Layered Structure and Order-to-Disorder Transition in a Block Codendrimer Caused by Intermolecular Hydrogen Bonds

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Introduction. It has been demonstrated that linear−linear block copolymers can form spherical, cylindrical, gyroidal, or lamellar microdomain structures via a microphase separation in the melt.[1] These block copolymers can self-organize into micelles or vesicles in selective solvents.[2] The most important parameters controlling the structure formation are the ratio of two blocks, Flory−Huggins segmental interaction parameter, χ, and the degree of polymerization, N. These supramolecular structures are normally in the nanometer to tens of nanometers depending on the total molecular weight of the block copolymers. These ordered structures in the solid state can be disordered by elevating the temperature to above the order-to-disorder transition temperature, T_{ODT}. In recent years, these microdomain or supramolecular structures have been utilized directly or as templates to prepare nanomaterials.[3]

Monodendrons and dendrimers are novel macromolecules with well-defined architectures.[4] Their unique architecture allows dendrimers to act as fundamental building blocks that self-organize into spherical or cylindrical supramolecular objects.[5] It has been shown that these objects can further self-organize into giant crystals.[6] In 1992, Hawker and Fréchet reported their pioneering work in the preparation of the segmented and layered codendrimers based on ester and ether monodendrons.[7a] Since these initial reports, a limited number of studies have been conducted with diblock codendrimers[7b−d,e] or Janus dendrimers.[7f] Recently, this group was the first to report that a block codendrimer composed of two third-generation monodendrons of poly(benzyl ether) (PBE) and poly(methallyl dichloride) (PMDC) can construct supramolecular objects, such as vesicles, via self-organization in selected solvents.[8] From this initial study, it can be concluded that the codendrimer architecture could allow the formation of strongly segregated microdomains difficult to achieve in other materials. Microdomain formation in the melt of block codendrimers was predicted on the basis of mean-field theory.[9] This pioneering study delivers a conclusion that the double-dendritic architectures could cause a difficulty to achieve the strongly segregated regime. To date, there are no reports focusing on the microdomain structures in the melt of block codendrimers. Herein, we report the first work regarding the formation of a layered structure in an amphiphilic block codendrimer caused by intermolecular hydrogen bonds and its thermal transition from an ordered state to a disordered state. Furthermore, the formation of a layered structure due to the formation and alternation of intermolecular hydrogen bonds between PMPA (methylpropionic acid) blocks was observed.

Results and Discussion. Scheme 1 shows the synthetic procedure for the block codendrimers. A third-generation Fréchet-type poly(benzyl ether) (*g3*-PBE) monodendron based on 3,5-dihydroxybenzyl alcohol[10a,b] and the third-generation aliphatic polyester monodendron based on 2,2-bis(hydroxymethyl)propionic acid (*g3*-PMPA)[10c,d] comprise the codendrimer. The monodendrons were synthesized according to convergent synthetic approaches from the literature.[10] The first block codendrimer **1**, denoted as *g3*-PBE-*b*-*g3*-PMPA, was prepared by directly coupling two different monodendrons together via esterification in dichloromethane with *N*,*N*′-dicyclohexylcarbodiimide (DCC) and using 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) as a catalyst.[11] The four acetonide protecting groups on the periphery of the *g3*-PMPA block were removed in methanol and dichloromethane (1:3) with Dowex H^+ 50W-X2 resin to give codendrimer **2** (*g*3-PBE-*b*-*g3*-PMPA-$(OH)_8$), which has eight hydroxyl groups on the periphery.[11]

The formation of the two codendrimers was verified using ^{1}H NMR and ^{13}C NMR spectrometries, MALDI-TOF mass spectrometry, and FT-IR spectrometry. The MALDI-TOF MS spectra in Figure 1A show that the molecular masses are in agreement with the theoretical molecular masses: 2606 for codendrimer **1** and 2428 for codendrimer **2**, indicating a high purity and a monodistribution. The monodistribution separates these materials from most block copolymers prepared by conventional polymerization. The FT-IR spectra in Figure 1B show a broad absorbance in the wavelength range of 3100−3700 cm^{-1} for codendrimer **2** indicative of OH groups. The disappearance of absorbances at 2995 and 1084 cm^{-1} (not shown) indicates a loss of methyl groups, further supporting the deprotection of the acetonide groups.

At room temperature codendrimer **1** is transparent while codendrimer **2** is slightly turbid. The DSC thermograms in Figure 1C show a *single* glass transition temperature for codendrimer **1** (30.2 °C) and for codendrimer **2** (24.2 °C) in the temperature range −40 to 120 °C. The wide-angle X-ray diffraction patterns in Figure 1D show broad halos in the range of $2\theta = 5°-30°$ indicative of an amorphous state of the two codendrimers at room temperature.

The microdomain morphology and morphological transition of codendrimer **2** in the temperature range of −30 to 135 °C were investigated using small-angle X-ray scattering (SAXS). Figure 2a is a three-dimensional graph showing the changes of scattering intensity and peaks with increasing temperature in the range of scattering vector q from 0.5 to 6 nm^{-1} ($q = 4\pi \sin \theta/\lambda$, where λ is the wavelength of X-rays). Figure 2b,c shows the temperature dependence of the *d*-spacing and scattering intensity (shown by the peak area). In Figure 3a there are two scattering peaks (a strong peak at lower q values and another weak peak at larger q values) that can be clearly observed below 50 °C. The corresponding *d*-spacings are 4.60 and 2.36 nm, respectively. The ratio is very close to 2, indicating the formation of a layered structure with a long spacing of 4.6 nm, as shown schematically in Figure 2d. Increasing temperature causes a great reduction in the scattering intensity of the peak at lower q values at 50 °C, and the peak at higher q values completely disappears (see Figure 2c). This indicates a transition from an ordered layered structure to disordered melt occurring at 50 °C, that is,

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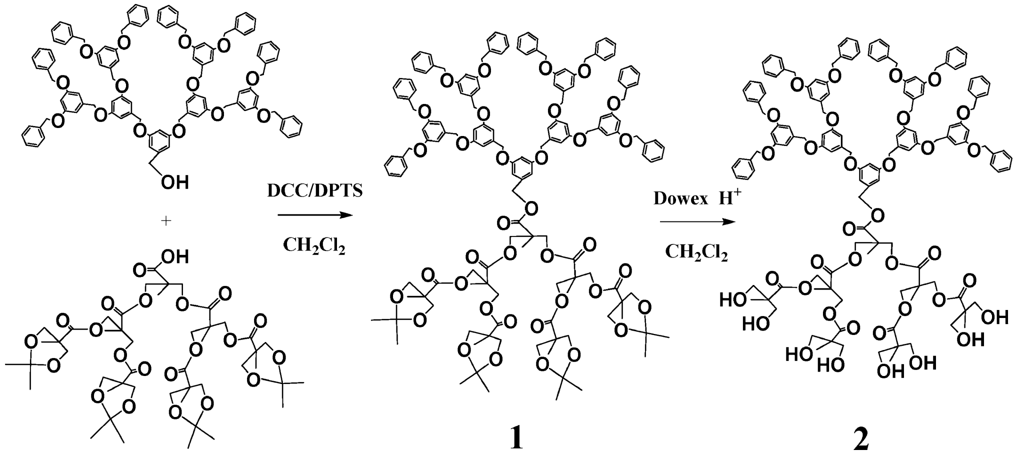
Scheme 1. Synthetic Route for Block Codendrimers: *g3*-PBE-*b*-*g3*-PMPA (1) and *g3*-PBE-*b*-*g3*-PMPA(OH)$_8$ (2)



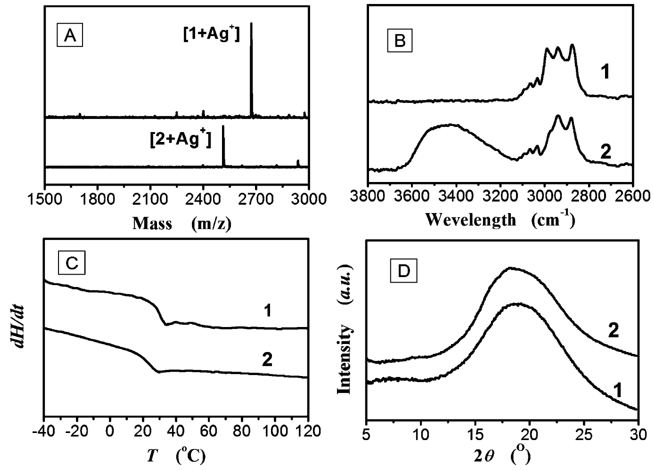


Figure 1. Spectral characterizations for the codendrimers **1** and **2**: (A) MALDI-TOF MS spectra; (B) FT-IR spectra of between 2660 and 3800 cm^{-1}; (C) DSC thermograms (second heating: 10 °C/min); (D) WAXD diffraction patterns.

$T_{\mathrm{ODT}} \cong 50$ °C. The weak scattering appeared at $T > 50$ °C is related to the density fluctuation in the disordered state.

The formation and change of the layered structure were further explored using temperature FT-IR spectroscopy. Figure 3a shows the change of absorbance at 3100−3700 cm^{-1} for codendrimer **2** when heated from 30 to 150 °C. The peak shape and position are greatly altered with increasing temperature. These changes demonstrate the sensitivity of the hydrogen bonding with the dendritic materials with respect to temperature. To gain some qualitative information regarding the hydrogen-bonding processes in the materials, the −OH band was fit by three Gaussian functions[12] (see Figure 3b). Clearly there are more than three modes of hydrogen bonding possible. In the simplified model, three distinct species are assumed to be present: free hydroxyl groups, intramolecularly hydrogen bonded hydroxy groups, and intermolecularly bonded hydroxyl groups. A gradual broadening of the peaks was observed with decreasing wavelength. The following assignments were made: the peak at $\upsilon \approx 3750$ cm^{-1} corresponds to the free hydroxy groups, the peak at $\upsilon \approx 3450$ cm^{-1} corresponds to the hydroxy groups involved in intramolecular hydrogen bonding between hydroxymethyl groups in the same PMPA blocks, and the peak at $\upsilon \approx 3320$ cm^{-1} corresponds to the hydroxy groups which participate in intermolecular hydrogen bonding between hydroxymethyl groups in the different PMPA blocks. In the temperature range investigated the peak positions of the three vibration modes do not vary significantly (see Figure 3c). The temperature dependence of the areas of these peaks was most interesting. The peak area at $\upsilon \approx 3750$ cm^{-1} is the smallest one and remains nearly unchanged with increasing temperature. The peak areas at $\upsilon \approx 3450$ and 3320 cm^{-1} become less intense upon heating, indicating a reduction in hydrogen bonding with increasing temperature, in particular for the intermolecular hydrogen bonding.

It can be inferred that the formation of the layered structure is driven by intermolecular hydrogen bonding. The formation of inter- and intramolecular hydrogen bonds can cause a molecular segregation leading to alternating hydrophobic PBE layers and hydrophilic PMPA layers. For the codendrimer studied here, the formation of the layered structure is very sensitive to the degree of which the intermolecular hydrogen bonding exists. From Figure 3d it can be seen that upon heating the sample above 50 °C the amount of the intermolecular hydrogen bonding was reduced. This slight change caused a dramatic transition from ordered layered structure to disordered melt, as demonstrated in Figure 2.

It is interesting to mention again that a single glass transition temperature for codendrimer **2** was detected. This indicates that the layered structure formed in this codendrimer could be different from the phase-separated structures of linear−linear block copolymers which normally exhibit two glass transitions.[1a,b,d] This amphiphilic codendrimer did not show two glass transition temperatures in the ordered state because the 4.6 nm thickness of the layered structure was smaller than the critical micro-domain size in polymer multiphase systems that can be detected by DSC.[13]

Some detailed information about the layered structure can be obtained using one-dimensional correlation analysis.[14] The results show that the volume fractions of the two layers were determined to be $\varphi_{\mathrm{PBE}} = 0.61$ and $\varphi_{\mathrm{PMPA}} = 0.39$. These values are similar to linear−linear block copolymers that demonstrate a lamellar structure in the range of a volume fraction from 0.40 to 0.60.[1d] The layer thicknesses of the two blocks that were calculated from the volume fractions are $L_{\mathrm{PBE}} = 2.8$ nm for the PBE layer and $L_{\mathrm{PMPA}} = 1.8$ nm for the PMPA layer. These values are reasonable because of different sizes of the two blocks. The mean-square radius of gyration of *g*3-PBE is $R_{\mathrm{g}} = 1.26{-}1.39$ nm in deuterated benzene (a good solvent) and 0.99−1.10 nm in THF or deuterated THF (a bad solvent).[15] No literature values were reported for the PMPA dendron. Its size, however, should be between that of the PBE monodendron and a third generation aliphatic polyether monodendron (ca. 1.0 nm).[5h]

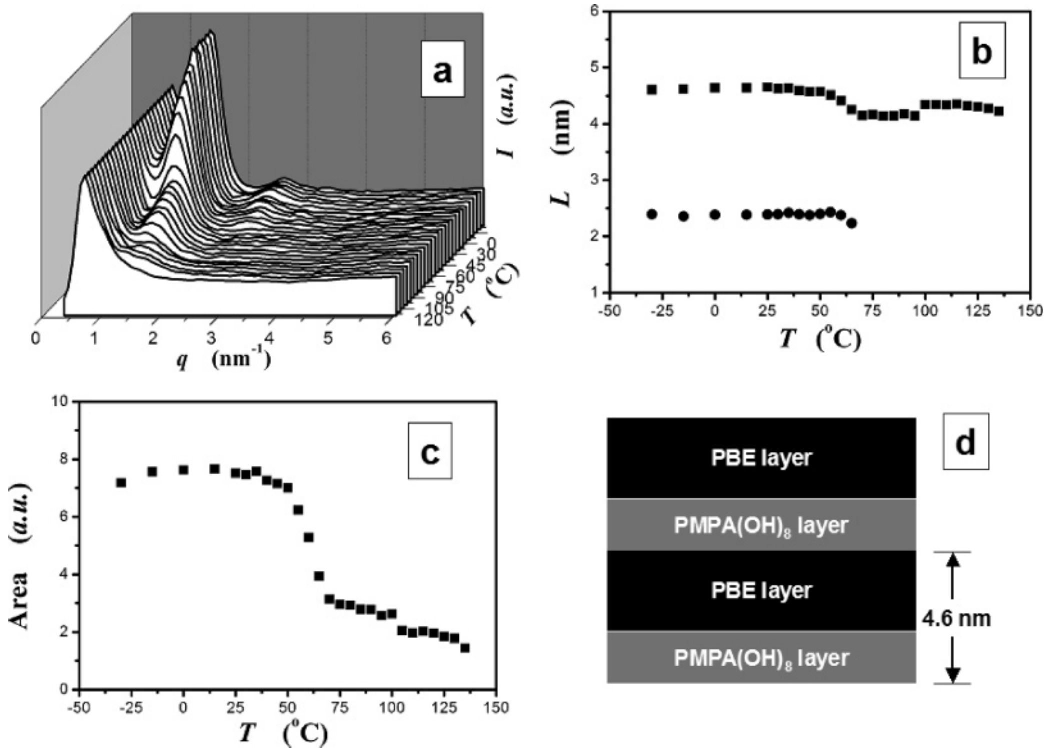


Figure 2. (a) SAXS diffraction patterns for codendrimer **2** obtained at different temperatures. (b) Temperature dependence of the *d*-spacing. (c) Temperature dependence of the scattering intensity. (d) Layered model depicting the expected arrangement of alternating blocks with the corresponding *d*-spacing.

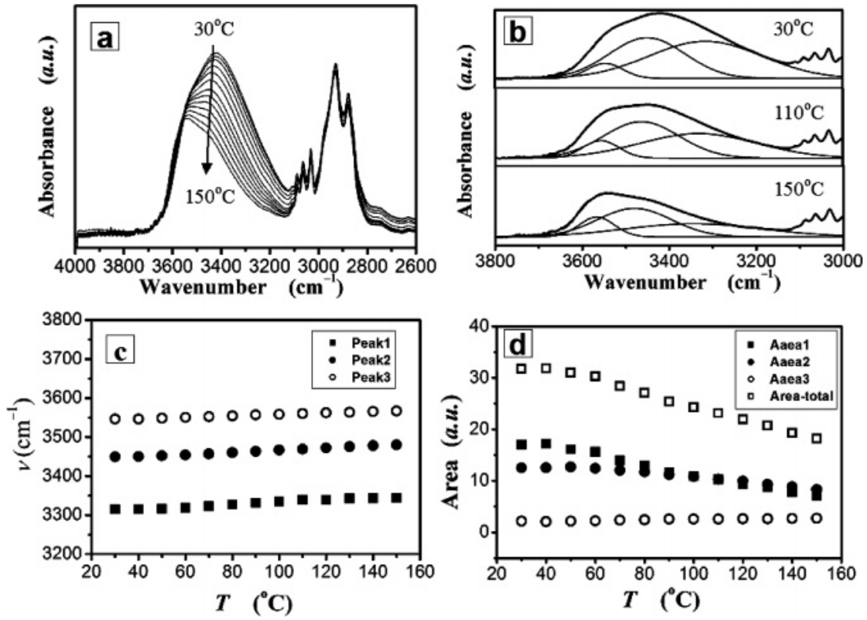


Figure 3. (a) Temperature-dependent FT-IR spectra from 30 to 150 °C, 10 °C as a step for **2**. (b) Gaussian fitting of the spectra obtained at 30, 110, and 150 °C. (c, d) Temperature dependence of the peak positions and areas.

A simple computer simulation using Chemdraw software shows that the PMPA block is spherical, but PBE block is fan-shaped. This is reasonable because PMPA block is more flexible than the PBE block. Because the *d*-spacing was 4.6 nm and the diameter of the codendrimer was about 3.0 nm as detected in THF solution using dynamic laser light scattering, an interdigitated arrangement of molecules is a rational model of the layered structure composed alternatively of PBE layers and PMPA layers. Such an arrangement of block codendrimer would allow a denser packing of the molecules. This is similar that we found in our previous study.[8] The difference between the *d*-spacing and the molecular diameter indicates that the molecules were depressed along the interfacial areas. The unique shapes of two monodendrons is also an important factor that causes the 4.6 nm *d*-spacing much smaller than those of linear−linear block copolymers having an identical molecular weight.[1d]

Previous studies[5,6] show that supramolecular objects were formed by "copolymers" composed of a dendritic core and long alkyl chains due to the unique shape of the dendrons, immiscibility of the dendritic core and the alkyl chains, and crystallization of the alkyl chains. Normally, the objects are spherical or cylindrical. The strong tendency of long alkyl chains to crystallize can produce a lamellar structure.[5h] The present work utilizes two different monodendrons to construct a block codendrimer having a nonlinear molecular shape or architecture. Surface functionalization of one block was used to induce the molecular segregation leading to a smaller *d*-spacing.

Conclusion. In summary, a block codendrimer composed of third-generation PBE and PMPA monodendrons was synthesized and was then converted to an amphiphilic block codendrimer with hydroxy groups on the periphery of the PMPA block by removing the protecting groups. The SAXS diffraction patterns showed the presence of a layered structure at a temperature range below 50 °C, and an order-to-disorder transition occurred at 50 °C. The FT-IR determination indicated the intermolecular hydrogen bonds cause a molecular segregation, which gives rise to a layered structure. The disruption of hydrogen bonding at 50 °C causes the transition to the disorder melt. The architectures of two blocks and the molecular diameter detected in solution suggested an interdigitated molecular arrangement within the layers which can rationally describe the layered structure of this block codendrimer. Work is underway to better understand the organizational properties of these and closely related amphiphilic codendrimers.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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