifluoroacetic acid in 1,4-dioxane, while no micellization proceeded in THF. The micelles should be formed on the basis of the van der Waals interaction through the pyridinium salt formation. Figure 12 shows the $^1$H NMR spectra of the copolymer in 1,4-dioxane-$d_8$ and in THF-$d_8$ in the presence of trifluoroacetic acid. The signal intensities at 4.50, 7.43, and 8.57 ppm based on the PySt moieties were reduced by the micellization. By comparing the spectrum for the micelles prepared by trifluoroacetic acid in 1,4-dioxane-$d_8$ with that of the micelles by maleic acid (Fig. 3, MA/PySt=3), a remarkable change was seen in the shape of the signal at 7.43 ppm. The signal was more broadened in the presence of trifluoroacetic acid. The copolymer formed firm micellar cores of the PPySt blocks by trifluoroacetic acid, resulting in that the PPySt blocks were more protected from the magnetic field.

## Conclusion

The micellization of the PPySt-*b*-PSt diblock copolymer was attained in nonselective solvents by the bifunctional and trifunctional carboxylic acids. The micellization proceeded through the hydrogen bond cross-linking between the pyridine moiety via the carboxylic acid and through the interaction among the carboxylic acids. This was based on the fact that the copolymer needed the acid over an equivalent to the PySt unit to complete the micellization. The acid with a strong acidity showed a tendency to produce larger micelles with a higher aggregation number. The CMC was also dominated by the acid strength. It was found that the micellar size, aggregation number, and CMC were dependent not only on the acid strength but also on the type of acid and the functionality. This is because phospholic acid with the higher acidity than citric acid produced the smaller micelles at the lower CMC. Furthermore, the micellization was affected by the solvent quality. The micellization proceeded more efficiently in 1,4-dioxane than in THF. The monofunctional carboxylic acid with a strong acidity also promoted the micellization, producing micelles with firm cores of PPySt blocks.

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