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Self-Organization of Dendron-Poly(ethylene glycol) Conjugates in an Aqueous Phase

Kyoung Taek Kim, Im Hae Lee, Chiyoung Park, Yumi Song, and Chulhee Kim*

Department of Polymer Science and Engineering, Hyperstructured Organic Materials Resaerch Center, Inha University, Incheon 402-751, Korea

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Abstract: We have prepared amide dendrons having alkyl peripheral units and various focal moieties through a convergent synthetic approach. The amphiphilic properties, due to hydrophilic amide branches and the hydrophobic peripheral units, provide an opportunity for the amide dendrons to self-organize in water. The dendritic architecture itself is also one of the critical factors in the self-organization of the amide dendrons in water. In particular, functionalization was performed at the focal point to elucidate the relationship between the focal functionality and the self-organized structures of the dendritic building blocks in the aqueous phase. The dendron having a short poly(ethylene glycol) monomethyl ether (MeO-PEG) unit (M_n = 750) as the focal moiety formed a vesicular organization in water. As the size of the hydrophilic focal MeO-PEG increased to M_n = 2,000 and 5,000, the self-organized structures became rod-type and spherical micelles, respectively. Our observation of multiple morphologies for amide dendrons is in good agreement with previous reports that indicated that the micellar structures changed from vesicles to rod-types and then to spheres upon increasing the size of the hydrophilic moiety of the amphiphiles.

Keywords: dendrimer, amide dendron, self-organization, amphiphile, poly(ethylene glycol).

Introduction

Self-assembly of dendritic building blocks using noncovalent interactions as driving forces has shed lights on the well-defined novel supramolecular structures with functions.[1-8] In this research area, there are challenging topics such as the effect of chemical structures of building blocks on assembled structures and the endowment of specific functions to the supramolecular structures.[9-13] In general, the self-organization of dendritic building blocks can be induced in several conditions such as thermotropic fashion, in organic media, or in aqueous phase.[14] Intriguing examples on the self-assembly of in aqueous phase have shown that various nanoscale assemblies could be formed from dendritic building blocks.[15-18] In particular, Meijer *et al.* demonstrated that multiple morphologies such as vesicle, sphere, and rod were observed with an amphiphilic linear-dendritic block copolymer system based on hydrophobic polystyrene and hydrophilic propyleneimine dendrimer.[19,20] The three different self-organized structures were induced by varying the generation number of the hydrophilic propyleneimine dendrimer block. As described in our previous report,[21,22] some amide dendrons self-organize in organic media to form supramolecuar nanoassemblies. Interestingly enough, the amphiphilic nature, originated from hydrophilic amide branches and hydrophobic peripheries, would provide an opportunity for the amide dendrons to self-organize in an aqueous phase as well. Since the initial discovery of the vesicular organization of **1-Me** in water, special emphasis in our research has been placed on the elucidation of the possibility of the multiple self-organization behavior by changing the focal functionality $\mathbf{R_2}$.

We report the synthesis and self-organization characteristics of the amide dendrons in aqueous phase. In particular, we investigated the characteristics of multiple morphologies in self-assembly of amide dendrons by varying the molecular weight of the hydrophilic PEG focal moiety.

Experimental

Materials and Equipment. 1,1'-Carbonyldiimidazole (CDI), lauric acid, 1,3-dicyclohexylcarbodiimide (DCC), palmitic acid, 4-(dimethylamino)pyridine (DMAP), and ethylene glycol from Aldrich were used as received. *N*-(3-aminopropyl)-propanediamine (Aldrich) was purified by vacuum distillation under calcium hydride. Triethylamine (TEA) (Aldrich) was purified by distillation under calcium hydride. Succinic anhydride (Aldrich) was recrystallized from *n*-hexane/acetone (2 : 8, v/v) before use. Three samples of poly(ethylene glycol) monomethyl ether (MeO-PEG, M_n

*e-mail: chk@inha.ac.kr
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= 750, 2,000 and 5,000, Aldrich) were purified by precipitation from methylene chloride into *n*-hexane. Dendron **1** and **1-Me** were synthesized by the reference procedure.[21,22] All the solvents were purified by the literature procedure.[23] ^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA 400 at 400 and 100 MHz respectively and were referenced to TMS. FT-IR spectra were obtained using Perkin-Elmer System 2000 FT-IR spectrophotometer. Molecular weights and molecular weight distributions were estimated using a GPC equipped with a Waters Associates 410 RI detector, 510 HPLC pump and μ-Styragel columns with pore size 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 the matrix.

Synthesis.

Synthesis of 1-OH. A solution of dendron **1** (1.0 g, 0.72 mmol) and CDI (140 mg, 0.86 mmol) in chloroform (50 mL) was stirred at 45 °C for 12 h under nitrogen. Then, a chloroform solution (10 mL) of ethylene glycol (0.99 g 13.0 mmol) was subsequently added. After stirring for 8 h at 60 °C, the solvent was removed under reduced pressure. The product mixture was recrystallized from chloroform/ethyl acetate (1 : 9 v/v) (yield 1.0 g, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 7.0 Hz, 12H, $C\underline{H}_3$-CH_2-), 1.18-1.20 (s, 64H, -$C\underline{H}_2$-), 1.54-1.78 (br, 20H, -$C\underline{H}_2$-CH_2-CO-, -NH-CH_2-$C\underline{H}_2$-CH_2-N-), 2.07-2.12 (m, 8H, -$C\underline{H}_2$-CO-), 2.46-2.59 (br, 12H, -CO-$C\underline{H}_2$-$C\underline{H}_2$-CO-), 3.07-3.29 (m, 24H, -CO-NH-$C\underline{H}_2$-, -$C\underline{H}_2$-N-CO-), 3.72 (t, J = 4.6Hz, 2H, -CO-O-CH_2-$C\underline{H}_2$-OH), 4.16 (t, J = 4.6Hz, 2H, -CO-O-$C\underline{H}_2$-CH_2-OH); ^{13}C NMR (100.64 MHz, $CDCl_3$) δ 13.92, 22.48, 25.67, 25.71, 27.53, 27.95, 28.37, 29.15, 29.26, 29.37, 29.43, 29.47, 30.90, 31.72, 36.09, 36.27, 36.42, 36.61, 42.69, 45.08, 60.38, 65.97, 171.68, 172.09, 172.23, 172.30, 172.67, 173.20, 173.42, 173.79; IR (KBr) υ = 3311, 3085, 2919, 2851, 1732, 1635, 1554, 1467, 1380, 1252, 1174, 1119, 1091, 721; MS (MALDI-TOF) calcd for $C_{80}H_{151}N_9O_{12}$ 1431.13, found 1431.85.

Synthesis of 1-P75: A methylene chloride solution (20 mL) of DCC (223 mg, 1.08 mmol) was added to a solution of dendron **1** (2.0 g, 1.44 mmol), MeO-PEG (M_n = 750) (1.3 g, 1.73 mmol), and DMAP (0.11 g, 0.9 mmol) in methylene chloride (100 mL). After stirring at 45 °C for 8 h, the precipitated urea was filtered off. The solvent was evaporated under reduced pressure and the product mixture was purified by repeated precipitation from methylene chloride into *n*-hexane (yield 2.53 g, 82%).

^{1}H NMR (400MHz, $CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 12H, $C\underline{H}_3$-CH_2-), 1.18-1.29 (s, 64H, -$C\underline{H}_2$-), 1.59-1.85 (br, 20H, -$C\underline{H}_2$-CH_2-CO-, -NH-CH_2-$C\underline{H}_2$-CH_2-N-), 2.11-2.17 (m, 8H, -$C\underline{H}_2$-CO-), 2.52-2.68 (br, 12H, -CO-$C\underline{H}_2$-$C\underline{H}_2$-CO-), 3.12-3.39 (m, 27H, -CO-NH-$C\underline{H}_2$-, -$C\underline{H}_2$-N-CO-, -O-$C\underline{H}_3$), 3.51-3.72 (m, 63H -$OCH_2C\underline{H}_2$-OCH_3, -$OC\underline{H}_2C\underline{H}_2$-O-, -CO-O-$CH_2$-$C\underline{H}_2$-O-), 4.20 (t, J=5.2Hz, 2H, -CO-O-$C\underline{H}_2CH_2$-O-); IR (KBr) υ = 3311, 3083, 2919, 2851, 1731, 1638, 1555, 1467, 1381, 1252, 1115, 953, 721; M_n = 2,110 (MALDI-TOF), 2,530 (GPC), M_w/M_n = 1.01 (GPC).

Synthesis of 1-P200: A methylene chloride solution (20 mL) of DCC (0.38 g, 1.84 mmol) was added to a solution of dendron **1** (2.0 g, 1.44 mmol), MeO-PEG (M_n = 2,000) (3.46 g, 1.73 mmol), and DMAP (0.11 g, 0.9 mmol) in methylene chloride (100 mL). After stirring at 45 °C for 8 h, the precipitated urea was filtered off. The product mixture was column chromatographed on a silica gel with chloroform. Further purification was performed by repeated precipitation from methylene chloride into *n*-hexane (yield 3.56 g, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 12H, $C\underline{H}_3$-CH_2-), 1.17-1.29 (s, 64H, -$C\underline{H}_2$-), 1.58-1.84 (br, 20H, -$C\underline{H}_2$-CH_2-CO-, -NH-CH_2-$C\underline{H}_2$-CH_2-N-), 2.11-2.17 (m, 8H, -$C\underline{H}_2$-CO-), 2.52-2.68 (br, 12H, -CO-$C\underline{H}_2$-$C\underline{H}_2$-CO-), 3.11-3.39 (m, 27H, -CO-NH-$C\underline{H}_2$-, -$C\underline{H}_2$-N-CO-, -O-$C\underline{H}_3$), 3.51-3.68 (m, 175H, -$OCH_2C\underline{H}_2$-OCH_3, -$OC\underline{H}_2C\underline{H}_2$-O-), 3.79 (t, J = 4.8Hz, 2H, -CO-O-CH_2-$C\underline{H}_2$-O-), 4.20 (t, J = 5.0Hz, 2H, -CO-O-$C\underline{H}_2$-CH_2-O-); IR (KBr): ν = 3311, 3082, 2887, 2742, 2695, 1959, 1636, 1557, 1467, 1343, 1280, 1242, 1112, 964, 843, 721; M_n = 3,280 (MALDI-TOF), 4,040 (GPC), M_w/M_n = 1.05 (GPC).

Synthesis of 1-P500: A methylene chloride solution (20 mL) of DCC (223 mg, 1.08 mmol) was added to a solution of dendron **1** (2.0 g, 1.44 mmol), MeO-PEG (M_n = 5000) (8.65 g, 1.73 mmol), and DMAP (0.11 g, 0.9 mmol) in methylene chloride (150 mL). After stirring at 45 °C for 8 h, the precipitated urea was filtered off. The product mixture was purified by column chromatography on a silica gel with chloroform. Further purification was performed by the repeated precipitation from methylene chloride into *n*-hexane (yield 5.7 g, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 6.8Hz, 12H, $C\underline{H}_3$-CH_2-), 1.17-1.29 (s, 64H, -$C\underline{H}_2$-), 1.59-1.84 (br, 20H, -$C\underline{H}_2$-CH_2-CO-, -NH-CH_2-$C\underline{H}_2$-CH_2-N-), 2.10-2.16 (m, 8H, -$C\underline{H}_2$-CO-), 2.52-2.68 (br, 12H, -CO-$C\underline{H}_2$-$C\underline{H}_2$-CO-), 3.12-3.39 (m, 27H, -CO-NH-$C\underline{H}_2$-, -$C\underline{H}_2$-N-CO-, -O-$C\underline{H}_3$), 3.51-3.70 (m, 447H, -$OCH_2C\underline{H}_2$-OCH_3, -$OC\underline{H}_2C\underline{H}_2$-O-), 3.79 (t, J = 4.8 Hz, 2H, -CO-O-CH_2-$C\underline{H}_2$-O-), 4.20 (t, J = 4.8 Hz, 2H, -CO-O-$C\underline{H}_2$-CH_2-O-); IR (KBr): ν = 3314, 3084, 2890, 2741, 2695, 1973, 1637, 1555, 1467, 1342, 1283, 1107, 963, 843, 719; M_n = 6,330 (MALDI-TOF), 8,430 (GPC), M_w/M_n = 1.08 (GPC).

Synthesis of 2: Dendron **2** was synthesized via a convergent pathway.[21,22] Palmitic acid (30.7 g, 120 mmol) was treated with CDI (21.4 g, 132 mmol) in chloroform (300 mL), and subsequently reacted with *N*-(3-aminopropyl)-1,3-propanediamine (7.7 g, 58 mmol) to generate secondary amine at the focal point, which was then reacted with succinic

anhydride (7.0 g, 70 mmol). The identical procedure was repeated for the preparation of the second generation dendron **2** (yield 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J=6.8 Hz, 12H, $C\underline{H}_3$-CH_2-), 1.17-1.22 (s, 96H, -$C\underline{H}_2$-), 1.58-1.81 (br, 20H, -$C\underline{H}_2$-CH_2-CO-, -NH-CH_2-$C\underline{H}_2$-CH_2-N-), 2.11-2.17 (m, 8H, -$C\underline{H}_2$-CO-), 2.48-2.64 (br, 12H, -CO-$C\underline{H}_2$-$C\underline{H}_2$-CO-), 3.10-3.40 (m, 24H, -CO-NH-$C\underline{H}_2$-, -$C\underline{H}_2$-N-CO-); ^{13}C NMR (100.64 MHz, $CDCl_3$) δ 14.04, 22.63, 25.77, 25.83, 27.36, 27.68, 28.21, 28.61, 29.31, 29.40, 29.53, 29.61, 29.66, 31.20, 31.41, 31.87, 36.27, 36.42, 36.58, 36.75, 36.85, 42.83, 45.35, 172.31, 172.64, 172.75, 173.68, 173.95, 174.03, 174.98; IR (KBr): ν = 3315, 2918, 2850, 1723, 1637, 1554, 1467, 1380, 1251, 1173, 1120, 722; MS (MALDI-TOF) calcd for $C_{94}H_{179}N_9O_{11}$ 1611.51, found 1611.93.

Synthesis of 2-Me: A solution of dendron **2** (1.0 g, 0.62 mmol) and CDI (150 mg, 0.93 mmol) in chloroform (50 mL) was stirred for 12 h at 45 °C under nitrogen. Then, methanol (10 mL) was subsequently added. After stirring for 6 h at 60 °C, the solvent was removed under reduced pressure and the product mixture was recrystallized from chloroform/ethyl acetate (1 : 9 v/v) (yield 866 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J=6.8 Hz, 12H, $C\underline{H}_3$-CH_2-), 1.17-1.22 (s, 96H, -$C\underline{H}_2$-), 1.58-1.84 (br, 20H, -$C\underline{H}_2$-CH_2-CO-, -NH-CH_2-$C\underline{H}_2$-CH_2-N-), 2.11-2.17 (m, 8H, -$C\underline{H}_2$-CO-), 2.50-2.66 (br, 12H, -CO-$C\underline{H}_2$-$C\underline{H}_2$-CO-), 3.12-3.35 (m, 24H, -CO-NH-$C\underline{H}_2$-, -$C\underline{H}_2$-N-CO-), 3.66 (s, 3H, -CO-O-$C\underline{H}_3$); ^{13}C NMR (100.64 MHz, $CDCl_3$) δ 13.90, 22.48, 25.68, 26.94, 27.38, 27.52, 27.82, 27.93, 28.31, 28.92, 29.16, 29.25, 29.37, 29.50, 30.84, 31.72, 36.18, 36.32, 36.36, 36.47, 36.52, 36.57, 36.60, 42.84, 45.22, 51.61, 171.49, 172.13, 172.26, 172.39, 172.47, 172.74, 172.82, 173.64, 173.69, 174.00, 174.08; IR (KBr): ν=3311, 3084, 2955, 2917, 2850, 1737, 1644, 1557, 1467, 1440, 1378, 1269, 1251, 1173, 721; MS (MALDI-TOF) calcd for $C_{95}H_{181}N_9O_{11}$ 1625.54, found 1627.02.

Preparation of Micellar Solutions. The typical procedure is as follows. A 5 mg of **1-Me** was placed into the 100 mL round bottom flask and dissolved with 3~5 mL of THF. Doubly distilled water (50 mL) was added slowly in the flask with gentle stirring. After vigorous stirring for 15 min, THF was evaporated with a rotary evaporator at 40 °C. Resulting solution with slight blue hue was filtered with a syringe filter (0.45 μm). The concentrations of the micellar solutions in this study were set to 0.1 g/L.

Dynamic Light Scattering Experiments. Dynamic light scattering (DLS) measurements were performed using a Brookhaven BI-200SM goniometer and BI-9000AT digital autocorrelator. All the measurements were carried out at room temperature. The scattered light of He-Ne laser (Research Electro-Optics 35 mW) operated at 632.8 nm was measured at an angle of 90°, and collected on an autocorrelator. The sample solutions were purified by passing through a Millipore 0.45 μm filter. The hydrodynamic diameters (d) of vesicles were calculated 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.

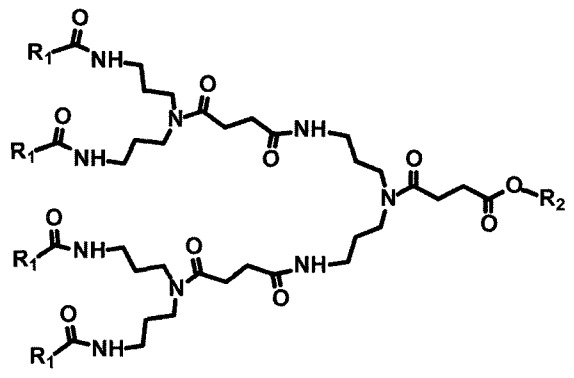
Transmission Electron Microscopy Experiments. Transmission electron microscopy (TEM) was performed using a Philips CM 200, operated at an acceleration voltage of 80 kV. For the observation of size and distribution of vesicle particles, a drop of sample solution was placed onto a 200-mesh copper grid coated with carbon. About 2 min after deposition, the grid was tapped with filter paper to remove surface water, followed by air-drying. The sample on the grid was shadowed with Au/Pd of 10~14 Å thickness at 20° tilt angle or negatively stained with uranyl acetate (2% aqueous solution).

Gel Filtration Experiments.[24,25] An aqueous solution of resorufin sodium salt (0.14 mM, 10 mL) was added dropwise to a mildly-stirred THF solution of an amphiphile (0.5 mg of 1-P75). Then, THF was removed on a rotary evaporator. The solution (0.5 mL) was passed through a sephadex G-100 column (2.520 cm) to collect 40~50 fractions (2 mL each). All the fractions were subjected to dynamic light scattering and fluorescence measurements to obtain elution profiles and confirm the existence of water entrapped in the self-organized aggregates.

Results and Discussion

Amide dendrons **1** and **2** with alkyl peripheral unit and carboxyl focal moiety were prepared by the convergent method reported previously.[21] The focal functionalities of the dendrons were modified by using DCC or CDI as the coupling agent for the reaction between the carboxyl unit at the focal point and hydroxyl groups of methanol or MeO-PEG.

Previously, we reported that some amide dendrons self-organize in organic media.[21,22] In addition, it was expected that the amphiphilic nature based on the hydrophilic amide branches and the hydrophobic alkyl chains at the periphery would be responsible for the amide dendrons to self-organize in aqueous phase as well. Therefore, we investigated self-organization characteristics of the amide dendrons, particularly multiple morphologies depending on the focal functionality. For the preparation of aqueous micellar solutions of the dendrons, a solvent evaporation method was employed by using THF as an organic solvent. All the aqueous micellar solutions prepared in this work were stable at room temperature for several weeks without formation of precipitates. During that period, there were no remarkable changes in size and shape of the aggregates observed by DLS and TEM. The dendrons were prepared up to the third generation, which could not be dispersed but precipitated in water. However, the second generation dendrons described in Figure 1 could form very stable self-organized structures



R_1 = n-undecyl, R_2 = H : **1**
R_2 = Me : **1-Me**
R_2 = CH_2CH_2OH : **1-OH**
R_2 = MeO-PEG 750 : **1-P75**
R_2 = MeO-PEG 2000 : **1-P200**
R_2 = MeO-PEG 5000 : **1-P500**

R_1 = n-pentadecyl, R_2 = H : **2**
R_2 = Me : **2-Me**

Figure 1. Amide dendrons with different focal groups.

in neutral or basic water without sonication.

When the peripheral moiety was replaced by small alkyl groups such as methyl or *t*-butyl group, the amide dendrons were freely soluble in water, which suggests that more hydrophobic periphery would be required to obtain amphiphilic balance. The dendrons with long alkyl periphery and focal carboxyl group (**1** and **2** in Figure 1), which self-assemble in organic media as described previously,[21,22] could not be dispersed to stable micellar solutions in neutral water. However, they formed bar-shaped micellar aggregates in basic water (10 mM NaOH) as shown in Figure 2A. The dendrons with methyl ester focal functionality, **1-Me** and **2-Me**, which are freely soluble in organic solvents such as THF, CH_2Cl_2, and methanol, formed very stable vesicular organizations in neutral water as shown in Figure 2B. The mean diameters of the vesicles of **1-Me** and **2-Me**, measured by using DLS, were 165 and 173 nm respectively. The first and third generation dendrons with methyl ester focal functionality did not form stable suprastructures but precipitated immediately, suggesting that the dendritic architecture of the second generation is critical in balancing the hydrophilicity of amide branches and hydrophobicity of alkyl periphery, and thus forming self-organized structures in water.

Interestingly, the vesicles of **1-Me** and **2-Me**, which do not possess charged surface, fused into gigantic tubular structures in the presence of divalent cation such as Ca^{2+} (Figure 3A).[26-30] Fusion of vesicles mediated by divalent cations or ionophores had been observed in synthetic vesicles with charged surfaces. The fusion of vesicles consisting of amide dendrons with uncharged surface may be derived possibly due to the

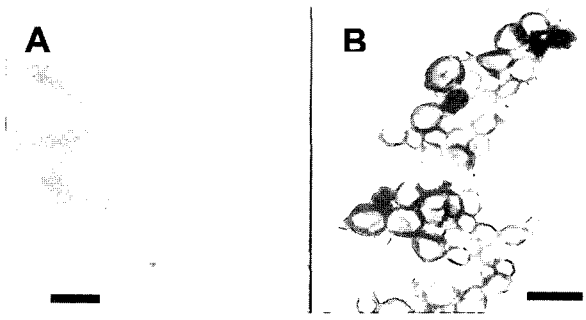


Figure 2. TEM images of the aggregate of **1** in 10 mM NaOH solution (A) and **2-Me** in neutral water (B). Bars represents 200 nm (A) and 500 nm (B), respectively.

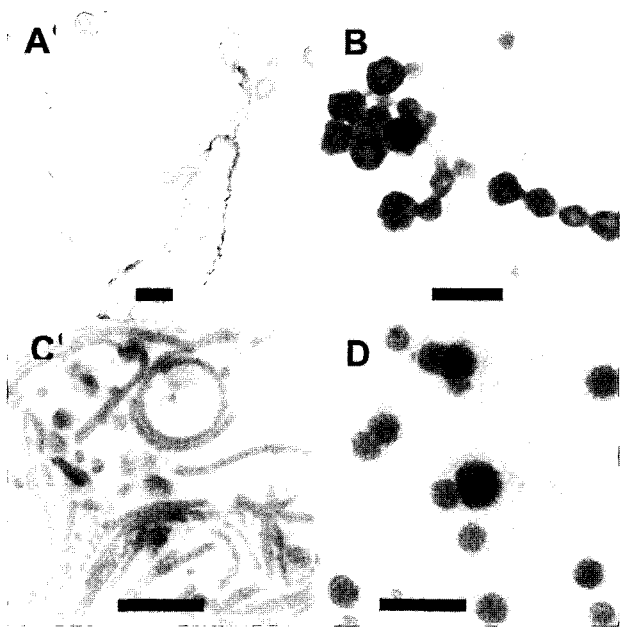


Figure 3. Fused vesicles of **1-Me** in 0.3 mM $CaCl_2$ in aqueous solution (A); self-organized structures of **1-P75** (B), **1-P200** (C), and **1-P500** (D) in water. Bars represent 200 nm (A), 500 nm (B), 500 nm (C), and 200 nm (D), respectively.

electrostatic interactions between Ca^{2+} and carbonyl oxygens of hydrophilic amide branches.

The structural difference in the self-organized assembly of **1** and **1-Me** suggests that the structure of the focal moiety in the amide dendrons strongly affects the self-organization process of the dendrons, and determines the nature of the assembled structure. Therefore, further functionalization at the focal point was carried out to elucidate the relationship between the focal functionality and the self-organized structures of the amide dendrons in aqueous phase. The dendron **1-OH** where $\mathbf{R_2}$ is OCH_2CH_2OH, formed a stable vesicular organization with the average diameter of 160 nm. The dendrons with MeO-PEG focal units of different molecular

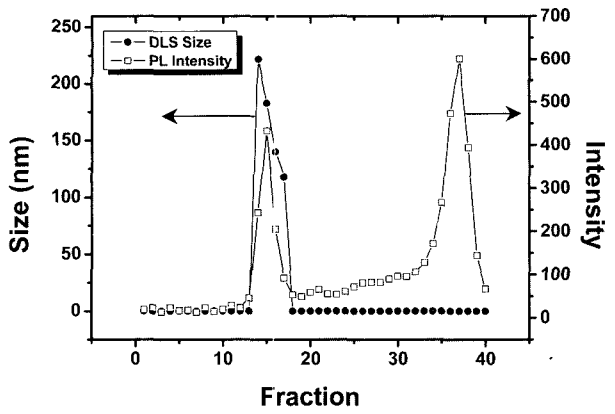


Figure 4. Elution profile in gel filtration of **1-P75**.

weights were also prepared in order to investigate the effect of size of the hydrophilic focal moiety on the self-organized architecture. The dendron with a short MeO-PEG focal unit (M_n = 750), **1-P75**, formed stable vesicles (average diameter, 170 nm) in water as evidenced by TEM (Figure 3B) and gel filtration results (Figure 4). As the size of the hydrophilic focal MeO-PEG increases to M_n = 2,000, the self-organized structures in water shifted to rods with the diameter in the range of 40~60 nm (Figure 3C). The amide dendron with focal MeO-PEG of M_n = 5,000 self-organizes into spherical micelles with an average diameter of ~ 60 nm as shown in Figure 3D.

The observation of multiple morphologies from the amide dendrons by varying the size of the focal PEG unit is in good agreement with Israelachvili's prediction in that the micellar structures changed from vesicles to rod-type and then to spheres with increasing the size of hydrophilic moiety of amphiphiles.[31-35] Particularly, for a dendrimer system in water, linear polystyrene-propyleneimine dendrimer diblock copolymers exhibit vesicle, rod, and spherical organizations as the generation of the hydrophilic propyleneimine dendrimer block increases.[19,20] However, this work shows that multiple morphologies of the self-organized structures of amide dendrons can be controlled simply by attaching different functionalities at the focal moiety of the identical amide dendron building block.

Conclusions

In summary, the amide dendrons with hydrophobic alkyl periphery and amide branches self-organize to exhibit multiple morphologies in aqueous phase. The dendritic architecture is one of critical factors in forming self-organized structures in water. The nature of the focal functionality of the amide dendrons determines the supramolecular morphology in water. The transition of the self-organized structure from vesicles to rod-type and spherical micelles was triggered by the increase of the surface area of the hydrophilic PEG focal moiety of the amide dendron. Currently, the incorporation of functional elements at the surface of the self-organized assemblies is being investigated by the modification of the focal end moiety. The self-organization characteristics of the amide dendrons in aqueous phase provide a new route to the supramolecular nanomaterials.

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