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Enhancing Gelation Ability of a Dendritic Gelator through Complexation with a Polyelectrolyte

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Abstract: A poly(urethane amide) (PUA) dendron with long alkyl chains on its periphery was synthesized and then attached to the backbone of a polyelectrolyte, in which each unit contained a positive charge, by ionizing the carboxyl groups on the apexes of the dendrons to form a dendronized polymer. We found that both the PUA dendron and the dendronized polymer could form organogels in toluene. Interestingly, both the minimum gelation concentration and the gelation time of the dendronized polymer gelator were greatly reduced compared with the dendron alone. Our investigations showed that in the gel phase the intermolecular hydrogen bonding between adjacent dendrons creates similar supramolecular structures in both the dendron and the dendronized polymer gelator, which immobilize solvent molecules by means of interactions between dendrons and solvent molecules. Further studies on the gelation kinetics indicated that the polyelectrolyte backbone plays an important role in prearranging the attached dendritic gelators orderly and quickly into the supramolecular structures through a nucleation–elongation mechanism. Therefore, the gel-forming ability of the dendritic PUA gelator is enhanced by being complexed with the polyelectrolyte. In this work, this positive macromolecular effect is discussed in detail.

Keywords: dendrimers · gels · polyelectrolytes · polymers · self-assembly

Introduction

Gels, which possess both the appearance of liquid and the property of a solid,[1] are well known and gelatinous products have been widely used as an important class of soft materials.[2] Depending on their molecular mass, there are low-molecular mass (LMM)[3] and polymer[4] gelators that form gel-phase materials in different ways. The polymer-based gels, particularly those prepared from natural macromolecules, in organic or aqueous media were the first system that was intensively investigated.[4,5] In gel phases, polymer chains, in which repeating units are connected together with covalent bonds, play a key role in creating a three-dimensional (3D) network through chemical (covalent) or physical (noncovalent) cross-linking to immobilize the solvent phase.[4] The comprehensive studies on polymer gelators and their gels have demonstrated that these gel-phase materials have many advantages in practical applications, and as a result, many commercial products are available that utilize them.

In recent years, LMM gelators have received considerable attention because their gelation in organic or aqueous media is an ordering process of molecular self-assembly, which usually forms supramolecular aggregates of fibers, strands, or tapes.[3,6,7] Therefore, both organogels and hydrogels of LMM gelators are supramolecular, meaning that LMM gelators are connected through noncovalent bonds so their gels contain primary, secondary, and tertiary structures varying in a wide range from the angstrom to the millimeter scale. Most previous studies mainly dealt with the complex relationship between the molecular structure of LMM gelators and the nature of their molecular assemblies.[3,6,7] In recent years, the gelation mechanism and kinetics of LMM gelators have also been studied intensively to understand their ability in forming stable gels.[8] One of the main forces driving the further discovery and exploration of LMM gelators is their potential applications in several fields[3a] among which biological ones are the most promising because the

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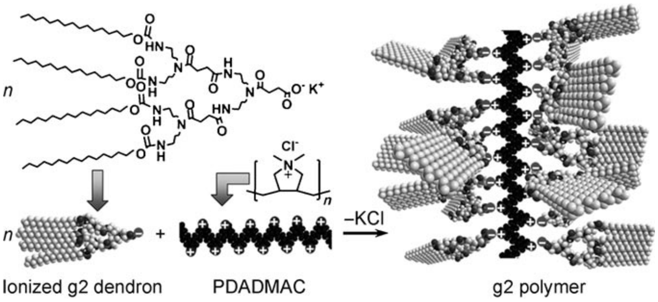
gel-phase materials in which gelators are held together by noncovalent forces may be easily biodegraded.[9]

Dendrimers[10] and dendronized polymers[11] are special molecules or macromolecules having well-defined architectures and diverse functionalization. They have demonstrated an extraordinary ability in self-assembling into spherical or cylindrical supramolecular objects.[12–14] In recent years, it has been found that some dendrons,[15] dendrimers or bolaform dendrimers,[16–18] dendronized polymers,[19] and diblock codendrimers[20] are good candidates for constructing gel-phase materials in organic or aqueous media. It is worth detailing some important achievements in this field. Aida and co-workers[15a,f] reported the first work describing the dendritic physical gel of dipeptide-core poly(benzyl ether) dendrimers in organic solvents through hierarchical self-organization. Kim and co-workers performed systematical studies on the supramolecular assemblies in organogels of amide dendrons,[15c] as well as their dimers,[15c] dendrimers,[16e] and dendronized polymers,[19b] and found that the supramolecular structures range from lamella to columnar hexagonal arrays with increasing dendron generation. Other systematical investigations, carried out by Smith and co-workers,[17,18] on one- and two-component dendritic gels from lysine-based peptide dendrimers in organic media demonstrated that the intermolecular and/or intramolecular hydrogen bonds among amide groups play an important role in the gel-phase assembly. Jia and co-workers reported their studies on the organogels of a series of natural amino acid based dendritic gelators[15g] and extended their interest in functionality to the functional groups at the focal point.[15i] In our previous work we explored the gelation ability of a series of amphiphilic diblock codendrimers consisting of poly(urethane amide) (PUA) and poly(methallyl dichloride) (PMDC) dendrons to understand the effects of high polarity and multiple molecular interactions on self-assembled ribbonlike aggregates.[20] From these studies we found that for such gelators, precisely controlling the three-dimensional molecular architecture by adjusting the generation and explicitly manipulating multiple molecular interactions by placing functional groups at the focal point, on branched units, and at the periphery of the dendrons can enable the assembly ability at the molecular level and then the gelation ability at the macroscopic level to be tuned.[15–20] Evidently, this is an ideal system for gaining a better understanding of the relationship between the molecular structure and the assembly.

It is believed that the supramolecular aggregation of LMM gelators may occur through a nucleation-growth or spinodal decomposition process.[21] However, investigation of their gelation kinetics, particularly at a molecular level, has been relatively limited.[8] Consequently, it is hard to correctly evaluate the gelation ability of most LMM gelators. From the viewpoint of practical applications, a good gelator should meet, at least, the following two criteria: they can gel 1) at a minimum gelation concentration (c_{mgc}) as low as possible and 2) in a gelation time (t_g) as short as possible. In this article, we report a conceptual work for promoting gelation of a dendritic gelator through complexing the gelator molecules with a polyelectrolyte. We synthesized a second-generation PUA dendron (denoted as "g2 dendron" hereafter) that contains a carboxyl group at its apex and can gel alone in organic solvents, by following the procedure of Kim et al.[15c,22] Then, the apex-ionized g2 dendrons were attached to the backbone of poly(diallyldimethylammonium chloride) (PDADMAC), which is a kind of linear polyelectrolyte,[23] to obtain a complex of the polyelectrolyte and the dendritic surfactants (denoted as "g2 polymer" hereafter) by means of an ionic interaction, as shown in Scheme 1. Surprisingly, the g2-polymer gelator gelled at a lower minimum concentration and in a shorter time than that of the g2-dendron gelator alone in toluene, that is, the gelation rate of the dendritic gelator is greatly accelerated after complexation with PDADMAC. More intriguing is that the multiple hydrogen bonding, existing in-between the g2 dendrons, may be the force driving the assembly of similar supramolecular structures that immobilize solvent molecules by means of interactions between gelators and solvent molecules. These cause gelation of both the gelators in toluene. A further investigation at the microscopic level of the gelation kinetics shows that the PDADMAC backbone can effectively accelerate the self-assembly of the dendritic gelator to form ordered supramolecular structures during gelation. Herein, we discuss this positive macromolecular effect on the formation of the supramolecular gels.



Scheme 1. Schematic drawing showing the preparation of the g2 polymer by complexation of the g2 dendrons with PDADMAC.

Results and Discussion

Formation of the dendronized polymer complex: Complexation of surfactants with polyelectrolyte is an efficient way to prepare new functional materials.[24] Recently, this method has been utilized to prepare dendronized polymers by using dendritic surfactants.[25] During our preparation of the dendronized polymers the appearance of a precipitate in aqueous media is evidence of the formation of the g2-polymer complex owing to neutralization of the positive and negative charges. To further prove the combination of the g2 dendron with PDADMAC by means of ionic interactions, we performed ^1H and ^{13}C NMR spectroscopy experiments on both the g2-dendron and g2-polymer samples. Figure 1 shows the ^{1}H NMR spectra of the two samples in $CDCl_3$ obtained over a measuring time of 12 h. The signal at $\delta=12$ ppm for the g2-dendron sample is contributed by the hydrogen atom of the carboxyl group at the apex of the dendron. The disappearance of this signal in the spectrum of the g2-polymer sample proves that all of the g2 dendrons have been linked to PDADMAC by ionic bonds. The shift of the peak from $\delta=2.64$ to 2.55 ppm, associated with the hydrogen atoms in the CH_2 groups next to the carboxyl group, also shows the combination of the dendrons with the linear polymer by ionic interactions. It is worth noting that most signals of the PDADMAC backbone do not appear in the spectrum of the dendronized polymer. The possible reason for this is that the mobility of the PDADMAC backbone, which is wrapped up by the dendritic molecules, is low in $CDCl_3$ so that the signals related to the backbone are shielded.

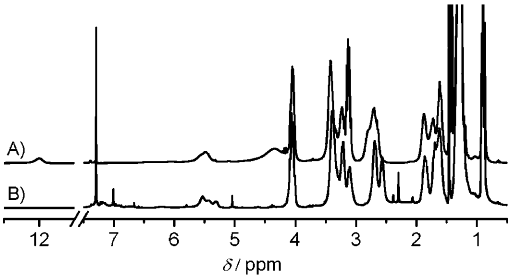


Figure 1. ^{1}H NMR spectra of the g2 dendron (A) and the g2 polymer (B) recorded over 12 h in $CDCl_3$.

Figure 2 shows the ^{13}C NMR spectra of the two samples. The major change of the signals appears in the range from $\delta=172$ to 174 ppm due to the change of the environment of the carboxyl groups. As shown in the left-hand side of the figure, the signal peaks at $\delta=172.35$, 172.47, 172.60, and 172.79 ppm for the g2 dendron shifted to $\delta=172.50$, 172.66, 172.92, and 173.52 ppm for the g2-polymer complex. This is because of the change of the chemical environment of the carboxyl group, especially for the focal carbon atom, which undergoes the greatest shift. These results also prove that the dendritic molecules were indeed connected to the polyelectrolyte backbone rather than being a simple mixture of the two compounds.

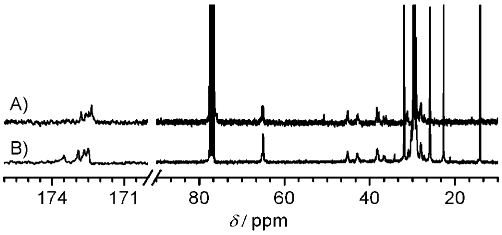


Figure 2. ^{13}C NMR spectra of the g2 dendron (A) and the g2 polymer (B) in $CDCl_3$.

Macroscopic observation of the gelation process: The transparent gels in toluene can be prepared by rapidly cooling the solution from 70 to 18 °C. The gelation was thermally reversible. The enhancement of the gelation ability of the dendritic gelators through forming the dendronized polymer complex was evaluated by comparing the changes of the minimum gel concentration (c_{mgc}) and the gelation time (t_g) between the two gelators. By using the "inverting-bottle method" we ascertained that c_{mgc} is about 1.5 mg mL^{-1} for the g2 dendron and about 0.5 mg mL^{-1} for the g2 polymer in toluene at 18 °C.[26] Clearly, c_{mgc} decreased to one third after forming the dendronized polymer complex. The gelation time of the two gelators was determined by using the same method. Because the difference of t_g between the two samples is too large at the same concentration near c_{mgc}, the comparison experiments were performed at different concentrations, that is, 5.0 mg mL^{-1} for the g2 dendron and 0.5 mg mL^{-1} for the g2 polymer.[27] Figure 3 shows the resulting gels obtained under identical conditions except for concentration. The solution of the g2 polymer in toluene (0.5 mg mL^{-1}) needed only 10 h to form an immobile gel,

Figure 3. Photos of the gels after the bottles have been inverted. In each photo the g2-dendron sample is on the right and the g2-polymer sample is on the left. The following gelation times were recorded from directly after the solutions had been cooled from 70 °C: A) 4, B) 10, C) 28, and D) 52 h.

whereas the solution of the g2 dendron in toluene (5.0 mg mL^{-1}) required about 52 h. The decrease of both the minimum gel concentration and gelation time of the g2-polymer gelator compared to the g2 dendron reveals that the dendronized polymer is a stronger gelator than the parent dendritic molecules.

Gelation kinetics microscopically tracked by ^{1}H NMR spectroscopy: Scattering and rheological methods have been widely used for tracking gelation kinetics because they can detect the formation of nanostructured aggregates or their three-dimensional aggregate network.[3b,4b,8c] To further investigate the transition kinetics of both the gelators from the sol phase to the gel phase, we carried out time-dependent ^{1}H NMR spectroscopy experiments to track the gelation process at the molecular level. To obtain a suitable gelation speed for the gelators, the initial concentration of the gelators was different: 10.0 mg mL^{-1} for the g2 dendron and 0.5 mg mL^{-1} for the g2 polymer.

Figure 4 shows the ^{1}H NMR spectra of a solution of the g2 polymer in [D$_8$]toluene obtained at different times after being cooled down from 70 to 18 °C. With increasing time the strength of all the signals that are associated with the groups in the g2-dendron segments clearly decreases and the peak positions shift to a higher field because of the mobility loss of the molecules or the groups in the gel phase. So, this characteristic was used to track the gelation process at the molecular level.

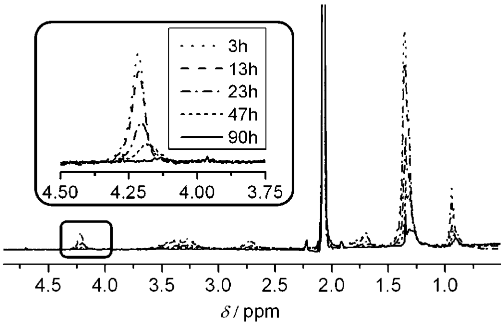


Figure 4. ^{1}H NMR spectra of the g2 polymer in [D$_8$]toluene taken with a time range from 3 to 90 h.

To track the gelation process we chose the peak in the ^{1}H NMR spectra at around $\delta = 4.2$ ppm, which corresponds to the hydrogen atom in a CH$_2$ group nearest the urethane-amide groups, so its change can promptly reflect the gelation progress driven by the hydrogen bonds between urethane-amide groups (see the next subsection). As clearly shown in the inset in Figure 4, the area under the peak decreased with increasing time. The quantitative descriptions of the gelation are illustrated in Figure 5 in which the normalized areas, $A_N(t) = (A(t) - A(\infty))/(A(0) - A(\infty))$, in which $A(0)$, $A(t)$, and $A(\infty)$ are the peak areas at a gelation time (t) of 0, t, and ∞, respectively, are plotted against t. Interestingly, the two gelators present totally different time dependences of the normalized areas. For the solution of g2 dendron in toluene with a concentration of 10.0 mg mL^{-1}, $A_N(t)$ linearly decreases with time (see the solid line in Figure 5A), which reflects a linear growth of the gelator molecules in constructing the assemblies in the system. For the solution of g2 polymer in toluene with a concentration of 0.5 mg mL^{-1}, the experimental data were fit using the sigmoidal function (see the solid curve in Figure 5B), which reflects a sharp transition from nonaggregation to aggregation of the gelator molecules after a lag time (t_c) of approximately 10 h. In this work, we define a time, $t_{1/2}$, at which $A_N(t) = 0.5$, to evaluate the gelation ability of the two gelators. Obviously, $t_{1/2} = 12.7$ h for the g2 polymer is shorter than $t_{1/2} = 38.6$ h for the g2 dendron although the concentration of the g2 polymer is much lower than that of the g2 dendron. This further indicates a higher gel-forming speed of the g2 polymer even at lower concentration. These dissimilarities should present differing mechanisms controlling their gelation.

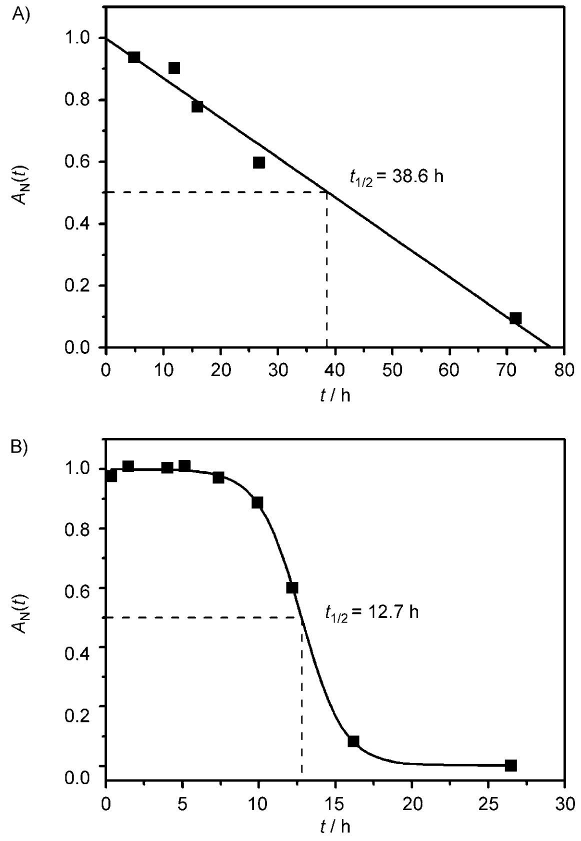


Figure 5. Plots of $A_N(t)$ versus t of A) the g2 dendron (10.0 mg mL^{-1}) and B) the g2 polymer (0.5 mg mL^{-1}).

Hydrogen bonding and hydrophobic interactions: We have recorded FTIR spectra to evaluate the hydrogen-bond interactions and hydrophobic interactions between the gelator molecules, which should be the main driving forces for gelation. Figure 6 shows four spectra of the two gelators in sol and gel phases. For the solution of the g2 dendron, we found that the peaks shift from 1722 (C=O stretching), 1526

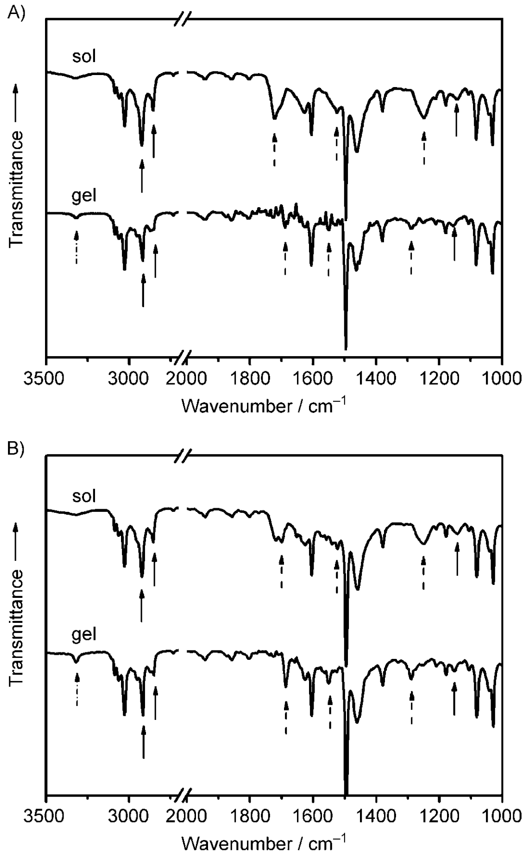


Figure 6. FTIR spectra of the g2 dendron (A) and the g2 polymer (B) in toluene in the sol or gel phase. The arrows point out the signals related to the hydrogen bonds and hydrophobic interactions.

(N–H bending), and 1248 cm^{-1} (C–N stretching) to 1688, 1550, and 1288 cm^{-1}, respectively, while the solution formed the gel. This indicates that the amides and urethanes form intermolecular hydrogen bonds with *trans* orientation during the gelation process.[15a,c,28] The signals at 2925, 2858, and 1143 cm^{-1} in solution and 2919, 2581, and 1156 cm^{-1} in the gel are contributed by the C–H stretching and rocking bands of the alkyl chains. Their shift to a lower wavenumber range after gelation is due to the denser packing of the alkyl chains in the gel. The IR spectra of the g2 polymer are very similar to those of the g2 dendron.[15c] Similarly, after gelation the C=O stretching, N–H bending, and C–N stretching bands shifted from 1701, 1526, and 1251 cm^{-1} to 1688, 1550, and 1291 cm^{-1}, respectively, and the C–H stretching and rocking bands of the alkyl chains shifted from 2925, 2858, and 1143 cm^{-1} to 2919, 2848, and 1153 cm^{-1}, respectively.

The similarity of the IR signals of the g2-dendron and g2-polymer samples in solution as well as in the gel phase is evidence that at the molecular level, the gelation driving forces of both are the same, that is, the intermolecular hydrogen bonds between the amides and urethanes, and the hydrophobic interactions between the alkyl groups and solvent molecules.

Aggregates in the gel phase: The supramolecular aggregates formed in the gel phase were further investigated by using AFM, SEM, and TEM methods. Figure 7 shows the AFM height (A) and phase (B) images, section profiles (C), and 3D image (D) of the aggregates. The assemblies are one dimensional. Arrows "a" point out several heads of the growing and primary aggregates. The surface profile clearly shows that the aggregate width is in the range of 60–140 nm and the height is about 19 nm on average. This means that the primary aggregates are ribbons. The 3D and phase images also clearly present a couple of primary ribbons

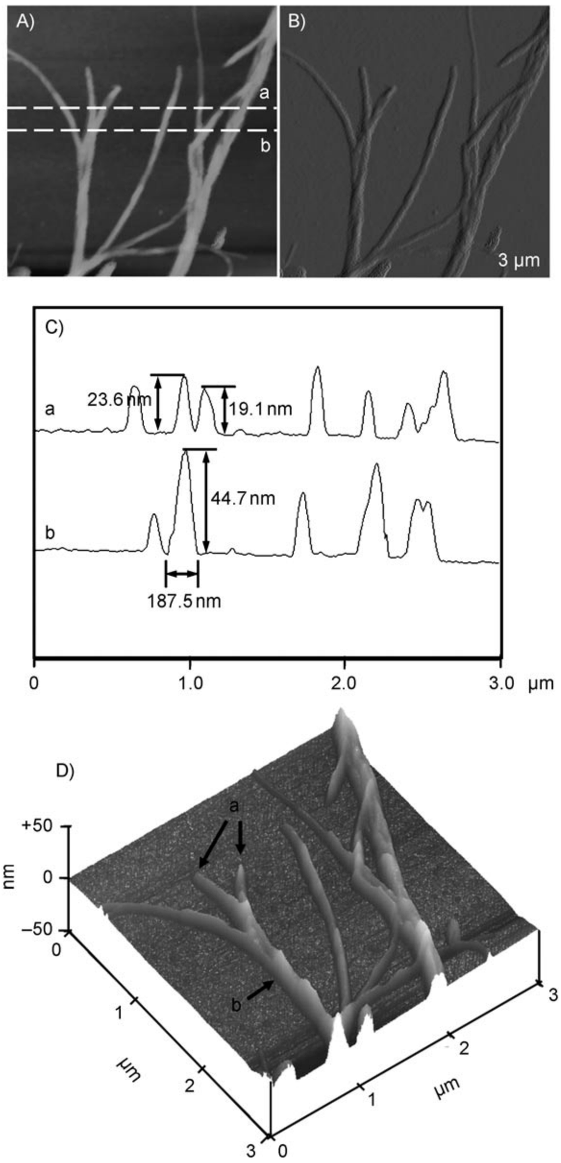


Figure 7. AFM characterization of ribbons of a g2-polymer gel. 3 μm × 3 μm AFM height (A) and phase (B) images. C) Surface profiles of the ribbons. D) A 3D-height image. In this image, arrows labeled "a" point out the growing and primary ribbons, and arrow "b" points out a typical braided ribbon.

braiding to form the intertwining ribbons, as pointed out by arrow "b". They should be the physical cross-linkages.

Figure 8 shows the SEM and TEM images obtained from the samples dried from the gel phases of the two gelators in toluene. These images show long, braided, and hyperbranched aggregates, the typical features of supramolecular structures that had been found frequently in gels of most LMM gelators.[3,6,8] Figure 9 shows an enlarged TEM image obtained by analyzing the gel phase of the g2 polymer. Arrows point out some branching points from which the wide and intertwining ribbons split or unbraid into two narrow and primary ribbons heading in different directions. The ribbon length between two splitting points changed from a couple of hundred nanometers to a few micrometers. The significance of these structural features is to indicate the formation of a three-dimensional ribbon network: The primary ribbons braid to form the braided ribbons (the physical cross-linking points) and then the braided ribbons unbraid to form the primary ribbons in-between two adjacent braided points.

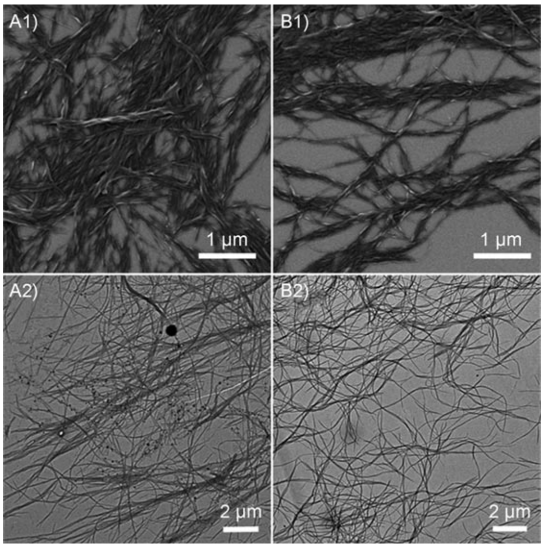


Figure 8. SEM (A1) and TEM (A2) images of the aggregates obtained from a dried sample of a g2-dendron gel at 5.0 g L^{-1} in toluene. SEM (B1) and TEM (B2) images of the aggregates obtained from a dried sample of a g2-polymer gel at 0.5 g L^{-1} in toluene.

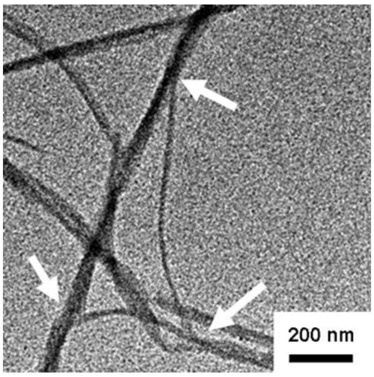


Figure 9. TEM image showing the three-dimensional network of the ribbons. Arrows point out the intertwining points of primary ribbons.

These results show that the supramolecular structures of the g2-dendron and g2-polymer gelators in gels are very similar. More precisely, the way that the g2-polymer gelators construct the supramolecular structures is similar to that used by most LMM gelators, but different from most conventional polymer-based physical gelators.[3] In addition, these finer supramolecular structures found in our observations are good evidence to indicate why our gels are transparent.

The basic structure of the ribbons: To investigate the fine structure within the individual ribbons, the molecular dimensions of the g2 dendron and the PDADMAC backbone were established. The calculated length and width of the g2 dendron are 4.09 and 1.67 nm, respectively, and the width of the PDADMAC backbone is 0.67 nm (see Figure S3 in Supporting Information). Small-angle X-ray scattering (SAXS) detections were also performed on dried samples of the gels. Figure 10 shows Iq^2 versus q plots (I = scattering intensity,

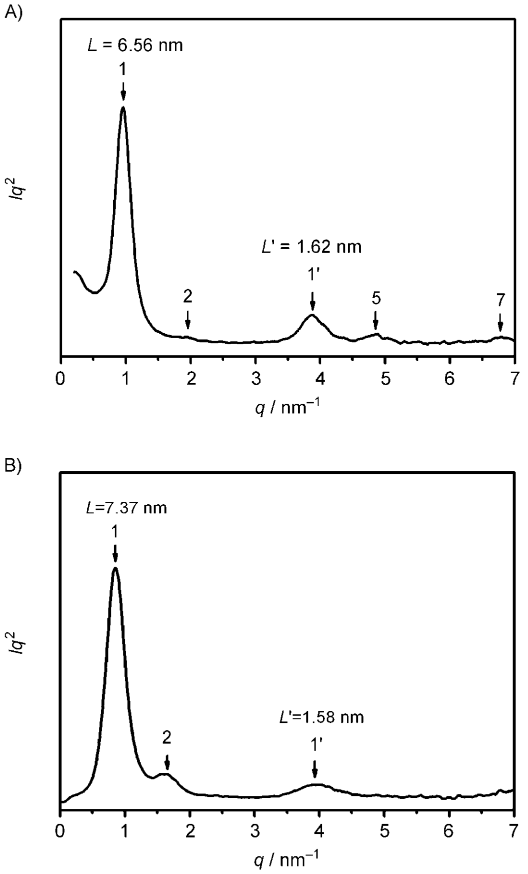


Figure 10. SAXS results of dried gel samples of the g2 dendron (A) and g2-polymer (B). The numbers 1, 2, 5 and 7 show the first, second, fifth and seventh scattering peaks of the layers within the aggregates; 1′ shows the scattering peak corresponding to the width of g2 dendron.

q = scattering wave vector) of the two gelators. Both plots show integer ratios (1, 2, 5 and 7) of the long period of the first peak with the long period of other peaks, which implies that a layered structure exists in the aggregates. The long period of the layer is 6.56 nm for the g2 dendron and 7.37 nm for the g2 polymer, thus suggesting that the primary ribbons in both the gels are constructed by a couple of layers with the thicknesses of $L = 6.56$ nm for the g2 dendron and $L = 7.37$ nm for the g2 polymer. Because the thickness of the primary ribbons is less than 20 nm, as shown in Figure 7, we can conclude that the ribbons only contain two or three layers. This is also the reason that the scattering peaks in Figure 10 are relatively wider according to the Scherrer formula.[29] The layer thickness of the g2-dendron ribbon ($L = 6.56$ nm) is smaller than the double molecular length of about 8.18 nm (see Figure S3 in Supporting Information). Therefore, for the g2-dendron gelator the most reasonable arrangement of the dendritic molecules in the layer is that the g2 dendrons are tightly linked by a hydrogen-bond interaction between the carboxyl groups with an angle of about 36° from the horizontal, as shown by the schematic drawing in Figure 11A. For the g2-polymer gelator the dendritic molecules have a similar arrangement, as shown in Figure 11B. The layer thickness of the g2 polymer is 0.81 nm larger than that of the g2 dendron. This value is close to the sum of the width of the PDADMAC backbone (0.67 nm) plus two ionic bonds between the dendrons and backbone. This increase in the layer width comes from the contribution of the PDADMAC backbone. We can conclude again that the polyelectrolyte backbones insert in-between the two layers of the g2 dendrons.

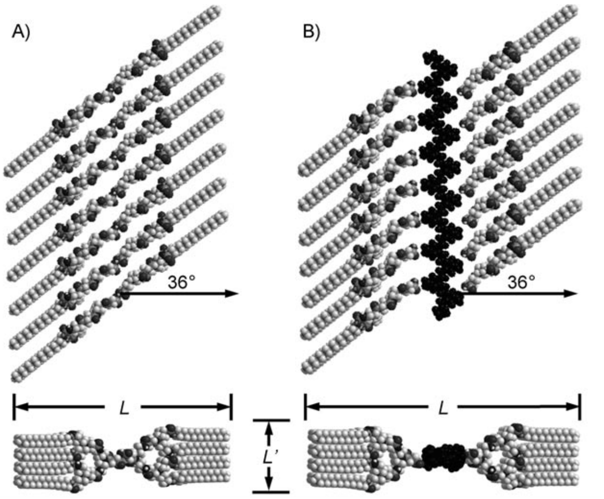


Figure 11. Schematic molecular arrangement of the g2 dendron (A) and the g2 polymer (B) in the layer.

In Figure 10 it is notable that in both plots we can find a middle-strong scattering signal. The d spacing (L') is 1.62 nm for the g2 dendron and 1.58 nm for the g2 polymer. This value corresponds to the width of the g2 dendron as shown in Figure S3 in Supporting Information. Therefore, we can ascribe this scattering to the layer thickness.

Mechanism of enhancing gelation ability by complexation: So far, our observations have illustrated that gelation of this dendritic gelator was greatly improved through forming a complex with PDADMAC. But it is very intriguing to see that for both the g2-dendron and g2-polymer gelators the intermolecular hydrogen bonding results in ribbonlike supramolecular structures in the gel phase. This similarity clearly reveals that it is the two amide groups, four urethane groups, and four long alkyl groups in the g2 dendrons that are the creators of the gel phase in toluene. The question is why gelation of the dendritic gelator can be accelerated after being complexed with PDADMAC.

As noted in the introduction, it is well known that the gel-phase formation of LMM gelators are normally divided into three steps.[6,7] In the primary step the gelators orderly arrange by means of molecular recognition to form aggregates that can grow in an anisotropic manner (the secondary step). In the final step, the long aggregates entangle into a three-dimensional network in which the solvent molecules can be trapped. Our observation shows that the g2-dendron gelator strictly follows these steps to form the gel phase. The hydrogen bonds between carbonyl groups at the focal points bring the two g2-dendron gelators together to form a unit. Another six hydrogen bonds between amides or urethanes on the PUA dendron body bring the individual units together to join the growing front of the ribbonlike aggregates, so they grow mainly in one direction, as schematically shown in Figure 12A. Key to this model is that the g2-dendron gelators recognize each other through hydrogen bonding so that they can join the ribbons in a one-by-one manner. In this case, the ribbon formation may be an isodesmic assembly.[30] Therefore, this model can rationally explain the linear consumption of the gelators, as found in Figure 5B.

The gelation of this dendronized polymer gelator is schematically represented in Figure 12B. For the g2-polymer gelator, the g2-dendron molecules have been tightly linked to the PDADMAC backbone by means of ionic interactions, so the PUA gelators can recognize each other more easily and quickly. It is rational to assume that the PDADMAC backbone could help the dendritic and side-group gelators easily arrange in order, at least partly, along the backbone to form a preordered macromolecule with a pseudo-one-dimensional structure. The driving force is the multiple hydrogen bonds forming in-between adjacent PUA gelator molecules. It is rational to assume that the solubility of the preordered macromolecules decreases. Therefore, they may join the growing front of the ribbonlike aggregates in an accelerating manner. Thus, this will cause a rapid growth of the aggregates, or a rapid gelation of the g2-polymer gelators. Consequently, the gelation time is shortened. Meanwhile, it has been reported that the PDADMAC backbone is relatively stiff.[31] We can rationally assume that the g2-polymer ribbons would be stiffer than the g2-dendron ribbons. This su-

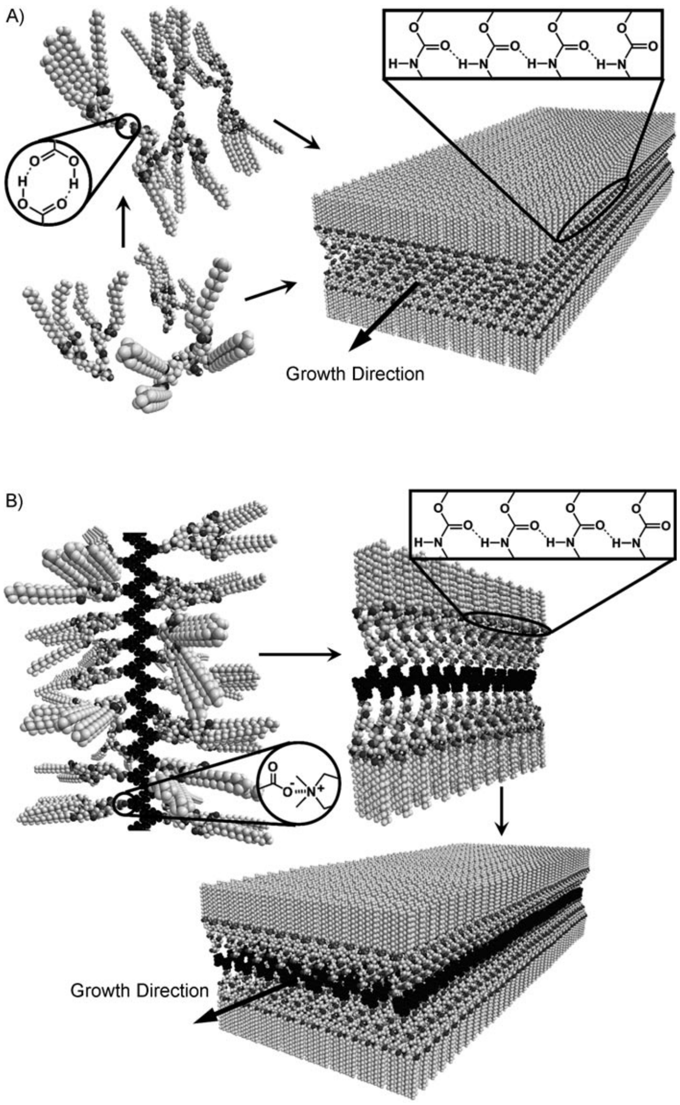


Figure 12. Suggested gelation processes of the g2 dendron (A) and g2 polymer (B).

periority in mechanical property further means that during the gelation of the g2 polymer fewer dendritic gelators are needed to construct ribbons that have a performance similar to those formed by g2-dendron gelators alone. For this reason, the minimum gel concentration could be reduced after forming the complex. Based on this suggested model it is possible to explain the gelation kinetics detected by NMR spectroscopy. In Figure 5B we can see that the changes of the normalized area with time are slow, fast, and slow again. The first slow change reflects the fact that all the PUA dendrons attached to the backbone seem to be in a state of free interaction in solution. The rapid change suggests groups rapidly lose their mobility because of a local rearrangement of side groups within the macromolecules. At this point the most preorganized macromolecules can rapidly join the ribbons. Further change becomes slow again. More interesting is that the ribbon growth is in a highly cooperative fashion caused by the PDADMAC backbone by means of a nucleation–elongation mechanism.[8g,h,30]

Macromolecular effect: It is well known that the ordering ability of macromolecules will normally decrease with increasing molecular weight because of increasing chain entanglements. One typical example is the crystallization ability of polymers in which the crystallization rate and crystallinity decrease with increasing molecular weight because of a reduction of the molecular mobility and increasing chain entanglements.[32] In the case of polymer-based gels the situation is complicated, and depends strongly on the gelation type. Normally, the minimum gel concentration and gelation speed of polymer physical gels decreases with increasing molecular weight because of the increase of chain entanglement.[4b] In this study we found a decrease in the minimum gel concentration but an increase in the gelation speed of the dendritic gelator after forming the dendronized polymer by complexation with PDADMAC. This is a positive macromolecular effect. The possible reason for this behavior is that the gelation mechanism of the dendronized polymer is different from common polymer physical gels.[4] In the dendronized polymer gelator, the real gel creators are still the PUA dendrons, not the PDADMAC backbone. As discussed in the previous subsection, the main roles played by the PDADMAC backbone are to assist the dendritic molecules to cooperatively assemble into a preordered layer structure easily and quickly, so the gelation rate is increased and, meanwhile, to reinforce the supramolecular aggregates, so the minimum gel concentration is decreased.

Conclusion

We synthesized a second-generation (g2) PUA-dendritic gelator and facilely complexed it with a linear polyelectrolyte (PDADMAC) by means of ionic interactions to form a dendronized polymer. Both the dendron and the dendronized polymer were able to form gels in toluene. The hydrogen bonding between the dendritic molecules and the hydrophobic interactions between the dendritic and solvent molecules are the driving force behind the creation of similar three-dimensional networks of ribbon aggregates, which cause gelation. However, macro- and microscopic observations of the gelation process demonstrated that the gelation of the dendritic gelator is greatly accelerated after being complexed with the dendronized polymer. This is reflected by our experimental observations: The minimum gel concentration was decreased and the gelation time was reduced. Further investigation into the gelation kinetics presented different consumption processes of the dendritic molecules before and after attachment on the PDADMAC backbone. During gelation in the system of the dendritic gelator in toluene, the resultant linear consumption shows that the g2-dendron gelators recognize each other through hydrogen bonding, which enables them to join the ribbons in a one-by-one manner. This indicates a noncooperative, isodesmic assembly. In the dendronized polymer, however, the dendritic gelators have been attached to the linear polyelectrolyte backbone by means of ionic bonds, so they can easily recognize each other by an arrangement within the macromolecules to form preordered macromolecules with a pseudo-one-dimensional structure. These preordered macromolecules cause a rapid growth of the ribbons, thereby resulting in rapid gelation. This shows that the ribbon grows by a co-operative nucleation–elongation mechanism. Meanwhile, the rigid PDADMAC backbone can reinforce the supramolecular ribbons, so the minimum gel concentration is reduced. The accelerated gelation rate and the reduced minimum gel concentration reveal that the gelation ability of the dendritic gelators was efficiently enhanced after being attached to the PDADMAC backbone. This is a positive macromolecular effect in the ordering process of aggregate formation and growth. This concept provides a new strategy for the design of new and efficient macromolecule-assisting LMM gelators. Finally, we hope that a similar concept can be applied in constructing novel functional or ordered materials through complexation of other LMM functional species with polyelectrolytes.

Experimental Section

Materials: 1,1-Carbonyldiimidazole (97%), succinic anhydride (99%), and 3,3′-diaminodipropylamine (99%) were purchased from Acros. PDADMAC (20 wt% in water, typical $g\,mol^{-1}$ detected by light scattering as shown in Figure S2 in the Supporting Information) was purchased from Aldrich. Cetyl alcohol (98%), triethylamine (99%), and other reagents were purchased from major chemical suppliers and used without further purification unless otherwise noted.

Techniques of analysis: ^{1}H and ^{13}C NMR spectra were recorded in [D$_1$]chloroform and [D$_8$]toluene on a Varian Unity Plus-400 NMR spectrometer. Elemental analysis was performed on an Elemental Vario MICRO CURE instrument. The molecular mass of the g2 dendron was recorded on a mass spectrometer (ESI). Infrared spectra (IR) were recorded on a Bio-Rad FTS-135 FTIR spectrometer. Transmission electron microscopy (TEM) observations were performed using a transmission electron microscope (Philips EM420) operated under an acceleration voltage of 120 kV. The samples were prepared by a slight touch of the gels onto carbon-film-coated copper grids. Scanning electron microscopy (SEM) observations were carried out using a LEO 1530 Gemini instrument with an acceleration voltage of 0.5 kV and using the in-lens mode. Small-angle X-ray scattering experiments were performed on a Bruker AXS NANOSTAR using a monochromatic X-ray beam and a two-dimensional detector for recording the scattering intensity. The distance between the samples and the detector was 270 mm. The plots of intensity versus scattering wave vector (q), which is calculated from $q=4\pi/(\lambda \sin(\theta/2))$ in which θ is the scattering angle and $\lambda=1.54$ Å for the radiation beam, were produced by integrating the two-dimensional scattering patterns. A MultiModel atomic force microscope (Digital Instrumental Nanoscope IV) was used to visualize aggregates on a silicon wafer surface at room temperature. The samples were prepared by dropping a drop of the solution on a freshly cleaned silicon wafer surface. The solvent was removed in vacuo. All measurements were performed in tapping mode. The X-ray diffraction (XRD) patterns were measured by using a Rigaku D/Max-2500 X-ray diffractometer equipped with a $Cu_{K\alpha}$ radiation ($\lambda=0.154$ nm) source operated at 40 kV/100 mA. Light-scattering (LS) experiments were carried out on an ALV/DLS/SLS-SP 5022F compact goniometer with an ALV 5000E/E correlator and a He–Ne laser ($\lambda=632.8$ nm). The experiments were measured in the range from 40 to 140° with a step of 10°. All the LS measurements were carried out at (25 ± 0.1) °C.

Synthesis of the g2 dendron: The synthesis was carried out following a route reported in previous work.[15a,24] ^{1}H NMR (400 MHz $CDCl_3$) (see Figure S3 in the Supporting Information): $\delta=0.86$ (t, 12 H; CH_3), 1.24 (s, 104 H; $(CH_2)_{13}$), 1.58 (m, 8 H; CH_2CH_2OCO), 1.63–1.87 (m, 12 H; $CH_2CONHCH_2CH_2CH_2NCOCH_2$), 2.54–2.74 (m, 12 H; $NCOCH_2CH_2CO$), 3.03–3.45 (m, 24 H; $CONHCH_2CH_2CH_2NCO$), 3.98–4.06 (m, 8 H; CH_2CH_2OCO), 5.18–5.51 ppm (s, 6 H; NHCO); ESI-MS (see Figure S4 in the Supporting Information): m/z: calcd for $[M-H]^-$: 1729.41; found: 1729.11; elemental analysis calcd (%) for $C_{98}H_{187}N_9O_{15}$: C 67.98, H 10.89, N 7.28; found: C 67.98, H 10.84, N 7.20.

Synthesis of the g2 polymer complex: The g2-dendron powder (173 mg, 0.1 mmol) was added to an aqueous KOH solution (0.02 wt%, 70 mL) and sonicated at room temperature until no granules were visible. The white turbid latex was then stirred at room temperature overnight. PDADMAC (20 wt%, 80.5 mg, 0.1 mmol calculated by N^+ group) was diluted and added dropwise into the latex. The mixed solution became more opaque and the white precipitate became apparent. The white precipitate was filtrated and washed with water several times, and then dried under vacuum for a week.

Preparation of the gels: Gels of both g2 dendron and g2 polymer were prepared by following a facile method. The gelators were weighted in a clean transparent transform bottle, and a volume of redistilled toluene was added to reach the aimed concentration. Then the bottle was sealed with Teflon tape and the mixture was sonicated for 5 min and heated at 70 °C for 5 min to get a clear solution. Then the bottle was left standing at 18 °C until a gel formed.

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[26] Due to the kinetic features of gelation, the determination of the minimum gel concentration (c_{mgc}) highly depends on the gelation time. In our experiments we obtained $c_{\mathrm{mgc}} = 1.5\ \mathrm{mg\,mL^{-1}}$ for the g2 dendron at $t_{\mathrm{g}} \approx 168$ h (or about one week) and $c_{\mathrm{mgc}} = 0.5\ \mathrm{mg\,mL^{-1}}$ for the g2 polymer at $t_{\mathrm{g}} \approx 20$ h.

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