Amphiphilic Linear PEO−Dendritic Carbosilane Block Copolymers

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ABSTRACT: A new class of amphiphilic linear−dendritic diblock copolymers based on hydrophilic linear PEO and hydrophobic dendritic carbosilane were synthesized using a divergent approach at the allyl end group of the allyl-terminated PEO. The amphiphilic nature of these block copolymers was highly dependent on the size of the hydrophobic dendritic block. The block copolymer with the dendritic moiety of a third generation could not be dispersed in water. The block copolymers with the first (PEO-Si-1G) and, the second (PEO-Si-2G) generation of dendritic carbosilane blocks form micelles in an aqueous phase. The critical micelle concentrations of PEO-Si-1G and PEO-Si-2G, determined by a fluorescence technique, were 82.6 and 2.3 mg/L, respectively. The mean diameters of the micelles of PEO-Si-1G and PEO-Si-2G, measured by dynamic light scattering, were 120 and 170 nm. The partition equilibrium constants, K_v, of pyrene in the micellar solution increased by increasing the size of the dendritic block, e.g., 9.13×10^3 for PEO-Si-1G and 1.75×10^5 for PEO-Si-2G. The steady-state fluorescence anisotropy values (r) of 1,6-diphenyl-1,3,5-hexatriene (DPH) were 0.08 for PEO-Si-1G and 0.10 for PEO-Si-2G. The r values were lower than the linear polymeric amphiphiles, suggesting that the microviscosity of the dendritic micellar core is lower than those of other polymeric micelles.

Introduction

The control of molecular architecture of synthetic macromolecules and their supramolecular structure has always been a challenging research target. Dendrimers have been of great interest due to their well-defined structure and consequent novel properties.[1−3] In particular, amphiphilic dendrimers are known to exhibit unique solution behaviors in an aqueous phase. Some amphiphilic dendrimers with ionic peripheral groups with hydrophobic interior structures show a characteristic behavior of unimolecular micelles.[4−6] In addition, the combination of dendrimers with linear chains provides an opportunity to design a well-defined amphiphilic linear−dendritic block copolymer system, which can bring about supramolecular aggregates in an aqueous phase.[7] Fréchet et al. reported on the behavior of linear PEO−dendritic benzyl ether amphiphilic block copolymers.[8,9] The block copolymers with long PEO chains behave as unimolecular micelles. Chapman and co-workers synthesized the block copolymers, which consisted of hydrophobic dendritic poly(L-lysine) and hydrophilic linear PEO.[10] In an aqueous phase, these polymers form self-aggregation, and the critical micelle concentrations of these linear−dendritic block copolymers were evaluated by measuring the surface tension. Meijer et al. also reported on the block copolymers with the linear polystyrene as a hydrophobic chain and the dendritic poly(propyleneimine) as a hydrophilic moiety.[11] They found out that the morphology of the amphiphilic linear−dendritic block copolymers in an aqueous phase changed from a vesicular structure to a spherical micelle with increasing the generation of the hydrophilic poly(propyleneimine). Other examples include poly(2-methyl-2-oxazoline)−PAMAM dendrimer and PEO−PAMAM dendrimer.[12,13] Their report deals mostly with solution behaviors and macroscopic morphology in an aqueous phase.

In this study, we report the synthesis of a new amphiphilic linear−dendritic diblock copolymers based on PEO as a hydrophilic linear block and polycarbosilane as a hydrophobic dendritic block. The micellar characteristics of these linear−dendritic block copolymers in an aqueous phase were investigated by using fluorescence techniques and dynamic light scattering.

Experimental Section

Materials and Equipment. Monomethoxy PEG (MW 750, Aldrich) was precipitated from methylene chloride into *n*-hexane and dried under vacuum. Allyl bromide from Aldrich was vacuum distilled over calcium chloride. Sodium hydride (Aldrich, 60% in mineral oil), trichlorosilane (Tokyo Chemical Industry), allylmagnesium chloride (Aldrich, 2 M solution in THF), Karstedt catalyst (platinum−divinyltetramethyldisiloxane complex, Gelest), Pyrene (Aldrich), and 1,6-diphenyl-1,3,5-hexatriene (DPH, Aldrich) were used without further purification. All the solvents were purified by the procedure described in the literature.[14] All reactions were performed under an atmosphere of dry nitrogen.

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 250 spectrometer at 250 and 63 MHz, respectively. Molecular weights and molecular weight distributions were determined using a GPC equipped with a Waters Associates 410 RI detector, 510 HPLC pump, and μ-Styragel columns with pore sizes of 10^2, 500, 10^3, and 10^4 Å. The eluent was THF, and the molecular weights were calibrated with polystyrene standards. MALDI spectra were obtained using a Voyager Biospectrometry time-of-flight mass spectrometer (PerSeptive Biosystem) operated at 25 kV accelerating voltage in reflector mode with positive ionization. Dithranol (solvent: $CHCl_3$) was used as matrix. Thermal analyses were carried out using a Perkin-Elmer DSC-7 instrument. Pyrene fluorescence spectra and steady-state fluorescence anisotropy values of DPH were recorded on an ISS K2 spectrofluorometer. The hydrodynamic diameters of micellar particles were determined using a He−Ne laser (Research Electro-Optics 35 mW) and a BI-200SM Brookhaven apparatus.

Synthesis of CH_3-PEO-allyl. A modified literature procedure was employed.[15] Sodium hydride (10.4 g, 60% in mineral oil, 260 mmol) in THF (100 mL) was added to a solution of monomethoxy PEG (20 g, 26 mmol) in THF (150 mL). The reaction mixture was stirred at room temperature for 4 h. After

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the evolution of H_2 ceased, a THF (150 mL) solution of allyl bromide (47.2 g, 390 mmol) was added to the reaction mixture and then stirred at room temperature for 20 h. The crude product was filtered, and the solvent was evaporated at reduced pressure. The polymer product was purified by the repeated precipitation from methylene chloride into *n*-hexane to give a colorless waxy product. Yield 20.5 g, 75%; $T_m = 20$ °C. ^{1}H NMR ($CDCl_3$): δ 3.35 (s, 3H), 3.50−3.67 (m, 64H),3.99 (d, $J = 5.4$ Hz, 2H), 5.11−5.26 (m, 2H), 5.70−5.81 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 58.8, 70.4, 72.0, 116.9, 134.6.

Synthesis of PEO-Si-1G. A THF (150 mL) solution of CH_3-PEO-allyl (10 g, 12.7 mmol), trichlorosilane (8.6 g, 63.3 mmol), and five drops of Karstedt catalyst was stirred at room temperature for 1 h and then at 45 °C for 10 h. After completion of the hydrosilylation reaction, the excess trichlorosilane was evaporated under reduced pressure, and then THF was refilled up to 100 mL, which was then added into a THF solution (190 mL, 2 N) of allylmagnesium chloride. After stirring at room temperature for 20 h, a few drops of water were added. After the filtration, the solvent was removed under reduced pressure. The product was purified by repeated precipitation from THF into cold *n*-hexane. The further purification was carried out by column chromatography on silica gel with methylene chloride and THF to give a viscous product. Yield 5.3 g, 45%; $T_g = -60$ °C; $T_m = 27$ °C. ^{1}H NMR ($CDCl_3$): δ 0.50−0.57 (m, 2H), 1.55 (d, $J = 8$ Hz, 6H), 1.60−1.66 (m, 2H), 3.35 (s, 3H), 3.35−3.37 (m, 2H), 3.51−3.63 (m, 64H), 4.80−4.96 (m, 6H). 5.65−5.85 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 7.3, 19.4, 23.5, 57.0, 59.0, 70.3, 113.6, 134.3.

Synthesis of PEO-Si-2G. The diblock copolymer, PEO-Si-2G, based on linear PEO and carbosilane dendritic moiety of second generation was synthesized with PEO-Si-1G as the starting material by following the identical experimental procedure for PEO-Si-1G (yield 63%). $T_g = -80$ °C; $T_m = 10$ °C. ^{1}H NMR ($CDCl_3$): δ 0.35−0.46 (m, 2H), 0.48−0.68 (m, 12H), 1.22−1.37 (m, 6H), 1.55 (d, $J = 8$ Hz, 18H), 1.74−1.86 (m, 2H), 3.35 (s, 3H), 3.35−3.37 (m, 2H), 3.51−3.67 (m, 64H), 4.78−4.95 (m, 18H), 5.64−5.84 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 8.0, 16.5, 17.3, 18.1, 19.6, 24.0, 57.0, 58.4, 70.5, 113.5, 134.4.

Synthesis of PEO-Si-3G. PEO-Si-3G was prepared with PEO-Si-2G as the starting material by following the identical experimental procedure described for PEO-Si-2G (yield 50%). $T_g = -83$ °C; $T_m = 3$ °C. ^{1}H NMR ($CDCl_3$): δ 0.37−0.46 (m, 2H), 0.46−0.70 (m, 48H), 1.21−1.40 (m, 24H), 1.55 (d, $J = 8$ Hz, 54H), 1.76−1.83 (m, 2H), 3.35(s, 3H), 3.35−3.37 (m, 2H), 3.51−3.67 (m, 64 H), 4.78−4.95 (m, 54H), 5.65−5.84 (m, 27H). ^{13}C NMR ($CDCl_3$): δ 8.0, 16.5, 17.4, 17.7, 17.9, 18.2, 18.5, 19.6, 24.0, 57.0, 58.4, 70.5, 113.5, 134.4.

Sample Preparation. To prepare the micellar solutions, doubly distilled water (20 mL) was added dropwise to a THF solution of linear−dendritic block copolymer. Then, THF was evaporated at 30 °C under reduced pressure. The micellar solution was diluted to obtain a concentration range from 2 to 1×10^{-4} g/L. For the measurement of fluorescence spectra, pyrene solution in THF (1.2×10^{-3} M) was added to doubly distilled water to give a pyrene concentration of 12×10^{-7} M, and THF was removed using a rotary evaporator at 30 °C. The pyrene solution was mixed with block copolymer solutions to obtain copolymer concentrations from 1 to 5×10^{-5} g/L. The pyrene concentration of the samples was 6.0×10^{-7} M. All the samples were sonicated for 10 min and were allowed to stand for 1 day before the fluorescence measurements. For the measurement of steady-state fluorescence anisotropy, samples were prepared by adding 4 μL of DPH solution (2.1×10^{-3} M in THF) to the 5 mL block copolymer solutions in water. The DPH concentration of the samples was 1.7×10^{-6} M. The samples were degassed by gently bubbling nitrogen into the solution for 30 min.

Fluorescence Measurements. All the fluorescence measurements were performed using an ISS K2 spectrofluorometer with a thermostat cell unit. Pyrene and DPH were used as fluorescence probes to analyze the block copolymers in the doubly distilled water. For the measurement of pyrene excitation spectra, emission and excitation slit widths were set at 2 and 0.5 mm, respectively. For the excitation spectra, $\lambda_{em} = 390$ nm, and the spectra were accumulated with an integration of 3 s/nm. The steady-state fluorescence anisotropy values of DPH were determined in the L-format geometry of detection. The excitation wavelength was 360 nm, and the emission was measured at 430 nm. The anisotropy value (r) was calculated from the following relationship:

$$r = \frac{(I_{VV} - I_{VV}^{S}) - G(I_{VH} - I_{VH}^{S})}{(I_{VV} - I_{VV}^{S}) + 2G(I_{VH} - I_{VH}^{S})} \qquad (1)$$

where I^S is the contribution of scattered light from a sample solution without DPH; G ($=I_{HV}/I_{HH}$) is the instrumental correction factor; and I_{VV}, I_{VH}, I_{HV}, and I_{HH} refer to the resultant emission intensities polarized in the vertical or the horizontal detection planes (second subindex)[16,17] when excited with vertically or horizontally polarized light (first subindex).

Dynamic Light Scattering Measurements. Dynamic light scattering measurements were performed using a Brookhaven BI-200SM goniometer and BI-9000AT autocorrelator. All the measurements were carried out at 25 °C. The amphiphilic block copolymer solutions were filtered through 0.45 μm filters from Millipore. The scattered light of a vertically polarized He−Ne laser (632.8 nm) was measured at an angle of 90° and was collected on an autocorrelator. The hydrodynamic diameters (d) of micelles were calculated by using the Stokes−Einstein equation $d = k_BT/3\pi\eta D$, where k_B is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and D is the diffusion coefficient. The polydispersity factor of micelles, represented as μ_2/Γ^2, where μ_2 is the second cumulant of the decay function and Γ is the average characteristic line width, was calculated from the cumulant method.[18] CONTIN algorithms were used in the Laplace inversion of the autocorrelation function to obtain micelle size distribution.[19]

Results and Discussion

Synthesis of Linear−Dendritic Block Copolymers. Amphiphilic diblock copolymers based on hydrophilic linear chain and hydrophobic dendrimer block are able to form supramolecular micellar aggregates in an aqueous phase, in which dendritic moieties are incorporated into a hydrophobic domain. In an effort to elucidate the characteristics of the dendritic hydrophobic core such as microviscosity or hydrophobicity as well as the macroscopic micellar behavior such as critical micelle concentration or micelle size, we synthesized a new class of amphiphilic linear−dendritic diblock copolymer which consisted of hydrophilic linear PEO and hydrophobic dendritic carbosilane blocks. As described in Scheme 1, the synthetic route begins with the preparation of CH_3-PEO-allyl, which then underwent repeated hydrosilylation and alkylation in a divergent fashion to build a carbosilane dendritic block onto linear PEO.[20] The allylation of monomethoxy PEO was achieved by allowing CH_3-PEO-ONa to react with allyl bromide.[15] The terminal allyl groups of linear PEO were reacted with trichlorosilane in the presence of Karstedt catalyst. To ensure the completion of hydrosilylation, the reaction mixture was monitored using ^{1}H NMR spectra. After the disappearance of vinyl protons of the allyl groups, allylmagnesium chloride was added to obtain the first generation linear−dendritic diblock copolymer, PEO-Si-1G. The second- and third-generation linear−dendritic block copolymers, PEO-Si-2G and PEO-Si-3G, were synthesized in an identical manner, i.e., repeated hydrosilylation and alkylation.

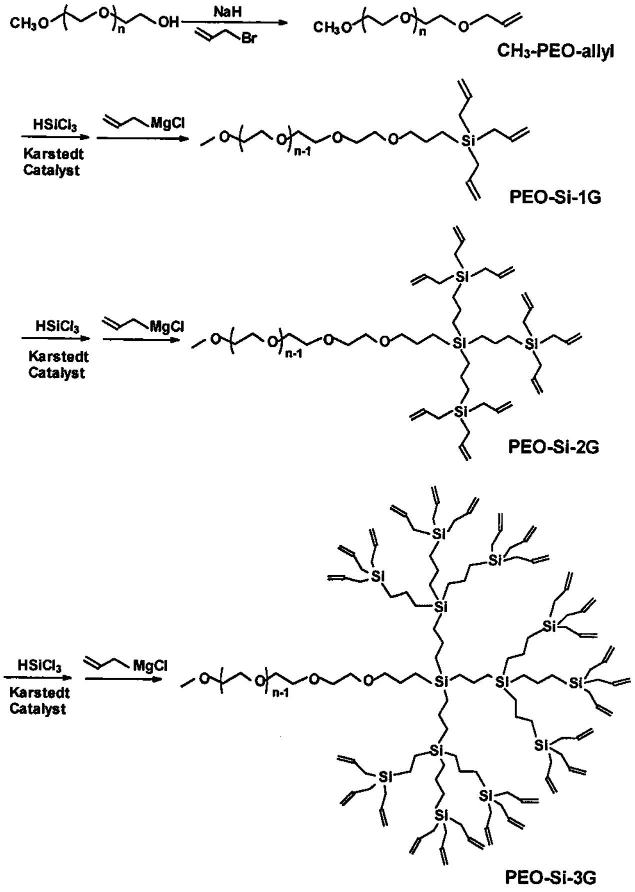
The structural characterization was carried out by ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra, relative peak integrations of allyl protons at 1.55, 4.88, and 5.75 ppm compared with PEO protons increased by

Table 1. Molecular Weights and Thermal Characterization of Linear−Dendritic Block Copolymers

	no. of end groups	$M_{n,\,theor}$	$M_{n,\,calcd}$[a]	M_n (MALDI-TOF)	wt % of hydrophobic dendrimer block	M_w/M_n	M_w/M_n	T_m[e] (°C)	T_g[e] (°C)
CH_3-PEO-allyl	1	815[a]	815	810	5.1	1.05[c]	1.06[d]	20	
PEO-Si-1G	3	1009[b]	1024	1022	19.3	1.05[c]	1.03[d]	27	−60
PEO-Si-2G	9	1488[b]	1488	1404	49.6	1.04[c]	1.03[d]	10	−80
PEO-Si-3G	27	2836[b]	2861	2886	72.8	1.06[c]	1.01[d]	3	−83

[a] Calculated by ^{1}H NMR spectra. [b] Theoretical values from CH_3-PEO-allyl (815). [c] Measured by GPC. [d] Measured by MALDI-TOF. [e] Measured by DSC (flow rate: 20 °C/min).

Scheme 1



increasing the dendritic generation of the carbosilane block as illustrated in Figure 1. For the second- and third-generation block copolymers, the methylene protons between silicon atoms gave resonance at 0.55, 0.60, and 1.30 ppm. Their relative peak integrations increased for the block copolymers of higher generations. The molecular weights of the polymers were determined by ^{1}H NMR, GPC, and MALDI-TOF as summarized in Table 1. The calculated M_n of CH_3-PEO-allyl from ^{1}H NMR spectrum was 815. The MALDI-TOF mass spectra showed similar molecular weight values compared with those of the calculated molecular weights. Molecular weight distributions (MWD) measured by MALDI-TOF and GPC were in the range 1.01−1.06. The thermal characterization was performed by using DSC and summarized in Table 1. The linear monomethoxy PEO showed glass transition at −89 °C and crystalline melting at 25 °C. The carbosilane dendrimer is amorphous. As the dendritic block becomes longer, the melting and glass transition temperatures become lower.

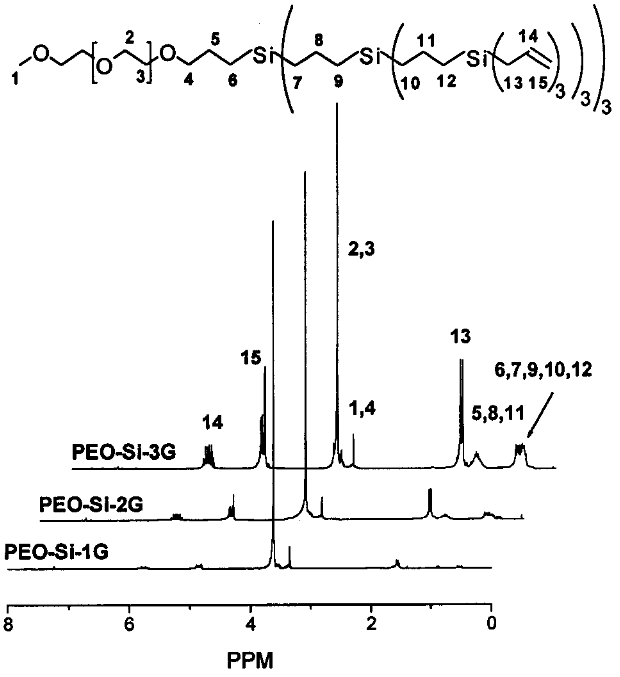


Figure 1. ^{1}H NMR spectra of linear−dendritic block copolymers.

Micelles of Linear−Dendritic Block Copolymers. The amphiphilic nature of the block copolymers, consisting of hydrophilic linear PEO and hydrophobic carbosilane dendrimer block, could be dispersed in an aqueous phase to form supramolecular micellar aggregates. The micellar characteristics of the block copolymers in an aqueous phase were investigated by using fluorescence techniques and dynamic light scattering. The critical micelle concentrations of the block copolymers in an aqueous phase were determined by a fluorescence technique using pyrene as a probe.[21−23]

In Figure 2, the excitation spectra of pyrene are shown at various concentrations of PEO-Si-1G. The characteristic feature of the pyrene excitation spectra, band (0,0) shift from 332 to 336 nm upon pyrene partition into micellar hydrophobic core, was utilized to determine the critical aggregation behavior of linear−dendritic block copolymers in water. Figure 3 shows the intensity ratios (I_{336}/I_{332}) of pyrene excitation spectra in the presence of PEO-Si-1G and PEO-Si-2G. At a low concentration range, a negligible change of intensity ratio (I_{336}/I_{332}) was detected. However, at a certain concentration the intensity ratios exhibited a substantial increase, suggesting that pyrene molecules are incorporated into the hydrophobic core region upon micellar aggregation. Therefore, the critical micelle concentrations were determined from the crossover point at the low concentration range in Figure 3.

The cmc values of PEO-Si-1G and PEO-Si-2G were 82.6 and 2.3 mg/L, respectively (Table 2). These values are much lower than that of low molecular weight surfactants, e.g., 2.3 g/L for sodium dodecyl sulfate

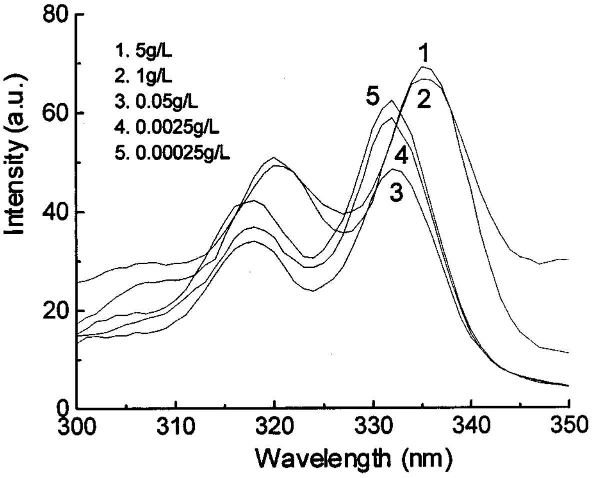


Figure 2. Excitation spectra of pyrene as a function of PEO-Si-1G concentration in water.

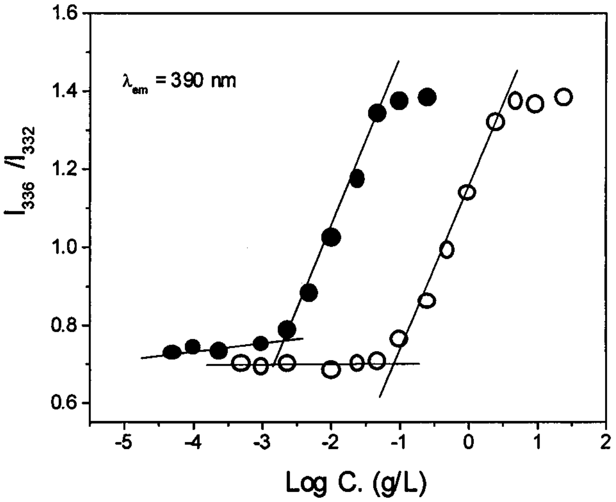


Figure 3. Change of intensity ratio (I_{336}/I_{332}) from excitation spectra of pyrene (6.0×10^{-7}M) depending on the concentrations of PEO-Si-1G (○) and PEO-Si-2G (●) in water.

Table 2. Micellar Characterization of Linear–Dendritic Block Copolymers

	cmc[a] (mg/L)	d[b] (nm)	μ_2/Γ^2 [c]	K_v	r[d]
PEO-Si-1G	82.6	120	0.047	9.13×10^3	0.08
PEO-Si-2G	2.3	170	0.158	1.75×10^5	0.10

[a] Measured at 25 °C. [b] Measured by dynamic light scattering. [c] Polydispersity factor. [d] Steady-state fluorescence anisotropy.

(SDS). The cmc of PEO-Si-2G is comparable with other polymeric amphiphiles,[21,22,24] while that of PEO-Si-1G is much higher due to the small portion of the hydrophobic block. As the hydrophobic dendritic composition became higher, a lower cmc value was observed. The third-generation block copolymer, PEO-Si-3G could not be dispersed in an aqueous phase possibly due to the large portion of the hydrophobic carbosilane dendritic block.

The mean diameters (d) of the micelles, measured by dynamic light scattering, were 120 and 170 nm respectively for PEO-Si-1G and PEO-Si-2G, suggesting that the hydrophobic dendritic block of higher generation induces larger micelles. This result is compatible with our previous observation with amphiphilic linear diblock copolymers based on poly(2-ethyl-2-oxazoline) and aliphatic polyesters.[25] The polydispersity factors (μ_2/Γ^2) of the PEO-Si-1G and PEO-Si-2G micelles, estimated by the cumulant method, were 0.047 and 0.158, respectively, suggesting a narrow size distribution.

Hydrophobicity of Dendritic Micellar Core. The hydrophobicity of micellar core was estimated by measuring the partition equilibrium constant (K_v) of a hydrophobic probe, pyrene, in the micellar solutions of the amphiphilic linear–dendritic block copolymers. The K_v values were calculated using the method of Wilhelm et al.,[19] in which pyrene binding to the micelles was considered as a simple equilibrium between a micellar phase and a water phase.[26] The K_v values of PEO-Si-1G and PEO-Si-2G were 9.13×10^3 and 1.75×10^5, respectively, suggesting that the hydrophobicity of the micelles increased by increasing the generation of the hydrophobic dendritic block. It is interesting to note that the K_v value of PEO-Si-1G is lower than that of sodium dodecyl sulfate (SDS) micelle (1.2×10^5) even though the sizes of their hydrophobic blocks are similar. This might be due to the dendritic architecture of the hydrophobic core of PEO-Si-1G in contrast to the stacking arrangement of linear aliphatic chains of SDS. The K_v value of PEO-Si-2G is comparable with those of other linear diblock copolymer system, but lie at the low edge. The K_v value of PEO–polystyrene block copolymer micelle was reported as 3.0×10^5.[27] In addition, poly(2-ethyl-2-oxazoline)–poly(ϵ-caprolactone) and poly(2-ethyl-2-oxazoline)–poly(L-lactide) exhibited K_v values in the range 1.79×10^5–5.88×10^5.[25]

Microviscosity of Micellar Core. The microviscosity of the hydrophobic dendritic core of the micelles was estimated by the measurement of the steady-state fluorescence anisotropy, which originated from the depolarization of DPH fluorescence due to the rotational diffusion of DPH in the micelle core.[16,28] The anisotropy value increases as the microviscosity of the micellar core increases because the rotational diffusion of DPH is increasingly hindered. The anisotropy values, r, of DPH measured for PEO-Si-1G and PEO-Si-2G were similar, e.g., 0.08 and 0.10, respectively. These values are similar to that of SDS (0.073) but much smaller than those of poly(ethylene-*co*-maleic acid) (0.187), poly(1-octadecene-*co*-maleic acid) (0.273), and other polymeric amphiphiles.[25,29] These low r values might be due to the branched dendritic structure of the micellar inner core rather than the well-packed core structure of the linear polymeric amphiphiles.

Conclusions

The linear–dendritic block copolymers with hydrophilic linear PEO and hydrophobic dendritic carbosilanes were synthesized via a divergent growth at the allyl end group of allyl-PEO. The amphiphilic nature of the linear PEO–dendritic carbosilane block copolymers provides an opportunity to form micelles in an aqueous phase, in which hydrophobic dendritic moieties are incorporated into the micellar core. Their micellar characteristics are highly dependent on the generation of the dendritic carbosilane units. The block copolymers with the dendritic carbosilane units of third generation were found not to disperse in an aqueous phase due to a large fraction of hydrophobic dendritic blocks. However, the block copolymers with the first and second generation of dendritic carbosilane blocks form micelles in water with the cmc's of 82.6 and 2.3 mg/L, respectively. The mean diameters of the micelles of the first- and second-generation block copolymers were 120 and 170 nm, respectively with a narrow unimodal distribution. The hydrophobic character of the micellar core was estimated by measuring the partition equilibrium constant, K_v, of pyrene in the micellar solution. The K_v values increased by increasing the generation of the dendritic block. The steady-state fluorescence anisotropy values (r) of DPH for PEO-Si-1G and PEO-Si-2G are similar but lower than the linear polymeric amphiphiles, suggesting that the microviscosity of the dendritic micellar core is lower than those of the linear polymeric amphiphiles.

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