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Amphiphilic Heteroarm Star-Shaped Polymers by Living Cationic Polymerization: A Unique Behavior in Aqueous Solution[1]

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Introduction. We have synthesized a variety of amphiphilic star-shaped polymers via polymer linking reactions with divinyl compounds based on living cationic polymerization.[2] These star polymers have properties that differ from those of the corresponding linear polymers. For example, amphiphilic star polymers with longer hydrophobic segments are superior in host−guest interaction with small organic molecules to the linear amphiphilic counterpart.[3] This is likely due to a high accumulation of polar functional groups that stems from the multibranched structures of star polymers.

The branched structure of star polymers consists of radially extended arms attached to a central core. Such a structure would make a star polymer unimolecular micelle or "reverse" micelle if they have amphiphilic arms. Although this hypothesis has already been mentioned, few empirical data for the conformation and/or properties of branched amphiphilic polymers in solution or solid state have been reported until now.[4] Recently, we found that amphiphilic star block or heteroarm star polymers of vinyl ethers (VEs) with shorter hydrophobic segments in the inner layer were able to solubilize hydrophobic dyes relative to the corresponding linear block polymers.[5] The higher ability of star polymers to solubilize small molecules is presumably because they behave as a unimolecular micelle.

In this study, therefore, we synthesized amphiphilic heteroarm star-shaped polymers and examined the properties of their aqueous solutions, which was then compared with those of the corresponding linear polymers. As reported previously,[6a] the treatment of linear living polymers (P*) of isobutyl vinyl ether (IBVE), prepared with the HCl−IBVE adduct/ZnI_2 initiating system, with a small amount of divinyl ether **1** gives a "living" star-shaped polymer **2** (Scheme 1). From the living sites in its core, an ester-containing VE (AcOVE) is polymerized to give a heteroarm star-shaped polymer **3**. Hydrolysis of the ester groups in **3** then leads to an amphiphilic heteroarm star polymer **4**.

In this communication, we specifically describe the surface tension of their aqueous solution as well as the effects of the concentration of star polymers on their solubilization of hydrophobic organic compounds. We selected heteroarm star polymers in this study because our preliminary results showed that they solubilize more small organic molecules than not only the linear counterpart but star block-type polymers do.[5]

Experimental Section. Purification of all chemicals and polymerization procedures were described before.[6] Hydrolysis of the pendant ester functions of star polymers was carried out as reported previously.[6a]

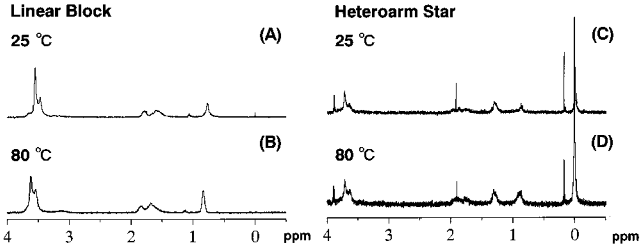

Figure 1. ^1H NMR spectra in D_2O at 25 °C (A and C) and at 80 °C (B and D): (A and B) linear block polymer **5** (IBVE/OH unit = 9/31); (C and D) heteroarm star-shaped polymer **4** (IBVE/OH unit = 11/29, 29 arms each).

Gel permeation chromatography (GPC) was performed in chloroform (flow rate: 1.0 mL/min) at 40 °C using a Shimadzu LC-10A liquid chromatograph system equipped with a Shimadzu LC-10AD pump, three polystyrene gel columns (Shodex K-803, 804, and 805), and refractive index/ultraviolet dual detectors. The polydispersity ratio (M_w/M_n) of the polymers was calculated from chromatographs relative to commercial polystyrene standards of which molecular weights range from 5.0×10^3 to 1.5×10^6. The weight-average molecular weight (M_w) of the star polymers was determined by multiangle laser light scattering (MALLS) in chloroform at 40 °C on a Dawn E instrument (Wyatt Technology; Ga−As laser, $\lambda = 690$ nm). ^1H NMR spectra were recorded at 400 MHz on a JEOL LA-400 spectrometer. The surface tension of aqueous polymer solutions was measured on a Kyowa Interface Science CBVP-Z automatic surface tensiometer.

The ability of star polymers to solubilize small organic molecules was evaluated as follows. A water-insoluble dye (15.0 mg) was added to an aqueous solution (5.0 mL) of **4**, and the mixture was maintained shaking at 40 °C for 20 h. After a part of the dye, which remained insoluble, was filtered off through a glass filter, the absorbance of the filtrate was measured by using a Hitachi U-3000 spectrophotometer ($\lambda = 700-200$ nm).

Results and Discussion. As illustrated in Scheme 1,[7] the linear living polymer of IBVE ($DP_n = 10$, $M_w/M_n = 1.12$) prepared with HCl−IBVE adduct/ZnI_2 was allowed to react with **1**, three equivalent to living ends ($r = [\mathbf{1}]_0/[P^*] = 3.0$) in toluene at −15 °C ($[IBVE]_0 = 0.10$ M, $[HCl-IBVE]_0 = 10.0$ mM, $[ZnI_2]_0 = 0.20$ mM). In 3 h, **1** and P* were consumed quantitatively, and the first star poly(IBVE) was obtained in high yield ($M_w/M_n = 1.50$).[8] On the addition of AcOVE,[9] its polymerization was immediately ensued from the living growing sites in the core of **2** and completed in 6 h to give heteroarm star precursor **3** [M_w(GPC-MALLS) = 1.59×10^5, $M_w/M_n = 1.50$, 29 arms each].

The pendant ester groups of the AcOVE units were hydrolyzed into hydroxyl moieties in 1,4-dioxane under basic conditions to give an amphiphilic heteroarm star polymer (**4**) (Scheme 1: see Experimental Section). The observed segment composition (IBVE/AcOVE = 11/29) of a star polymer determined from the ^1H NMR peak intensity ratio was in good agreement with the calculated value (11/30) from the monomer feed ratio. The formation of amphiphilic heteroarm star polymers by hydrolysis was also confirmed by ^1H NMR spectroscopy.

Figure 1 shows ^1H NMR spectra of an amphiphilic star polymer and the corresponding linear block amphiphile in D_2O. With the block polymer, on going from room temperature (Figure 1A) to 80 °C (Figure 1B), the

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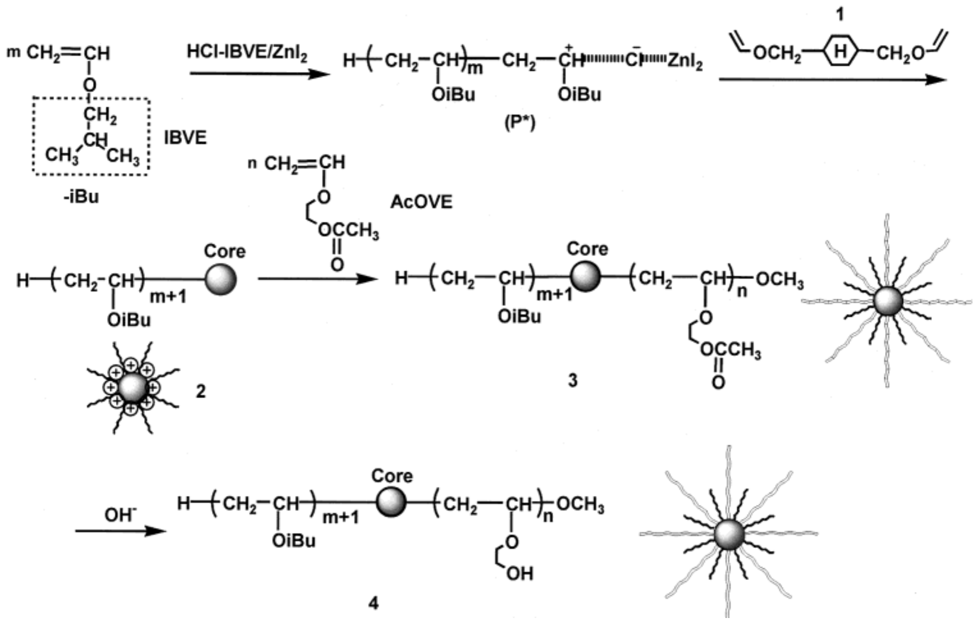
Scheme 1



signal (0.8−0.9 ppm) of the pendant methyl group of the IBVE unit, which is rather small and broad at room temperature, became stronger in intensity and sharper in shape. This arises from the destruction of the micelle structure where thermal motions of the hydrophobic segments are restricted. In contrast, with the star polymer, the broadness of the signals was still observed with those signals at the higher temperature (Figure 1C,D), although they became slightly stronger in intensity. This is consistent with the structure of heteroarm star polymers studied herein, where hydrophobic arms and a core are encapsulated by hydrophilic arms.

Figure 2 plots surface tension values for star polymer **4** and the corresponding linear polymer as a function of their concentrations. The degree of polymerization (*m* and *n*) of their hydrophobic and hydrophilic segments are ca. 10 and 30, respectively. The concentrations of linear block polymer **5** were set so as to give the hydroxyl groups equivalent to those in the heteroarm counterpart to be compared with. In aqueous solution, **5** remarkably lowered the surface tension from 72.8 mN/m for pure water down to ca. 30 mN/m, as can be seen with general nonionic surfactants. In contrast, star polymer **4** induced little decrease in surface tension, which would be caused by some organic impurities. This implies that star polymers do not pack at the air−water interface but are mostly dissolved into water at any concentration.

No effect of star amphiphiles on the surface tension of their aqueous solutions means that they are likely to behave as a unimolecular micelle, which was also suggested by our previous study[4] and the results of ^{1}H NMR study herein. These findings prompted us to examine the surface activity of heteroarm star polymers, which was evaluated by their ability to solubilize a hydrophobic organic compound into their aqueous solutions, and comparing with that of the corresponding linear block copolymers with the same composition.

A water-insoluble dye (**6**) was added to an aqueous solution of **4**, and the mixture was maintained shaking at 40 °C for 20 h. After an insoluble fraction was filtered off, the filtrate was measured by using a UV−vis spectrometer. In the absence of amphiphiles, a colorless filtrate was obtained, and no absorption was observed. In contrast, with amphiphiles, the initially colorless solution turned light red, and the filtrate showed absorption assigned to **6**. Figure 3 plots the absorbance at 495 nm of the filtrates with linear and star polymers against their concentrations, which were set in the same way for surface tension measurement. As shown in Figure 3, star polymer **4** solubilizes **6** more than the linear counterpart does.

Figure 3 also reveals that star polymer **4** is invariably superior in solubilization to the corresponding linear polymer at any concentration. More important, the amount of **6** dissolved in the solution is larger with the

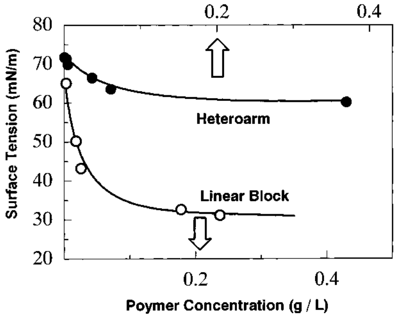


Figure 2. Surface tension of heteroarm star polymer **4** (IBVE/OH unit = 11/29, 29 arms each) and block polymer **5** (IBVE/OH unit = 9/31) against their concentration in water at 25 °C.

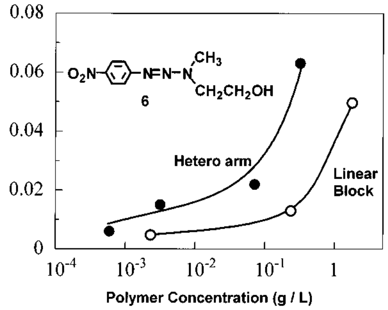


Figure 3. Relationships between the absorption (λ_{max} = 495 nm) of **6** solubilized in water by amphiphiles (**4** and **5**) and their concentration.

star polymer than that with the linear counterpart even below critical micelle concentration for **5**, which is assumingly around 0.1 g/L judging from the results of surface tension (see Figure 2). These results suggest that amphiphilic heteroarm star polymers not only act as a unimolecular micelle but also surpass the corresponding linear amphiphiles in solubilization.

In conclusion, we demonstrated that amphiphilic heteroarm star-shaped polymers show no critical micelle concentration and that they solubilize a water-insoluble dye into their aqueous solutions than the corresponding linear polymers do at any concentration. These results presented in this communication suggest that amphiphilic heteroarm star-shaped polymers behave as a unimolecular micelle, which is now under further investigation.

References and Notes

(1) This work was presented in part at the following meetings: (a) 50th Annual Meeting of the Society of Polymer Science, Japan, Osaka, May 2001; paper IIPf028: Kanaoka, S.; Hayase, N.; Fujita, Y.; Nakata, S.; Yamaoka, H. *Polym. Prepr., Jpn.* **2001**, *50* (2), 266. (b) 50th Symposium on Macromolecules, the Society of Polymer Science, Japan, Tokyo, Sept 2001; paper IIIC07: Kanaoka, S.; Koyama, C.; Nakata, S.; Yamaoka, H. *Polym. Prepr., Jpn.* **2001**, *50* (8), 1535.

(2) For a review, see: Sawamoto, M.; Kanaoka, S.; Higashimura, T. In *Hyper-Structured Molecules I: Chemistry, Physics and Applications*; Sasabe, H., Ed.; Gordon and Breach Science Publisher: Amsterdam, 1999; pp 43−61.

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(6) (a) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6407. (b) Kanaoka, S.; Fujita, Y.; Higashimura, T. *Macromol. Rapid Commun.* **2000**, *21*, 218. (c) Kanaoka, S.; Hayase, N.; Higashimura, T. *Polym. Bull. (Berlin)* **2000**, *44*, 485.

(7) Zinc iodide was employed instead zinc chloride because the yield of heteroarm star polymers was invariably higher with zinc iodide than that with zinc chloride.

(8) The molecular weight of the first star polymer was so small for light scattering measurement that we found no reproducibility for the M_w determined by MALLS.

(9) The living polymerization of an ester-containing VE needs a larger amount of ZnI_2 than that for alkyl vinyl ethers. Accordingly, in the second-phase polymerization of an ester-containing VE from the core, an additional dose of ZnI_2 ($[ZnI_2]_{add} = 3.0$ mM) was added to the reaction mixture as soon as the second VE was added. (a) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 5741. (b) Sawamoto, M.; Okamoto, C.; Higashimura, T. *Macromolecules* **1987**, *20*, 2693.

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