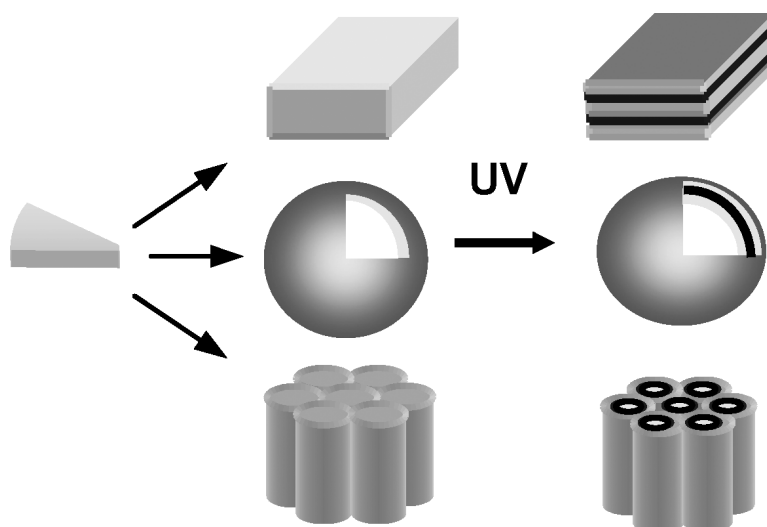


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Stabilization of Supramolecular Nanostructures Induced by Self-Assembly of Dendritic Building Blocks

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Dendrons with amide-urethane branch units and topochemically polymerizable diacetylene moieties at the alkyl periphery were synthesized via a convergent method. They form organized nanostructures in organic media and also in water. In organic media, they form lamella or columnar hexagonal structures depending on the dendron generation. By changing the solvent from organic to aqueous phase, the identical dendritic building blocks self-organize into a vesicular structure. The noncovalent interactions such as hydrogen bonding of the dendritic branches and van der Waals interactions of the alkyl periphery are critical for the construction of organized structures. These supramolecular nanostructures induced via self-assembly of dendritic building blocks could remarkably be stabilized by in situ photopolymerization of topochemically polymerizable diacetylene moieties incorporated at the periphery of the dendrons in organized states.

Introduction

Recent advances in self-assembly of dendrimers or dendrons provide a unique methodology for creation of supramolecular nanomaterials.¹ In particular, self-organization of dendrons into ordered suprastructures has been demonstrated in thermotropic or lyotropic fashion.² We have reported on the formation of thermoreversible supramolecular gels through self-organization of some amide dendrons in organic media, and the formation of lamella or columnar hexagonal arrays in the dry state depending on the structures of the dendritic building blocks.³ In addition, the amide dendrons form organized supramolecular nanostructures such as vesicles in the aqueous phase. This type of supramolecular assembly of dendrons is expected to be very effective for the construction of nanomaterials

which have functional elements in the core or on the surface of the nanostructure. These self-organizations of the dendrons are induced by noncovalent interactions such as hydrogen bonding of the dendritic branches or van der Waals interactions of the alkyl peripheries. Therefore, those self-organized nanostructures could be labile in an environment which can solubilize the noncovalent interactions between the building blocks. For example, addition of a small amount of methanol into the wet gel in chloroform results in formation of homogeneous solution by dissolving gels possibly due to breakup of hydrogen bonds.

In this report, we present photopolymerizable dendritic building blocks which can self-organize not only in organic media but also in aqueous phase, so that the self-assembled supramolecular nanostructures could be stabilized by in situ photopolymerization in organized states. For this purpose, diacetylene moieties were introduced at the periphery of the amide-urethane dendrons as described in Scheme 1. Diacetylene moieties can undergo photopolymerization in an organized environment when the topochemical requirements are satisfied.⁴

Experimental Section

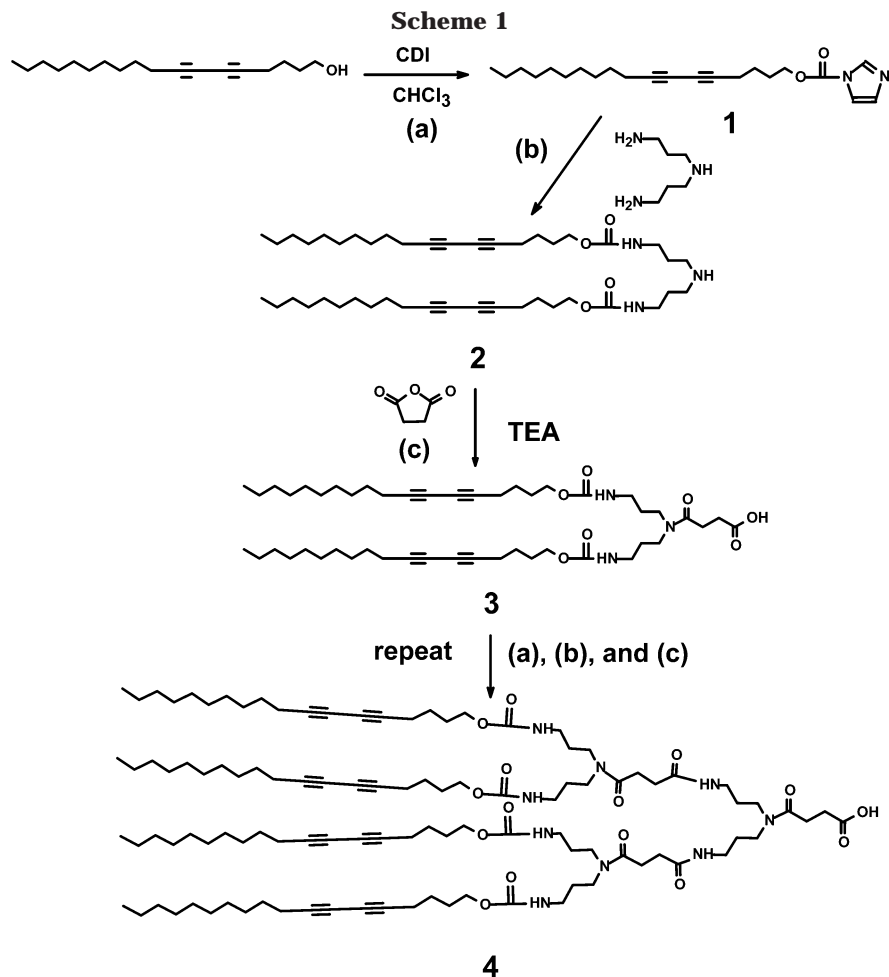
1. Materials and Equipment. 1,1'-Carbonyldiimidazole (CDI) and phosphotungstic acid hydrate from Aldrich were used as received. *N*-(3-Aminopropyl)-propanediamine (98%) and triethylamine (TEA) from Aldrich were purified by vacuum distillation under calcium hydride. Succinic anhydride from Aldrich was recrystallized from *n*-hexane/acetone (2:8, v/v). 5,7-Octadecadiyne-1-ol was synthesized by the reference procedure.⁵ Chloroform was distilled under calcium hydride. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 250

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spectrometer at 250 and 63 MHz, respectively, and were referenced to TMS. FT-IR spectra were obtained using a Perkin-Elmer System 2000 FT-IR spectrophotometer. Elemental analysis data were obtained using a CE Instrument EA 1110. The thermal transition temperatures were measured by using a Perkin-Elmer DSC 7 under nitrogen atmosphere at a heating rate of 5 °C/min. Mass data were obtained using an Agilent 1100 LC/MSG. UV-vis spectra were obtained using a Hewlett-Packard 8452A spectrophotometer. The photopolymerization was carried out by using a Ushio UV irradiation apparatus (UI-501C with a 500-W mercury lamp USH-500D).

2. Synthesis. *Synthesis of 1.* A chloroform solution (100 mL) of 5,7-octadecadiyn-1-ol (21.98 g, 83 mmol) was added to a solution of 1,1'-carbonyldiimidazole (16.15 g, 99.6 mmol) in chloroform (150 mL). After 3 h at 25 °C under nitrogen, the chloroform solution was washed with water and dried with magnesium sulfate. After evaporation of the solvent under reduced pressure, the product was obtained as a viscous liquid (yield 26.58 g, 90%).

¹H NMR (CDCl₃) δ 0.85 (t, J = 7.5 Hz, 3H, CH₃-CH₂-), 1.23 (br s, 14H, -CH₂-), 1.43–1.52 (m, 2H, -CH₂-CH₂-C \equiv C-), 1.61–1.70 (m, 2H, -CH₂-CH₂-CH₂-O-CO-), 1.85–1.94 (m, 2H, -C \equiv C-CH₂-CH₂-), 2.22 (t, J = 7.2 Hz, 2H, -C \equiv C-CH₂-), 2.31 (t, J = 6.8 Hz, 2H, -CH₂-CH₂-C \equiv C-), 4.41 (t, J = 6.5 Hz, 2H, -CH₂-O-CO-), 7.05 (s, 1H, -CO-N-CH=CH-N-), 7.40 (s, 1H, -CO-N-CH=CH-N-), 8.12 (s, 1H, -CO-N-CH=CH-N-). ¹³C NMR (CDCl₃) δ 13.8, 18.6, 19.0, 22.4, 24.5, 27.4, 28.1, 28.6, 28.9, 29.1, 29.2, 29.3, 31.7, 64.9, 66.2, 67.5, 75.6, 77.9, 116.8, 130.5, 136.8.

Synthesis of 2. A chloroform solution (100 mL) of compound 1 (26.2 g, 73 mmol) was added to a solution of *N*-(3-aminopropyl)propanediamine (4.79 g, 36.5 mmol) in chloroform (150 mL). After the solution was stirred for 12 h at 40 °C, the solvent was evaporated under reduced pressure and the product mixture was recrystallized from ethyl acetate (yield 23.7 g, 89%).

¹H NMR (CDCl₃) δ 0.85 (t, J = 7.5 Hz, 6H, CH₃-CH₂-), 1.23 (br s, 28H, -CH₂-), 1.45–1.70 (m, 16H, -CH₂-CH₂-C \equiv C-, -CH₂-CH₂-CH₂-CH₂-O-CO-, -CO-NH-CH₂-CH₂-CH₂-NH-), 2.19–2.28 (m, 8H, -CH₂-CH₂-C \equiv C-C \equiv C-CH₂-CH₂-), 2.62–2.67 (m, 4H, -NH-CH₂-CH₂-CH₂-NH-), 3.23–3.27 (m, 4H, -O-CO-NH-CH₂-CH₂-), 4.03 (t, J = 6.5 Hz, 4H, -CH₂-CH₂-O-CO-NH-), 5.37–5.39 (m, 1H, -CH₂-NH-CH₂-). ¹³C NMR (CDCl₃) δ 13.8, 18.7, 19.0, 22.4, 24.7, 28.1, 28.2, 28.7, 28.9, 29.1, 29.3, 29.4, 29.6, 31.7, 39.3, 47.3, 63.9, 65.1, 65.7, 76.4, 77.6, 156.6. MS calcd for C₄₄H₇₃N₃O₄, 708; found, 708 (m/z).

Synthesis of 3. A chloroform solution (150 mL) of compound 2 (23.7 g, 33 mmol) and triethylamine (3.67 g, 36.3 mmol) was added to a solution of succinic anhydride (3.36 g, 36.3 mmol) in chloroform (100 mL). After the solution was stirred for 12 h at 40 °C, the solvent was removed by using an evaporator, and the product was recrystallized from ethyl acetate and diethyl ether (yield 26.7 g, 98%). mp 103 °C.

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^1H NMR (CDCl_3) δ 0.84 (t, $J = 7.5$ Hz, 6H, $\text{CH}_3\text{--CH}_2\text{--}$), 1.23 (br s, 28H, $\text{--CH}_2\text{--}$), 1.45–1.68 (m, 16H, $\text{--CH}_2\text{--CH}_2\text{--C}\equiv\text{C--}$, $\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--O--CO--}$, $\text{--NH--CH}_2\text{--CH}_2\text{--CH}_2\text{--NH--}$), 2.18–2.29 (m, 8H, $\text{--CH}_2\text{--CH}_2\text{--C}\equiv\text{C--C}\equiv\text{C--CH}_2\text{--CH}_2\text{--}$), 2.62–2.69 (m, 8H, $\text{--N--CO--CH}_2\text{--CH}_2\text{--COOH}$), 3.05–3.39 (m, 8H, $\text{--O--CO--NH--CH}_2\text{--CH}_2\text{--}$, $\text{--CH}_2\text{--CH}_2\text{--N--CO--}$), 4.01 (t, $J = 6.5$ Hz, 4H, $\text{--CH}_2\text{--CH}_2\text{--O--CO--NH--}$), 5.02 (br, 1H, --NH--), 5.49 (br, 1H, --NH--). ^{13}C NMR (CDCl_3) δ 13.9, 18.7, 19.0, 22.5, 24.7, 27.6, 28.0, 28.2, 28.7, 28.9, 29.1, 29.3, 29.4, 31.7, 38.4, 42.9, 45.2, 64.0, 65.0, 65.7, 76.3, 77.7, 156.9, 172.0, 175.7. IR(KBr) cm^{-1} 3315, 3068, 2921, 2849, 2184, 2166, 2141, 1686, 1614, 1536, 1461, 1269, 1101, 1038, 827, 777, 722.; Anal. Calcd for $\text{C}_{48}\text{H}_{77}\text{N}_3\text{O}_7$: C, 71.34; H, 9.60; N, 5.20. Found: C, 71.43; H, 10.02; N, 5.20.

Synthesis of 4. For the preparation of second-generation dendron **4**, the convergent procedure identical to that employed for the synthesis of dendron **3** was repeated by using dendron **3** as the starting material. Dendron **3** was reacted with *N*-(3-aminopropyl)-propanediamine by using CDI as a coupling agent, and subsequently treated with succinic anhydride to yield dendron **4** (yield 88%).³ mp 49 °C.

^1H NMR (CDCl_3) δ 0.85 (t, $J = 7.5$ Hz, 12H, $\text{CH}_3\text{--CH}_2\text{--}$), 1.23 (br s, 56H, $\text{--CH}_2\text{--}$), 1.46–1.82 (m, 36H, $\text{--CH}_2\text{--CH}_2\text{--C}\equiv\text{C--}$, $\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--O--CO--}$, $\text{--NH--CH}_2\text{--CH}_2\text{--CH}_2\text{--N--CO--}$), 2.18–2.30 (m, 16H, $\text{--CH}_2\text{--CH}_2\text{--C}\equiv\text{C--C}\equiv\text{C--CH}_2\text{--CH}_2\text{--}$), 2.52 (br, 4H, $\text{--CO--CH}_2\text{--CH}_2\text{--COOH}$), 2.65 (br, 8H, $\text{--N--CO--CH}_2\text{--CH}_2\text{--CO--NH--}$), 3.05–3.35 (br, 24H, $\text{--O--CO--NH--CH}_2\text{--CH}_2\text{--}$, $\text{--CH}_2\text{--N--CO--}$), 4.03 (t, $J = 6.5$ Hz, 8H, $\text{--CH}_2\text{--O--CO--NH--}$). ^{13}C NMR (CDCl_3) δ 14.0, 18.7, 19.0, 22.5, 24.7, 27.1, 27.7, 28.0, 28.2, 28.7, 28.9, 29.1, 29.3, 29.4, 30.9, 31.7, 36.7, 37.7, 38.1, 42.5, 45.1, 63.9, 64.1, 65.0, 65.6, 76.5, 77.7, 156.7, 156.8, 172.2, 172.3, 172.5, 172.7. IR(KBr) cm^{-1} 3320, 3080, 2927, 2855, 2184, 2166, 2141, 1705, 1626, 1535, 1457, 1377, 1258, 1174, 1145, 1088, 1046, 777, 722. Anal. Calcd for $\text{C}_{106}\text{H}_{171}\text{N}_9\text{O}_{15}$: C, 70.28; H, 9.51; N, 6.96. Found: C, 70.04; H, 9.98; N, 7.08.

Dynamic Light Scattering. Dynamic light scattering measurements were performed using a Brookhaven BI-200SM goniometer and BI-9000AT digital autocorrelator. All the measurements were carried out at 25 °C. The scattered light of a 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 them through a Millipore 0.45- μm filter. The hydrodynamic diameters (d) of vesicles were calculated using the Stokes–Einstein equation $d = k_B T / 3\pi\eta D$, 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. 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 (concentration 60 mg/L) 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 and air dried. Negative staining was performed by using a droplet of a 0.2 wt % phosphotungstic acid solution. For observation of the gel morphology, the gel was gently contacted on the surface of the 200-mesh copper grid coated with carbon. The sample on the grid was air-dried, and shadowed with Au/Pd of 10–14 Å thickness at 20° tilt angle.

Results and Discussion

The urethane-amide dendrons with topochemically polymerizable diacetylene peripheral units were synthesized via a convergent pathway as described in Scheme 1. For the synthesis of first-generation dendron **3**, 5,7-octadecadiyne-1-ol was treated with CDI in chloroform, and subsequently reacted with *N*-(3-aminopropyl)-1,3-propanediamine to generate secondary amine at the focal point, which was then reacted with succinic anhydride to yield first-generation dendron **3**.

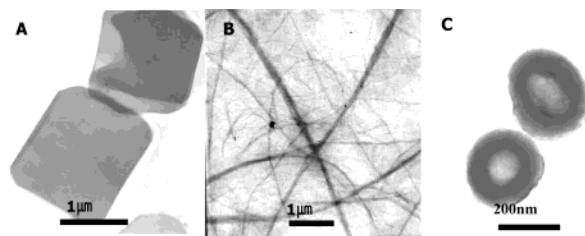


Figure 1. TEM images of aggregates of (A) dendron **3** in $\text{CHCl}_3/n\text{-hexane}$ (5:5); (B) dendron **4** in toluene; and (C) dendron **4** in water.

For the preparation of second-generation dendron **4**, the convergent procedure identical to that employed for the synthesis of dendron **3** was repeated as described in Scheme 1. Dendron **3** was reacted with *N*-(3-aminopropyl)-propanediamine by using CDI as a coupling agent, and subsequently treated with succinic anhydride to yield dendron **4**. For the preparation of second-generation dendron **4**, an identical divergent procedure was repeated.

The dendrons formed gels in selected organic media. For example, dendron **3** is soluble in $\text{CHCl}_3/n\text{-hexane}$ (5:5) above 50 °C, and dendron **4** dissolves in $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ (3:7) above 45 °C. However, after cooling to room temperature, the solutions turned into immobile gels after certain period of time.⁶ The organogel formation was thermoreversible, which is similar to that observed for the amide dendrons.³ The first-generation dendron, **3**, showed turbid immobile gel in organic solvents such as $\text{CHCl}_3/n\text{-hexane}$ (5:5, v/v) and THF/*n*-hexane (5:5). The second-generation dendron, **4**, initially exhibited a transparent gel in toluene, cyclohexane, and $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ (3:7), and then became translucent as the aggregation proceeded. The structure of the dry gels was examined by using transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. The TEM image of the dry gel from dendron **3** is shown in Figure 1A. The XRD results showed a lamellar structure with interlamellar spacing of 42 Å (Figure 2A). Considering the dimension of the stretched form of dendron **3** (31 Å), it is expected that each lamellar layer consists of dimeric building blocks of **3** which are hydrogen bonded at the focal carboxyl groups.

When the samples were exposed to X-ray or the electron beam of TEM, the gels showed colorimetric transition from very pale yellow to red indicating that the diacetylene units were polymerized. Therefore, there was no noticeable difference in TEM or XRD results before and after UV irradiation on the samples, even though UV irradiation induces drastic colorimetric change to deep red suggesting that the diacetylene units undergo topochemical polymerization. Before irradiation, the gel in $\text{CHCl}_3/n\text{-hexane}$ (5:5, v/v) did not exhibit absorption in the visible range. However, after irradiation, the gel showed broad absorption at 500–650 nm with maxima at 554 and 632 nm. After 2 h UV irradiation on the dry gel of **3**, 87 wt % of the irradiated sample became insoluble in organic solvents such as chloroform and methylene chloride at ~20 °C, whereas

(6) Typical procedure: A pulverized sample of **4** (0.1 g) was placed in a vial and methylene chloride/cyclohexane (3:7, 1 mL) was added. Upon heating to 50 °C, the mixture turned into a transparent solution. After 24 h at room temperature, a transparent gel formed. A dry gel was obtained by slow evaporation of solvent.

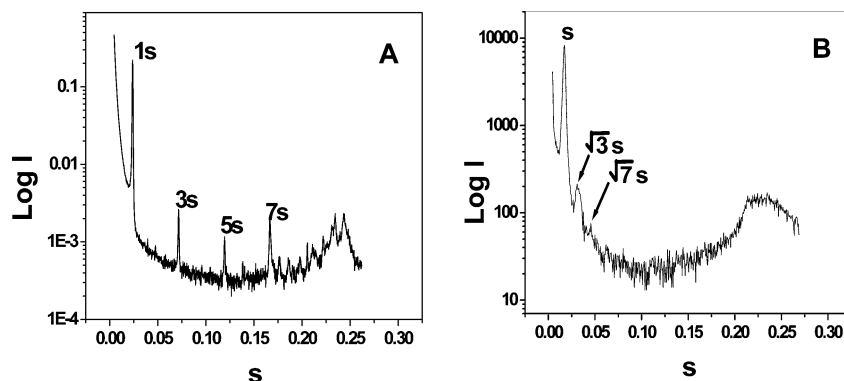


Figure 2. XRD data of suprastructures of dry gels from (A) dendron **3** and (B) **4**; $s(\text{\AA}^{-1}) = (n\lambda/2\sin\theta)$.

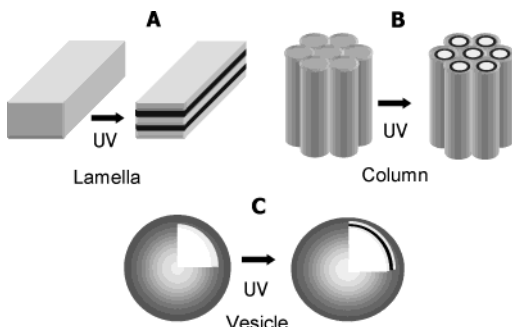


Figure 3. Schematic illustration of stabilized nanostructures induced by self-assembly of dendrons (■: polymerized area).

the unirradiated gels of dendron **3** were soluble in those organic solvents at room temperature. At elevated temperature, $\sim 50^\circ\text{C}$, however, the insoluble portion of the irradiated product became partially soluble in the above organic solvents while ~ 40 wt % of the sample was still insoluble. In addition, the insoluble portion maintained the identical lamellar structure. This result suggests that the lamellar structure induced by self-organization of dendron **3** is stabilized by photopolymerization of the diacetylene units at the periphery of the building blocks as illustrated in Figure 3A.

The gel of dendron **4** exhibited fibrous bundles in the TEM image (Figure 1B). The XRD results revealed a hexagonal columnar structure with the column diameter of 67 \AA (Figure 2B). Considering the dimension of the stretched form of dendron **4** (42 \AA), it is most likely that the column was formed by stacking the dimeric species of dendron **4**, where the hydrogen bonded carboxyl groups are located in the middle of the column and the alkyl peripheries with diacetylene units are organized outward.³ Therefore, the photopolymerization of the diacetylene moiety is expected to give rise to the polymerized shell in the column, which would stabilize the nanostructure (Figure 3B). The unirradiated gel did not exhibit absorption in the visible range. However, after UV irradiation on the gel of **4** in toluene, the color changed to deep red and a broad absorption appeared at $500\text{--}650\text{ nm}$ with a maximum at 626 nm , which indicates that the diacetylene units undergo polymerization. After 2 h UV irradiation on the dry gel of **4**, 30 wt % of the deep red sample became insoluble in organic solvents such as chloroform, methylene chloride, THF, DMF, and DMSO at room temperature, whereas the unexposed gel of dendron **4** was soluble in those organic media at room temperature. In addition, the insoluble

product maintained the identical columnar hexagonal structure.

Dendrons **3** and **4** have the capability not only to self-organize in organic media but also to form self-organized vesicular structures in aqueous phase as shown in Figure 1C. This can be attributed to the amphiphilic nature of the dendrons, i.e. hydrophilic dendritic branches and hydrophobic peripheries. It is interesting to note that the identical dendron building blocks show multiple morphologies just by employing different solvent systems. The average diameter of the vesicles determined by dynamic light scattering was 210 nm for dendron **3** and 205 nm for dendron **4**. The polymerization of diacetylene moiety at the vesicular membrane in water was performed by UV irradiation at 5°C . Upon irradiation, the color of the samples turned into blue, suggesting that the diacetylene polymerization occurred in an organized structure. Before irradiation, the vesicle solutions did not exhibit absorption in the visible range. But after irradiation, the absorption maxima of the vesicular solutions appeared at 638 nm for dendron **3** and 636 nm for dendron **4**. The change of vesicle size for dendron **3** was not noticeable before and after UV irradiation. However, the vesicle size for the dendron **4** decreased by $\sim 15\%$ after UV irradiation. The enhanced stability of the vesicular structure by the polymerization of diacetylene moiety at the vesicular membrane was confirmed by monitoring the vesicle fusion characteristics before and after polymerization. Addition of divalent cation, Ca^{2+} , induces a fusion of the nonionic vesicles of the dendrons which accompanies the partial disruption of the vesicular membrane, thus the increase of vesicle size. This fusion occurs most likely due to the electrostatic interaction between divalent cation and carbonyl oxygen. For example, before polymerization, the vesicle of dendron **4** exhibits size increase as shown in Figure 4, where the vesicle size was measured 30 min after the addition of CaCl_2 for each concentration. However, after polymerization, a drastic retardation in fusion can be noted possibly due to the enhanced stability of the polymerized vesicle membranes.

Conclusions

In summary, supramolecular nanostructures induced via self-assembly of dendritic building blocks could remarkably be stabilized by in situ topochemical photopolymerization of diacetylene moieties incorporated at the periphery of the dendrons. The amide-urethane

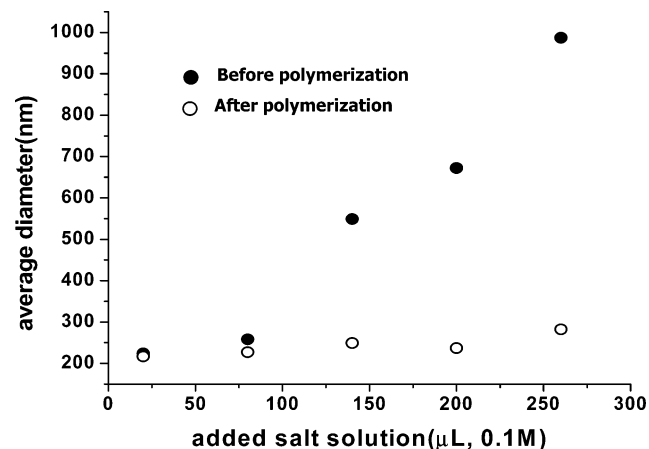


Figure 4. Comparison of calcium-induced vesicle fusion (dendron **4**) in water before and after polymerization.

dendrons **3** and **4** with topochemically polymerizable diacetylene moiety at the alkyl periphery form organized

nanostructures not only in organic media but also in water. In organic media, **3** and **4** respectively form lamella and columnar hexagonal structure. By changing the solvents from organic to aqueous media, the identical dendritic building blocks self-organize into a vesicular structure. The noncovalent interactions are critical for the construction of organized supramolecular nanostructures, which can be further stabilized by the photopolymerization of diacetylene moieties incorporated into the periphery of the building blocks in organized states.

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