Globular Organization of Multifunctional Linear Homopolymer Using Trifunctional Molecules

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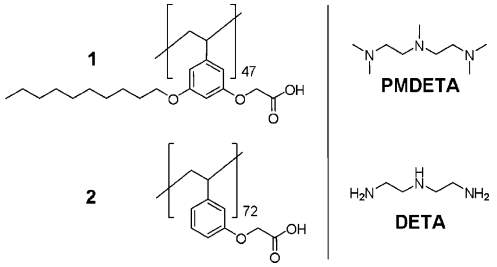
ABSTRACT: The influence of the microenvironment of chains on their self-organization has been studied using styrene-based linear polymers having two different pendant groups on every repeat unit. The noncovalent cross-linking of a polymer containing both carboxylic acid and alkyl (n-$C_{10}H_{21}$−) pendant groups with a multifunctional amine (PMDETA) in a nonselective solvent (DMF) resulted in thermally reversible supramolecular aggregates that were stable without interparticle cross-linking. The size of the aggregates was controlled on a sub-micrometer level by varying concentration. In the absence of the alkyl pendant group, control over the structure and properties of the aggregates was lost. These multifunctional polymers are model systems to investigate the three-dimensional organization of linear polymers by noncovalent cross-linking and the influence of chain structure on supramolecular organization.

Introduction

The organization of linear biomacromolecules, such as proteins, into 3-dimensional (3-D) constructs has inspired the design of synthetic self-assembling systems.[1] There have been numerous efforts to use specific noncovalent bondings, such as hydrogen bonding,[2] ionic bonding,[3] metal coordination,[4] or solvophobic interactions,[5] to fabricate a wide variety of supramolecular structures from synthetic molecules. The assembly of synthetic multifunctional macromolecules in solution states in the presence of complementary multifunctional molecules was not an exception for this exploration. Various block copolymer micelles[6a−d] or vesicles[6e] have been prepared using inter-polyelectrolyte complexes of block ionomers, i.e., neutral−ionic block copolymers. In these examples, because of the self-assembly of block copolymers and the presence of neutral blocks, the extent of the cross-linking reaction was regulated and discrete objects were obtained. This approach was also used to fabricate shell cross-linked micelles by cross-linking preformed micelles of a cationic block ionomer with anionic one.[6f] Pochan and co-workers showed that an amphiphilic triblock copolymer having a negatively charged component can form toroidal micelles through the interaction with a divalent organic counterion.[6g] Yoshida and Kunugi reported a nonamphiphilic diblock copolymer that assembled into micelles through a hydrogen bonding with a bifunctional cross-linker.[6h] The micellization of poly(ethylene glycol)-*block*-poly(vinylpyridium) in the presence of divalent anion has also been reported.[6i,j] Compared to block copolymers, the association of multifunctional homopolymers into discrete objects in the presence of multifunctional cross-linkers has been studied to a much lesser extent,[2e,7a] especially for stoichiometric complexes, partly because of the difficulty in controlling the extent of complexation. Jiang and co-workers observed the formation of hollow spheres by attaching difunctional rigid polyimide oligomers to a flexible poly(4-vinylpyridine) chains through hydrogen bonding.[7a] Though not a homopolymer, a random copolymer having diaminopyridine groups has been reported to form micron-sized giant vesicles[7b] or aggregates[7c] through the complementary hydrogen bonding with a random copolymer containing thymines or bis-thymine cross-linkers, respectively. In addition to the construction of noncovalently cross-linked discrete polymeric aggregates, control of the aggregate size has been investigated by varying the polymer concentration[6k,7a] or the cross-linker structure.[7c] However, getting a narrow size distribution still remains a challenge.

Scheme 1. Structures of Linear Polymers and Cross-Linking Molecules



Recently, we reported a new class of styrene-based linear homopolymers containing two different pendant groups, i.e., a carboxylic acid and a neutral group, on every repeat unit, and their self-assembly in solvents that were selective for one of the pendants.[8] The carboxylic acid moiety can function as a specific recognition site for complexing with an amine group through an acid−base type of interaction and possibly subsequent hydrogen bonding.[9] With the proper choice of the remaining pendant group, we can regulate the microenvironment of the repeat unit and, thereby, influence the assembly of the chains. Here, we report the effect of neutral pendant groups on the structure, stability, and reversibility of the aggregates brought

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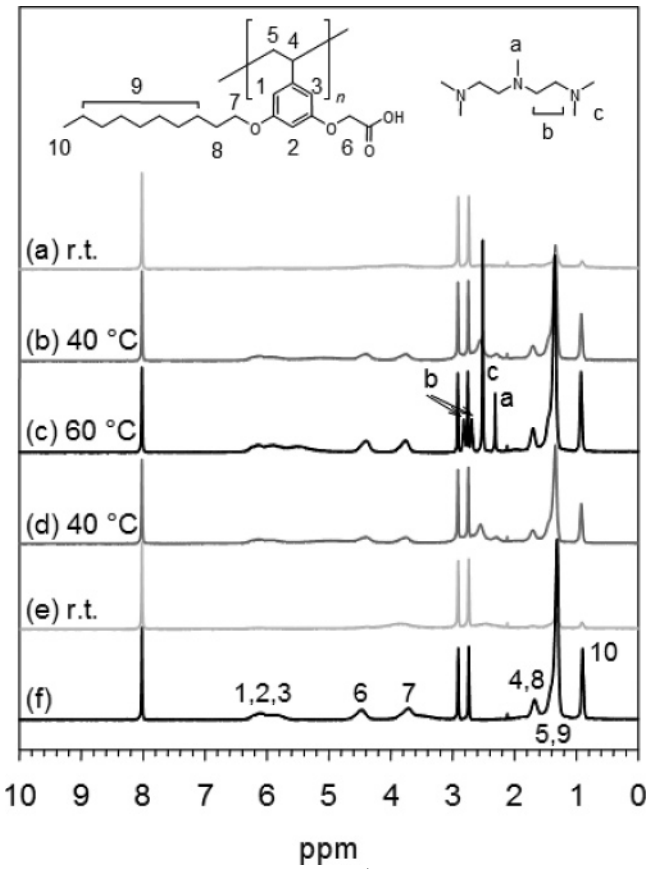


Figure 1. (a−e) Variable temperature ^{1}H NMR spectra of **1** (1 wt %) and PMDETA in DMF-d_7. (f) ^{1}H NMR spectrum of **1** (1 wt %) in DMF-d_7 ((a) → (c): heating; (c) → (e): cooling; (f) rt).

about by the noncovalent cross-linking with multifunctional small molecules.

Results and Discussion

Two different neutral pendants, i.e., an alkyl (n-$C_{10}H_{21}$−) group (polymer **1**) and hydrogen (for polymer **2**) (Scheme 1), were used in this study. For the cross-linking molecules, a trifunctional aliphatic amine, diethylenetriamine (DETA), and its *N*-methyl-substituted derivative, *N*,*N*,*N*′,*N*′*N*″-pentamethyldiethylenetriamine (PMDETA), were used. As discussed previously,[8] solvent is important in determining the organization of these homopolymers. To investigate the organization behavior of free chains by introducing cross-linkers into a homogeneous solution of the polymers, an amide-type polar aprotic solvent, DMF (*N*,*N*-dimethylformamide), was used. The carboxylic acid pendant groups and DMF have polar interactions. Although DMF is not a good solvent for long alkyl chains, *n*-decane is soluble in DMF by up to 60 μL in 1000 μL of DMF. This concentration of *n*-decane corresponds to the content of the alkyl group in a ∼10 wt % solution of polymer **1**. All of the DMF solutions of **1** were colorless and optically transparent for the concentrations ≤1.0 wt %. Dynamic light scattering (DLS) confirmed the absence of aggregates of **1** in DMF. Furthermore, the ^{1}H NMR spectrum of **1** (1.0 wt %) in DMF-d_7 at room temperature displayed all of the resonances corresponding to the protons of the polymer (Figure 1f), indicating that DMF solubilizes all parts of the polymer. Over the concentration range studied, DMF did not induce any discernible micellization or flocculation of polymer **1** or **2**.

After an addition of a stoichiometric amount of trifunctional amine cross-linker, DETA or PMDETA, the clear DMF solution of polymer **1** (1.0 wt %) turned turbid, indicating the formation of aggregates. As the concentration of **1** decreased, the solution became translucent and eventually transparent. After adding PMDETA, the ^{1}H NMR spectrum (Figure 1a) of **1** (1.0 wt %) in DMF-d_7 at room temperature did not show any observable resonances, except for the weak signals corresponding to the

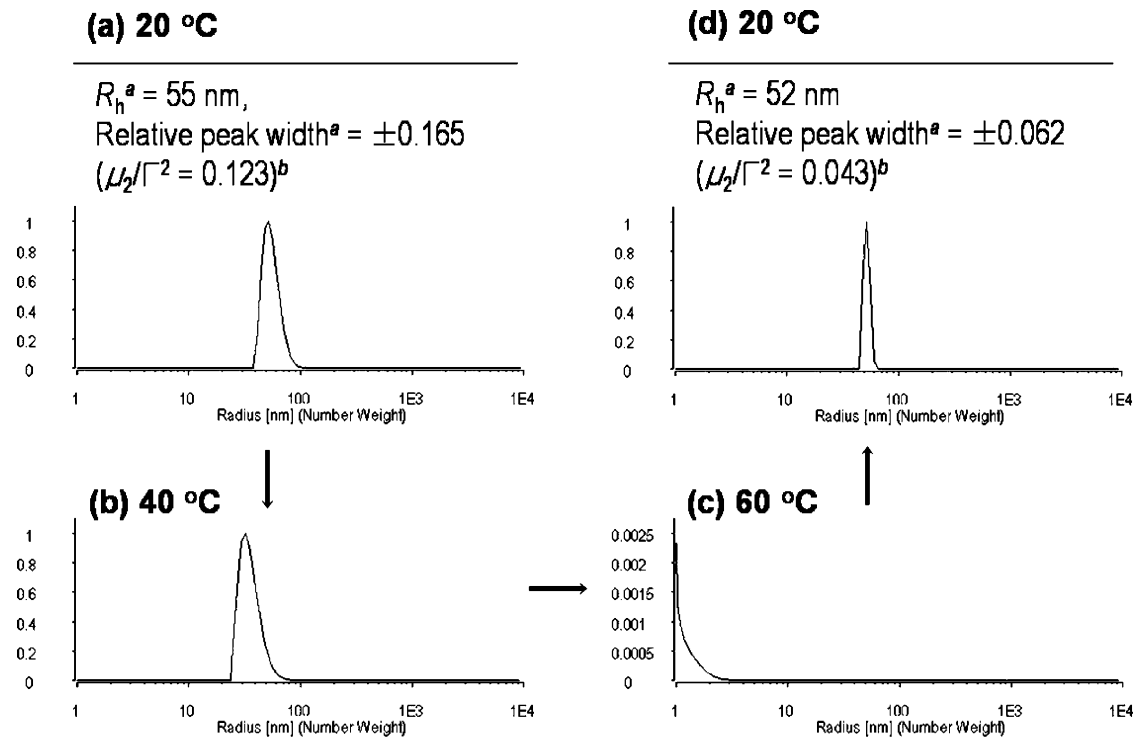


Figure 2. Change of hydrodynamic radius and its distribution of **1** (0.43 wt %) cross-linked with PMDETA in DMF during the first heating−cooling cycle.

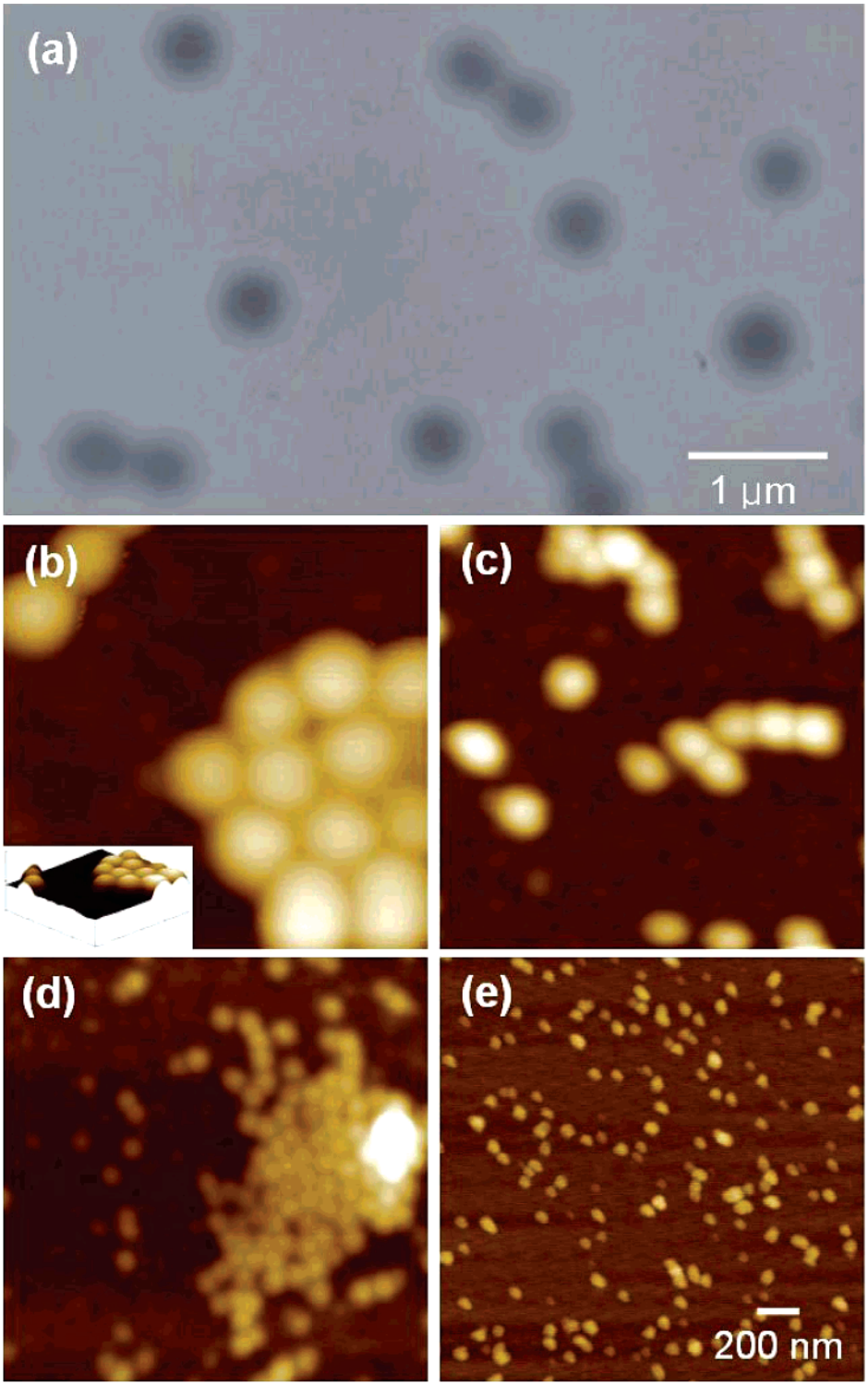


Figure 3. (a) TEM micrograph and (b−e) SFM images (height contrast, inset of (b): 3-D profile) of **1** cross-linked with PMDETA. The samples were prepared from a solution treated with a heating−cooling process. Initial concentration of **1** in DMF (wt %): (a, b) 1.0, (c) 0.85, (d) 0.43, and (e) 0.21.

protons of the alkyl pendant group ($\delta = 0.8-1.6$). These results indicate that the bonding between the carboxylic acids and amines is strong enough to overcome the interactions with DMF and produce dense aggregates of **1** and the cross-linking molecules. Upon heating, the turbid DMF solutions became optically clear, suggesting a dissociation of aggregates. Conversely, the aggregates prepared from **1** and DETA were not soluble in DMF even at 150 °C. Since PMDETA has the *N*-methyl-substituted structure of DETA, this different behavior can be understood by considering the effect of *N*-methyl substitution on the bond strength of the constituent amine−carboxylic acid complexes. Primary and secondary amines have hydrogens that can participate in the formation of additional hydrogen bonds with carboxylic acids to further strengthen the amine−acid interaction,[10] while tertiary amines do not have such hydrogens. Also, in crowded systems, like the aggregates, there is also a possibility of the formation of amide bonds between the primary or secondary amines of DETA and carboxylic acids. Upon cooling, the DMF solution containing **1** and PMDETA became turbid, suggesting the regeneration of the aggregates.

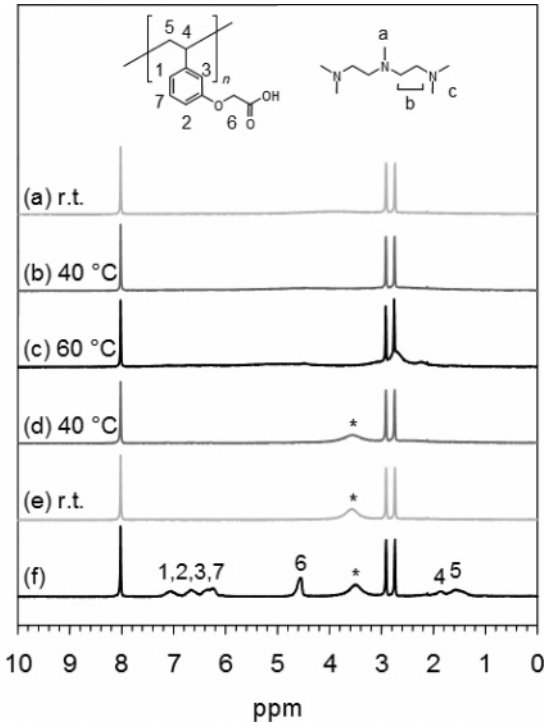


Figure 4. (a−e) Variable temperature ^{1}H NMR spectra of **2** (1.0 wt %) and PMDETA in DMF-d_7. (f) ^{1}H NMR spectrum of **2** (1.0 wt %) in DMF-d_7 ((a) → (c): heating; (c) → (e): cooling; (f) rt, *: peak from water).

Variable temperature NMR spectra of the aggregates consisting of **1** (1.0 wt %) and PMDETA in DMF-d_7 are shown in Figure 1. As the temperature increased to 60 °C, the ^{1}H NMR signals from both **1** (at $\delta = 3.6-6.4$ and $\delta = 0.8-1.8$) and PMDETA ($\delta = 2.2-2.9$) intensified and sharpened, indicating a substantial increase of interactions between each component (**1** and PMDETA) and DMF. When the solution was cooled to room temperature, the ^{1}H NMR signals were again suppressed, confirming the thermal reversibility of aggregate formation.

DLS experiments also indicated that the supramolecular assembly of **1** and PMDETA was thermally reversible in DMF (Figure 2). In the as-prepared solution of **1** (0.43 wt %) and PMDETA, the aggregates had a hydrodynamic radius (R_h) of 55 nm at 20 °C. Upon heating to 60 °C, the aggregates disappeared. When the solution was cooled to 20 °C, aggregates with R_h of 52 nm were regenerated. It should be noted that the size distribution (relative peak widths evaluated by CONTIN analysis: ±0.062) of the aggregates formed after the heating−cooling cycle was much narrower than that (±0.165) of the as-prepared aggregates. This result suggests that the addition of the cross-linking molecules into the polymer solution causes a nucleation and growth of the aggregates where nuclei form at different times. However, nucleation of the aggregates from a uniformly mixed solution of **1** and PMDETA, as it is cooled, occurs over a much smaller time interval.

This result suggests a route for the preparation of globular aggregates with controlled sizes and narrow size distribution from polymer **1** and PMDETA. Several solutions of **1** with differing concentrations were prepared, and stoichiometric amounts of PMDETA were added. The mixtures were subjected to a heating−cooling cycle before spin-coating on silicon substrates. As the initial concentration of **1** decreased from 1.0 to 0.21 wt %, the average diameter (D_{av}) of the globular aggregates decreased from 450 to 60 nm (Figure 3). This reduction in size with concentration can be explained by a competition between intra- and intermolecular cross-linking of the polymer chains: when the concentration is low, an intramolecular cross-linking is favored and smaller aggregates are generated. The aggregates exhibited a tendency to locally pack on a silicon substrate into regular monolayer arrays (Figure 3d), suggesting the stability of the aggregates in solution as well as in dried state. Transmission electorn microscopy (TEM) of the aggregates adsorbed on a carbon-coated copper grid (from 1.0 wt % solution of polymer **1** and PMDETA) also suggests that the aggregates are discrete globular objects (Figure 3a). The TEM micrograph showed a maximum contrast in the middle of the objects, indicating that the aggregates are not hollow. This was further supported by the fact that the SFM images displayed no indication of a depression in the middle of the objects.

The DMF solutions of polymer **2** (1.0 and 0.43 wt %), where hydrogen has replaced the alkyl group, also became turbid with the addition of PMDETA. Infrared (IR) experiments on both polymers **1** and **2** showed significant reductions of the peak intensity at ~1730 cm^{-1} (due to characteristic carbonyl stretching) with the addition of PMDETA or DETA. Other changes were hardly discernible probably due to overlaps with the intense

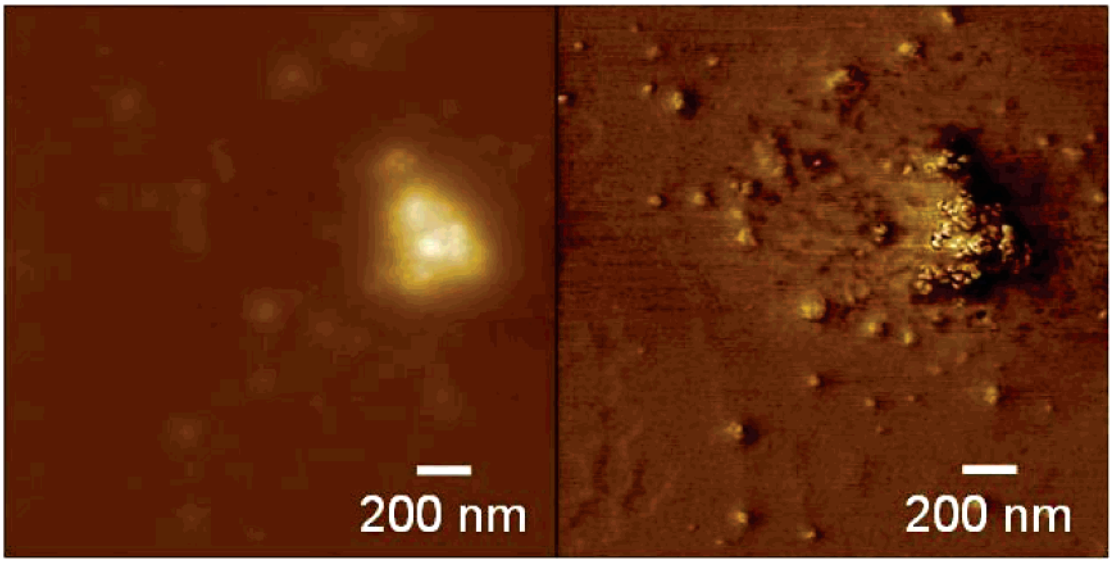


Figure 5. SFM images (left: height contrast; right: phase contrast) of **2** (0.43 wt %) cross-linked with PMDETA.

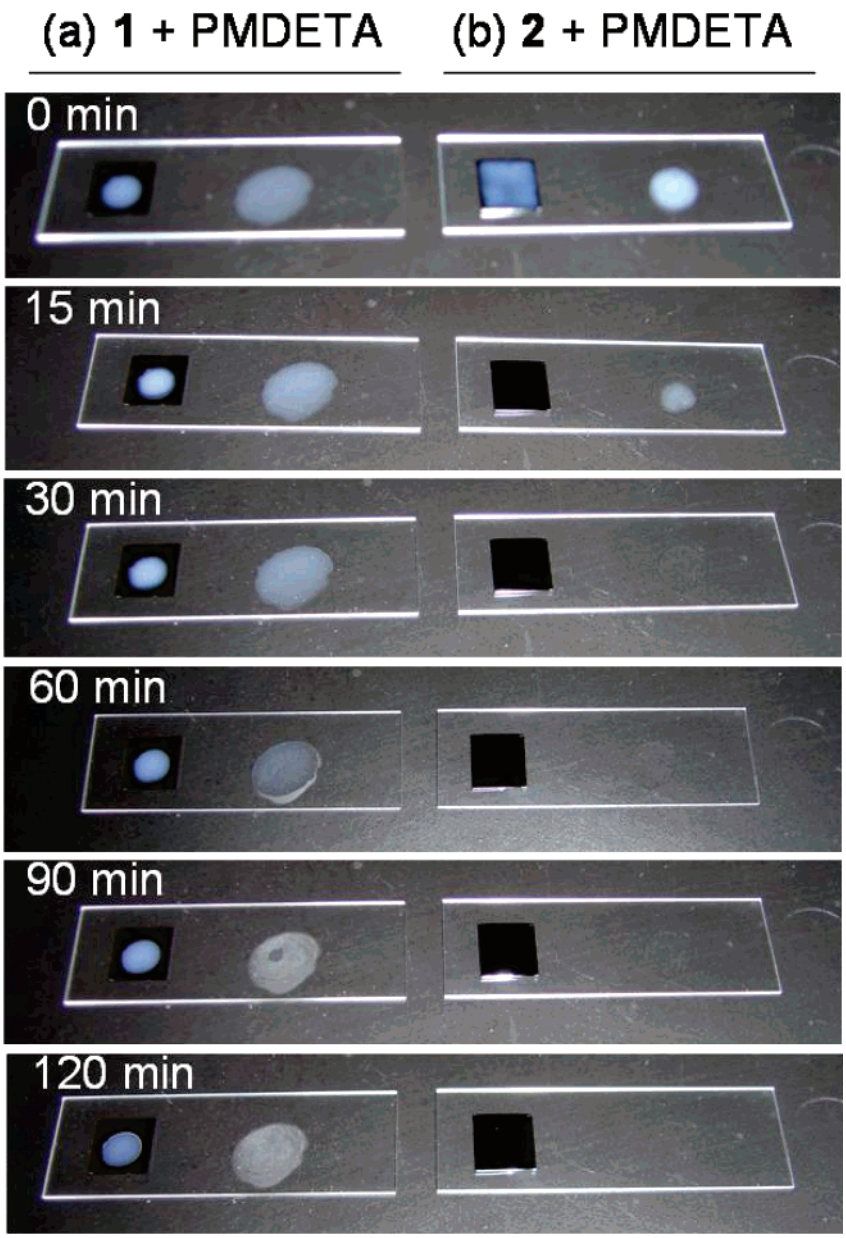


Figure 6. Slow solvent evaporation process of DMF solutions containing (a) **1** or (b) **2** (0.43 wt %) cross-linked with PMDETA (left of each: on silicon substrate; right of each: on glass slide).

polymer peaks. This result indicates that on a functional group level the nature of the amine−acid interaction is similar for all the considered polymer amine combinations. However, the properties of supramolecular aggregates might be different. The DMF solutions of polymer **2** and PMDETA did not become clear, even at 150 °C. The ^{1}H NMR spectra of DMF-d_7 solution containing **2** (1.0 wt %) and PMDETA did not show any observable resonances, regardless of the solution temperature (Figure 4). These observations imply that the aggregates consisting of **2** and PMDETA are so tightly cross-linked that the access of solvent molecules to the amine−acid bonds is restricted, and the dissociation of the amine−acid complexes does not occur even at high temperatures. Thus, the alkyl pendant group in each repeat unit of the polymer **1** is the key to the thermal reversibility of aggregation. Although this irreversibility might be a kinetic phenomenon, the dissociation of the aggregate of polymer **2** and PMDETA at elevated temperatures was not observed in the time frame of our experiment. When spin-coated, the mixture of polymer **2** and PMDETA showed large fragments of small particles (Figure 5), suggesting that the aggregates are not stable and prone to flocculation.

A drop of each solution containing polymer **1** or **2** (0.43 wt %) and PMDETA was placed on a silicon substrate or on a glass slide (Figure 6(0 min)). On the silicon substrate, the solution of **1** and PMDETA (mixture **1**) formed a droplet with a finite boundary, while the solution of **2** and PMDETA (mixture **2**) spread the entire surface. The silicon substrate has ∼2 nm thick native oxide layer on the surface. Therefore, these results indicate that mixture **1** was less hydrophilic than mixture **2**. Since the only difference between **1** and **2** is the presence of the alkyl pendant group on the monomer units, the reduced hydrophilicity of the mixture **1** can be attributed to the alkyl groups. As suggested by the NMR results discussed above, some of the alkyl groups are located on the exterior of the aggregates, thereby reducing the polarity of the whole mixture. On the glass slide, mixture **1** spread more than it did on the silicon substrate, while mixture **2** showed the opposite tendency. This is understandable, since the glass slides are less hydrophilic than silicon substrates unless they are scrupulously cleaned. When

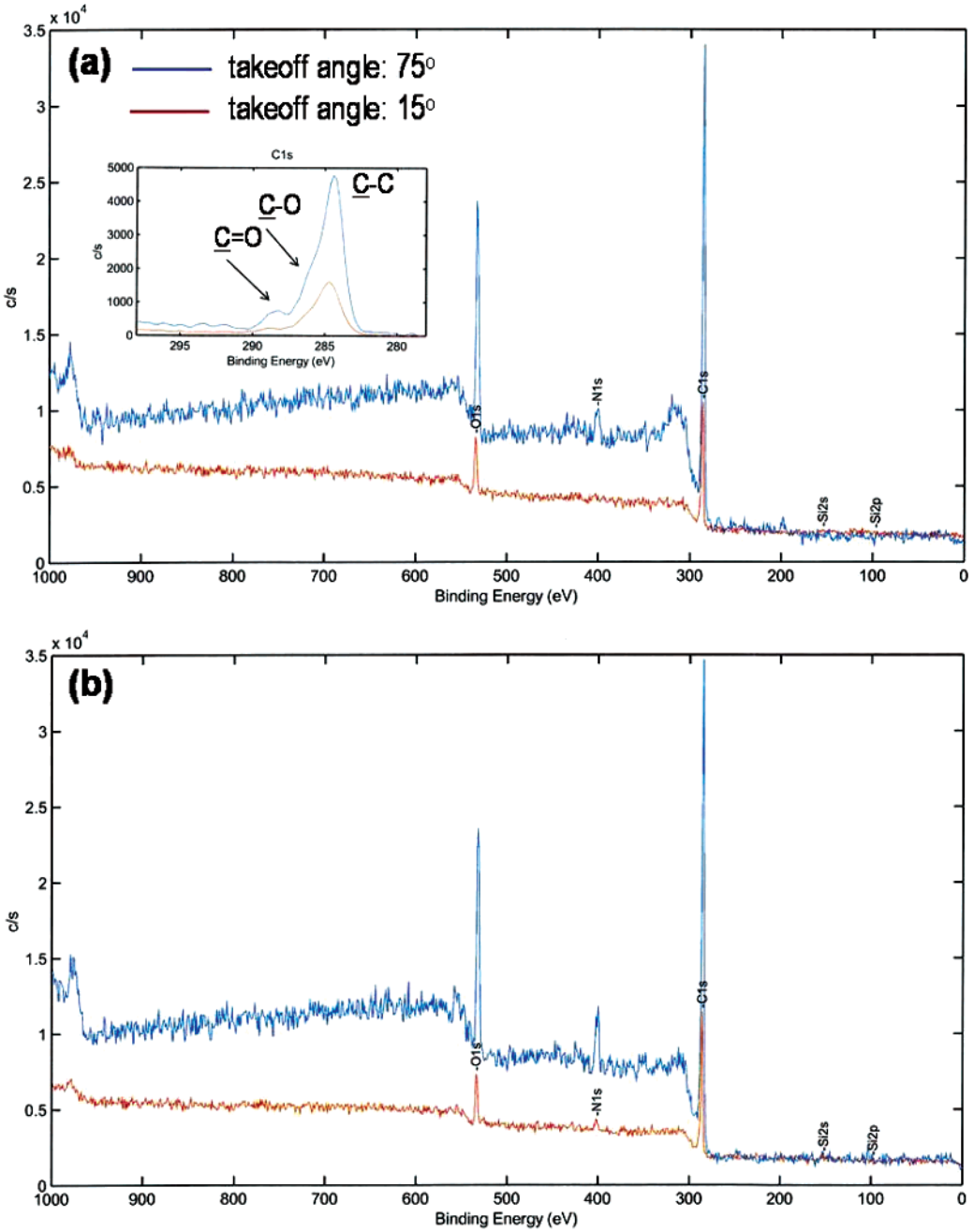


Figure 7. XPS spectra of the samples obtained after slow solvent evaporation of DMF solutions containing (a) **1** (inset: C 1s core-level spectra) or (b) **2** cross-linked with PMDETA.

the turbid mixture **2** was dried at ambient condition, it gradually cleared as DMF evaporated, producing a transparent film (Figure 6b). This can be understood by a fusion of the aggregates via an interparticle cross-linking. Conversely, mixture **1** maintained its turbidity and left a white powder after evaporation of the solvent (Figure 6a). An exterior layer of alkyl groups, as suggested by the wetting studies, would retard the fusion of the particles, leaving isolated particles upon drying.

X-ray photoelectron spectroscopy (XPS) measurements were performed on samples dried on silicon substrates (Figure 7). The X-ray takeoff angle was controlled to investigate the variation of compositions as a function of the sampling depth. At the takeoff angle of 75°, all of the three elements, carbon, oxygen, and nitrogen, were observed in the XPS survey spectra of both samples. At a shallow sampling depth (takeoff angle of 15°), the XPS survey spectrum obtained with the sample of **1** and PMDETA showed carbon and oxygen peaks but negligible nitrogen peak, while the spectrum obtained with the sample of **2** and PMDETA showed all of the three peaks. These data indicate that, in the case of aggregates of polymer **1** and PMDETA, nitrogen atoms (the elemental markers of PMDETA) were buried beneath a thin surface layer consisting of carbon and oxygen. The C 1s core-level spectrum, taken at the takeoff angle of 75°, of **1** and PMDETA contained the peak corresponding to the carbonyl carbon. On the other hand, the spectrum taken at a takeoff angle of 15° did not show this peak, suggesting that the alkyl groups, not the carboxylic acid groups, were located at the exterior of the aggregates, in agreement with the other measurements. But, considering the substitution pattern of the alkyl groups in the polymer **1** and the size of the globular aggregates, a large number of alkyl groups are expected to exist in the interior of the aggregates also.

The internal structure of the aggregates was investigated by X-ray scattering. Aggregates of polymer (**1** or **2**) and PMDETA

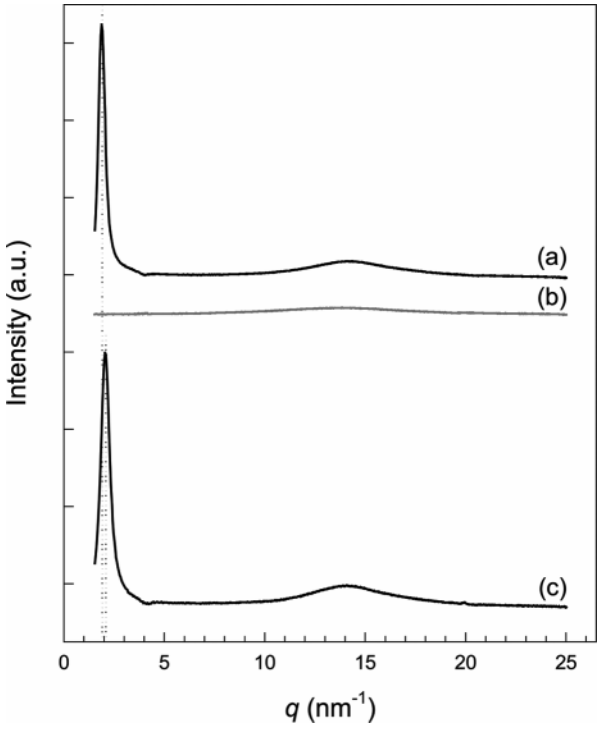
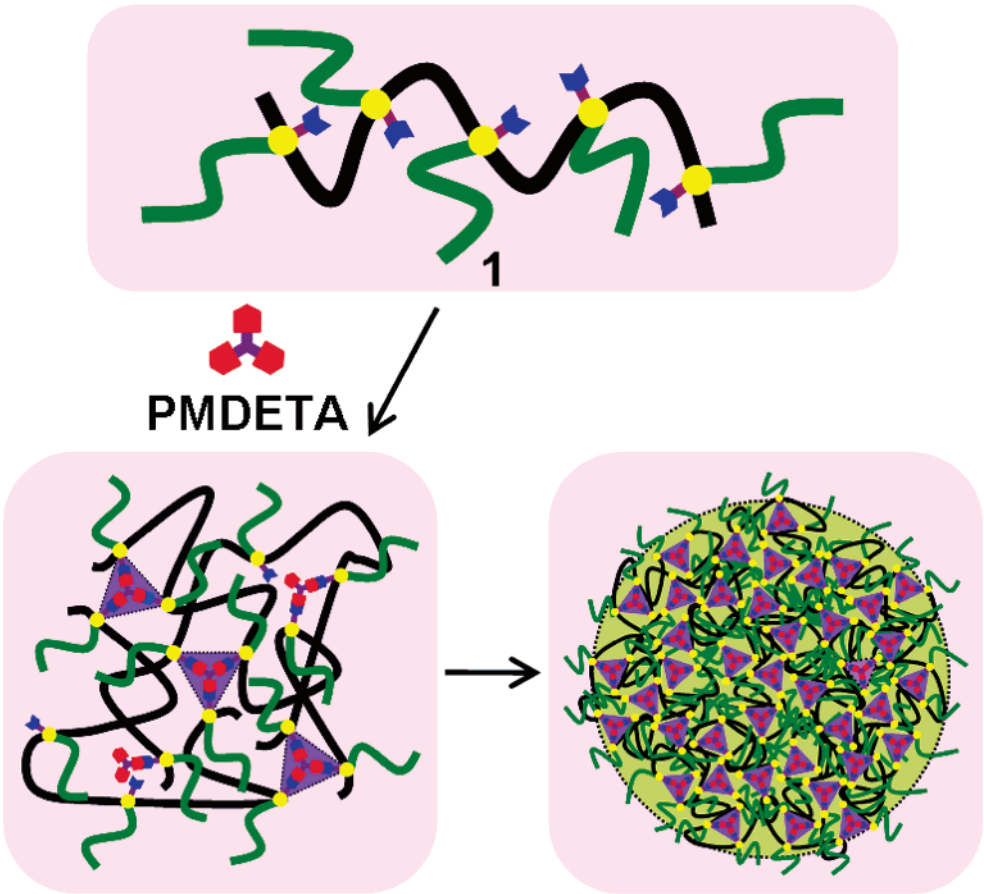


Figure 8. Wide-angle X-ray scattering patterns of samples dried from DMF solutions: (a) **1** or (b) **2** (0.43 wt %) cross-linked with PMDETA; (c) **1** itself. (The background scattering from Kapton window was subtracted.)

were collected by centrifugation from DMF solutions (the initial concentrations of polymer: 0.43 and 1.0 wt %), dried at an ambient condition, and sandwiched between Kapton films (25 μm thick). The samples (powdery states) of **1** and PMDETA consistently showed only one peak with a *d* spacing of 3.3 nm (Figure 8a). It is much smaller than the size of the aggregates, prepared at the corresponding initial concentrations, implying that the aggregates had a definite internal structure and a structural hierarchy. The absence of any other peaks indicates that the ordering is short range, with no ordering on the segmental level. The samples (transparent film states) of **2** and PMDETA did not show any peaks, regardless of the initial concentration of **2** (Figure 8b), even though they had the same amine−carboxylic acid complexes as the samples of **1** and PMDETA. This suggests that the alkyl groups of the polymer **1** played an important role in the formation of the hierarchical structures. Although the sample dried from DMF solution of **1** (without PMDETA) was an optically transparent film, it showed a very similar scattering pattern to that of sample of **1** and PMDETA except a slight shift of the peak toward higher *q* (Figure 8c, $q = 2.1$ nm^{-1}, $d = 3.0$ nm). Here, structure formation is, more than likely, due to hydrogen bonding between the carboxylic acid groups. Although this bonding was not strong enough to overcome the interactions with DMF, it could become dominant as the solvent evaporates. Comparing the size of the microstructure (3.0 nm) to the dimension of the repeat unit of **1** (~2.0 nm long), the alkyl pendant groups of the hydrogen-bonded repeat units are, more than likely, not extended. The increase in the spacing to 3.3 nm, as a result of the incorporation of PMDETA, can be understood by considering the flexible nature of PMDETA. Molecular models of PMDETA show that the average distance of nitrogen pairs varies from 0.29 to 0.49 nm, depending on its conformation. This indicates that PMDETA adopted a compact conformation in the aggregates.

Scheme 2. Schematic of the Structural Development of a Hierarchical Globular Aggregate from 1 and PMDETA



The structure of the aggregates can be described as Scheme 2. As PMDETA molecules interact with the acid groups and link, the chains of polymer **1** associate, the number of free acids decreases, and the local concentration of the chains increases. Such changes reduce the solubility of the associates in DMF and, consequently, induce a collapse of the associates into globular aggregates. The aggregates become even denser through further cross-linking of the remaining free acids and amines. The formation of an amine−acid bond forces the pendant groups to reorient due to their substitution pattern, in a way that the alkyl group faces opposite to the bond. As a result of such a pendant group reorientation, the globular aggregate has alkyl groups at the surface and remains stable without interparticle cross-linking. Similarly, the chains of **2**, having hydrogen instead of the alkyl pendant groups, are also able to form cross-linked aggregates when PMDETA is added. While the alkyl pendants (n-$C_{10}H_{21}$−) can make enough free volume in the collapsed aggregate to allow the access of solvent molecules to the amine−acid bonds, hydrogen is simply too small. Therefore, the aggregate of polymer **2** and PMDETA lacks thermal reversibility. The dense nature of the collapsed aggregates of **2** and PMDETA restricts the mobility of the remaining free acids and amines in the interior. Hence, the development of structure may be kinetically trapped, unlike the case of polymer **1**. Also, the small size of hydrogen presents little or no steric barrier to interparticle cross-linking as the solvent evaporates. The absence of a steric barrier in addition to the lack of thermal reversibility may be the origin for the inability of polymer **2** to generate regular objects with controllable size.

Conclusion

We have shown that a rationally designed synthetic polymer chain (**1**), the styrene-based linear macromolecule containing both carboxylic acid and an alkyl (n-$C_{10}H_{21}$−) pendant group on every repeat unit, can organize in a thermally revesible manner with controlled size into a stable hierarchical globular object in DMF through specific interactions with an organic cross-linker (PMDETA). The results showed that the organization behavior of this linear macromolecule can be regulated by the choice of pendant groups in the repeat units. In addition to the use of monomers having different pendants, block-wise construction could be another way to achieve a structural versatility of this kind of polymers. Therefore, our designed architecture could provide a model system to study the 3-D organization of linear polymers through noncovalent cross-linking and to investigate the effect of the chain structure on supramolecular organizations. With the thermal reversibility and the size control, in addition to the narrow size distribution, these noncovalently cross-linked globular supramolecular objects are expected to find their use as reaction supports for syntheses, templates for the growth or self-assembly of other organic or inorganic materials, carriers for the delivery of guest molecules or ions, colloidal materials for the optical devices, biotechnological materials, and more.

Experimental Section

Materials. Polymers **1** and **2** were synthesized according to the previously reported method using nitroxide-mediated living free radical polymerization.[8] Polymer **1** was synthesized from the styrene-based monomer having a *tert*-butyl ester group and an alkyl (n-$C_{10}H_{21}$−) group with ether linkages at each meta position relative to the olefinic group, followed by the hydrolysis of the *tert*-butyl ester group. The number-average molecular weight (M_n) of **1** determined by size exclusion chromatography (SEC), performed before the hydrolysis of *tert*-butyl ester group, was 15.6 kDa (PDI = 1.08, DP = 47). Polymer **2** (M_n = 13.0 kDa, PDI = 1.14, DP = 72) which has hydrogen as a neutral pendant, instead of the alkyl group, was also similarly prepared using the styrene-based monomer having a *tert*-butyl ester group with an ether linkage at one meta position relative to the olefinic group. Diethylenetriamine (Aldrich) and *N*,*N*,*N*′,*N*′*N*″-pentamethyldiethylenetriamine (Aldrich) were used as received. *N*,*N*-Dimethylformamide (Aldrich, 99.8%, anhydrous) was used without further purification.

General Measurement. ^{1}H NMR spectra were recorded on a Bruker Fourier transform AVANCE 400 (400 MHz for ^{1}H) spectrometer in *N*,*N*-dimethylformamide-d_7 using residual proton resonance of the solvent as internal standard. Infrared spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with an ATR accessory. Size exclusion chromatography (SEC) traces were obtained with a RI detector using tetrahydrofuran as an eluent. Number (M_n) and weight (M_w) average molecular weights were calculated on the basis of polystyrene standards. Dynamic light scattering (DLS) experiments were performed on an ALV/SP-125 compact goniometer system with an ALV-5000/E multiple tau digital correlator and an argon laser (λ = 514 nm). Transmission electron microscopy (TEM) measurements were performed using a JEOL 100CX operated at 100 keV without staining. Scanning force microscopy (SFM) measurements were performed using a Dimension 3000 of Digital Instruments Inc. in tapping mode. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Physical Electronics Quantum 2000 XPS spectrophotometer using a monochromatic Al Kα source. The XPS survey spectra were recorded at the pass energy of 117.40 eV, while the C 1s core-level spectra were recorded at the pass energy of 46.95 eV. Wide-angle and small-angle X-ray scattering studies were performed using an instrument from the Molecular Metrology Inc., equipped with a focusing multilayer monochromator (Osmic MaxFlux) with λ = 0.154 nm. The beam was collimated with three pinholes. For the small angle detection, a 2-D multiwire detector (sample-to-detector distance of 1.5 m) was used. To record the wide angle profiles, an image plate with a hole in the center was inserted into the beam path. For the wide-angle studies, the scattering peak of Kapton at $q = 4\pi \sin\theta/\lambda = 4.1$ nm^{-1} was used as an internal standard and a $CaCO_3$ standard (d_{111} = 0.3035 nm) was used for angular calibration. Silver behenate (d_{001} = 5.838 nm) was used for angular calibration of the SAXS measurements.[11]

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