Supramolecular Chemistry

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Self-Healing Supramolecular Gels Formed by Crown Ether Based Host–Guest Interactions**

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Self-healing, an ability of biological or artificial systems to spontaneously repair their damage, is one of the most amazing properties of these materials.[1] Among the three kinds of conceptual self-healing systems, capsule-based healing systems, vascular healing systems, and intrinsic healing polymers,[2] the last one has attracted much more attention these days not only owing to the automatic and intrinsic healing nature of the polymers, but also for their relatively easy modification as well as wide applications.[3] However, it is not easy to get polymeric materials with such excellent properties, because covalent bonds in current materials are susceptible to damage but difficult to restore to their original state.

A milestone in the development of self-healing materials can be dated back to 2001 when White et al. reported the autonomic healing of polymer composites by embedding monomers as liquid healing agent in microcapsules to heal cracks by releasing monomer followed by polymerization after mechanical damage.[4] Later, Wudl and co-workers developed a thermally re-mendable polymeric material that can repeatedly mend or "re-mend" itself under mild conditions based on the cross-linking of a trifunctional maleimide and tetrafunctional furan owing to the efficient thermal reversibility of cross-linking by Diels–Alder reactions.[5] In 2008, Leibler and co-workers demonstrated a thermoreversible rubber that consisted of fatty acids and diethylene diamine functionalized with urea and that showed self-healing at room temperature by supramolecular self-assembly.[6] Aida and co-workers reported a moldable hydrogel with remarkable mechanical strength and self-healing properties by mixing clay and a dendritic molecular binder, thereby giving insights for futuristic technological applications.[7] Recently, Rowan et al. developed optically healable metallosupramolecular polymers that absorb ultraviolet light and convert it into heat to trigger the healing process.[8] Although much progress has been made on self-healing materials, it is still a challenge to construct a system that can show both stimuli-responsiveness and self-healing properties.

Owing to the rapid development of supramolecular chemistry and self-assembly, materials linked by noncovalent bonds (supramolecular materials) have exhibited responsiveness to external stimuli, while retaining stability and functionality similar to covalently bonded systems.[9] Supramolecular gels are the most promising materials in this field and have been widely used across material science (smart or adaptive materials, information-recording materials) to medicine (drug release carriers).[10]

Host–guest interactions have been widely used in the construction of supramolecular polymers and supramolecular gels, because the combination of multiple noncovalent interactions, such as hydrogen bonding, π–π stacking, charge transfer, and hydrophobic interactions between two complementary compounds makes them not only show good binding affinity, but also form complexes with fixed host–guest geometry and directionality.[11] Although much progress has been made in the preparation of cross-linked supramolecular gels based on host–guest interactions,[12] the study of their properties was mainly focused on their stimuli-responsiveness; self-healing supramolecular gels have been rarely reported.[13] Herein, we prepared two noncovalently cross-linked polymer gels by mixing a poly(methyl methacrylate) (PMMA) polymer with pendent dibenzo[24]crown-8 (DB24C8) groups and two bisammonium cross-linkers with different end-group sizes (Scheme 1) under different conditions. It was expected that supramolecular networks would form when the DB24C8 moieties were cross-linked by bisammonium salts,[14] thereby leading to the formation of supramolecular gels (Scheme 1). The polymer (**1**, $M_n =$ 9.5 kDa and polydispersity index (PDI) = 1.37) was prepared by copolymerization of methyl methacrylate and a DB24C8 derivative (**7**, Scheme S1 in the Supporting Information).[15] There were approximately 7.2 DB24C8 units per single polymer chain for **1** as calculated based on proton NMR spectra and gel-permeation chromatography (GPC) data. The two cross-linkers (**2** and **3**) are bisammonium salts linked by long flexible alkyl chains with two different end groups, phenyl and cyclohexyl. When 10.0 mM **1** and 36.0 mM **2** (1:1 molar ratio, DB24C8/dibenzylammonium salt (DBAS)) were mixed in chloroform/acetonitrile ($v/v = 1:1$), supramolecular gel **4** formed immediately. However, supramolecular gel **5** constructed from polymer **1** and cross-linker **3** (1:1 molar

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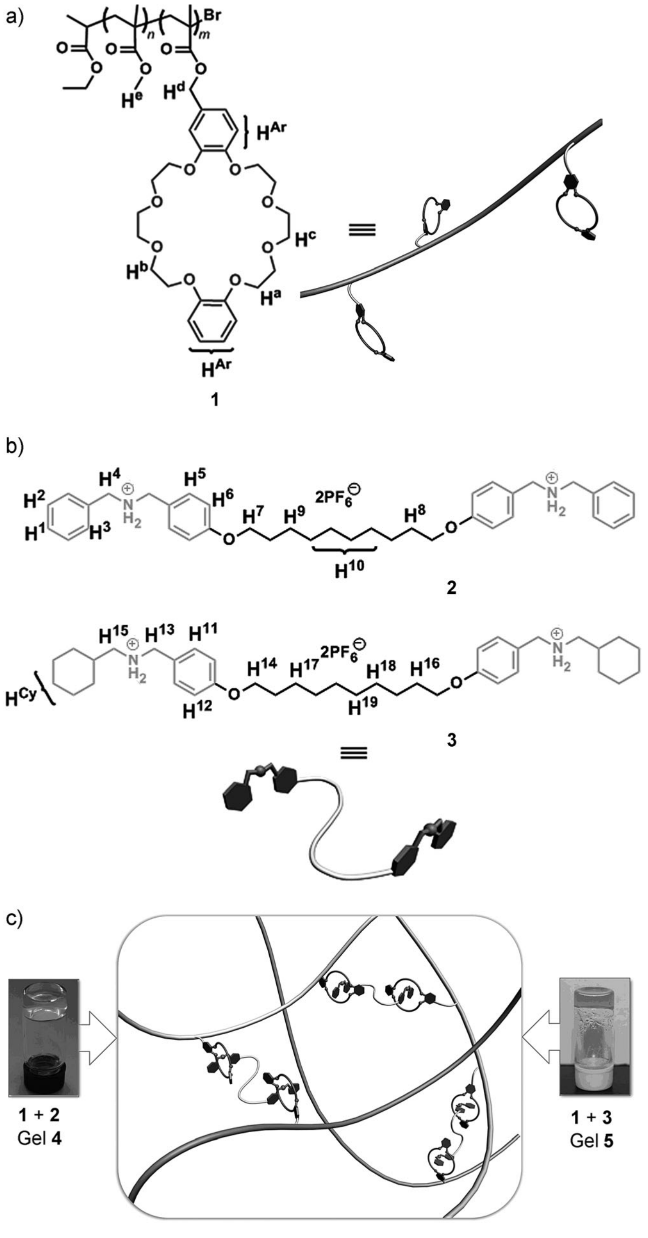

Scheme 1. Cartoon representations of a) polymer **1**, b) cross-linkers **2** and **3**, and c) supramolecular gels **4** and **5**.

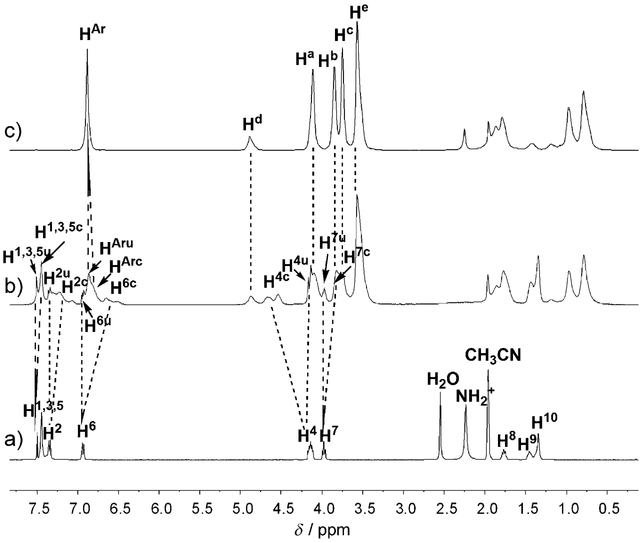

Figure 1. Partial ^{1}H NMR spectra (400 MHz, 1:1 $CDCl_3/CD_3CN$, 20 °C): a) cross-linker **2**; b) a mixture of cross-linker **2** (3.60 mM) and polymer **1** (1.00 mM); c) polymer **1**. Here "c" and "u" denote complexed and uncomplexed moieties, respectively.

ratio, DB24C8/ammonium ion) was prepared by heating for 30 days at reflux in chloroform/acetonitrile ($v/v = 1:1$) and stirring at room temperature for another 45 days,[16] because achieving equilibrium takes longer because of the larger size of the cyclohexyl unit.[17]

Proton NMR spectra gave important insights into the complexation behavior of polymer **1** with cross-linkers **2** and **3** in solution. Obvious changes in the chemical shift were observed by comparison of the ^{1}H NMR spectra of polymer **1**, cross-linker **2**, and their mixture (Figure 1). Because the complexation of DB24C8 and DBAS is a slow exchange system,[14a,18] the NMR spectra are complicated and each of the protons of DB24C8 and DBAS splits into two signals, corresponding to the complexed and uncomplexed species.[19] Upfield chemical shift changes were found for aromatic protons H^{1}, H^{2}, H^{3}, H^{5}, and H^{6} and benzyloxymethylene protons H^{7} of **2**, while the benzyl protons H^{4} shifted downfield after complexation, consistent with the well-known DB24C8/DBAS complexation systems.[14,18] This result indicated that the complexation of the DB24C8 units and DBAS moieties exists in the cross-linked supramolecular networks and leads to the formation of supramolecular gel **4** at high concentrations of polymer **1** and cross-linker **2**.

However, owing to the larger ring size of the cyclohexyl moiety relative to phenyl, DB24C8 would not complex the bisammonium salt with cyclohexane end groups **3** just by simple mixing.[17] Consistent with this expectation, no changes in chemical shift were observed by comparison of the ^{1}H NMR spectra of polymer **1**, cross-linker **3**, and their fresh mixtures even after excess **3** was added (Figure S1 in the Supporting Information). When polymer **1** (1.00 mM) and cross-linker **3** (3.60 mM) were heated at reflux, peaks corresponding to protons (H^{12}, H^{13}, and H^{15}) on complexed species became more and more obvious as time went on (Figure 2). Upfield shifts were observed for aromatic protons H^{12} while benzyl protons H^{13} and cyclohexylmethylene protons H^{15} shifted downfield, thus indicating the complexation of DB24C8 and bisammonium salts carrying cyclohexane end groups. Moreover, the solution of the mixture became more and more viscous, and gel **5** formed when the solution was evaporated to 10 % of its original volume.

Viscometry (Figure S2 in the Supporting Information) gave direct evidence of the existence of polymer networks in these two gels. Both the specific viscosities and reduced viscosities of the two gels are larger than those of polymer **1**. Notably the specific viscosities and reduced viscosities of gel **5** are much larger than those of gel **4**, thus indicating that the mechanical cross-linking in gel **5** was much more efficient than the noncovalent cross-linking in gel **4**.[20]

Rheological data were also collected to characterize gels **4** and **5** (Figure S3 in the Supporting Information). For gels **4**

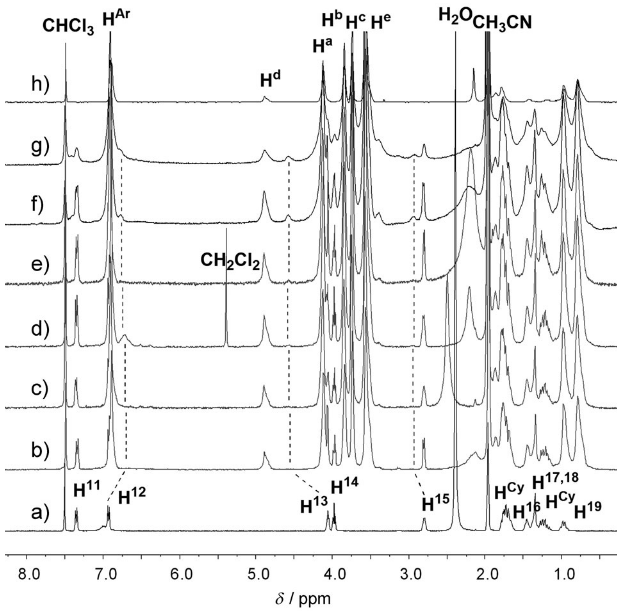

Figure 2. Partial ^{1}H NMR spectra (400 MHz, 1:1 CDCl$_3$/CD$_3$CN, 20 °C): a) cross-linker **3**; b–f) a mixture of cross-linker **3** (3.60 mM) and polymer **1** (1.00 mM) after being heated at reflux for b) 0, c) 3, d) 5, e) 15, and f) 30 days; g) (f) after further stirring at room temperature for another 45 days; h) polymer **1**.

and **5**, the storage modulus (G') is much larger than the loss modulus (G''), and the storage modulus G' is independent of the angular frequency ω, thus indicating the formation of organogels.[21] For a fresh mixture of **1** (10.0 mM) and **3** (36.0 mM) in chloroform/acetonitrile ($v/v = 1:1$), the moduli are very low (near the detection limit of the rheometer) and close to the moduli of the pure polymer **1** solution. The results here confirm that gel **5** only forms after a long time at high temperature.

To further investigate the formation of supramolecular gels and supramolecular networks, we considered the extent of cross-linking and calculated that the mean numbers of elastically active cross-linkers per chain (f^*) of gels **4** and **5** were 3.49 and 1.01, respectively.[22] From the data of f^*, it is inferred that 48.5 % and 14.0 % of the DB24C8 units are complexed to form elastically active cross-linkers in gels **4** and **5**, respectively. Therefore, we conclude that gel **4** involves a well-developed network structure, whereas gel **5** is a mixture of linear polymer, branched supramolecular polymer, and clusters of network structures.[15b,23]

Both **4** and **5** are stimuli-responsive supramolecular gels (Figure 3). Gel **4** experiences reversible gel–sol and sol–gel transitions by adding base (triethylamine, TEA) and acid (trifluoroacetic acid, TFA) because of the pH-controllable host–guest interaction between DB24C8 and DBAS (Figure S4 in the Supporting Information).[14d] However, gel **5** can be regarded as a degradable material, because it changed into a sol by adding TEA (Figure S5 in the Supporting Information) but was difficult to recover to its gel state by TFA addition, because once the mechanically interlocked structures (rotaxanes) in gel **5** were destroyed, rethreading could not be achieved in a short time.[17]

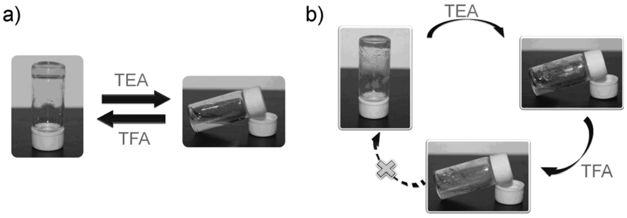

Figure 3. a) The reversible gel–sol transition of supramolecular gel **4** and b) the degradation of gel **5** upon adding TEA and TFA.

Then the self-healing properties of gels **4** and **5** were studied in detail. A sample of gel **4** was prepared by mixing polymer **1** with cross-linker **2** (1:1 CHCl$_3$/CH$_3$CN solution of 10.0 mM **1** and 36.0 mM **2**) by ultrasonication for one minute. A sample of gel **5** (10.0 mM, polymer concentration) was prepared by heating for 30 days at reflux in chloroform/acetonitrile ($v/v = 1:1$) and stirring at room temperature for another 45 days with a 1:1 molar ratio of DB24C8 units and secondary ammonium salt moieties.[16] It can be seen by eye that when the gels are broken, they heal themselves in a short time (Figure 4, Movies 1 and 2). The healing time was related to the size of the damage, the concentration, and the internal structures of the samples.

The self-healing properties of gels **4** and **5** were also confirmed by rheological data (Figure 5 and Figures S7 and S8 in the Supporting Information). Gel **4** recovers to 95 % of its original G' and G'' values in less than 30 s after damage (Figure S7 in the Supporting Information), while for gel **5**, its G' and G'' values could be fully recovered in less than ten seconds after damage (Figure S8b in the Supporting Information). In Figure 5, we show that G' and G'' of gel **5** are fully recovered in ten seconds even after 10000 % strain. The results here indicate that the self-healing of gel **5** is not caused by the threading of the secondary ammonium salt units of bisammonium cross-linker **3**; this threading has been demonstrated above to be very slow.[23]

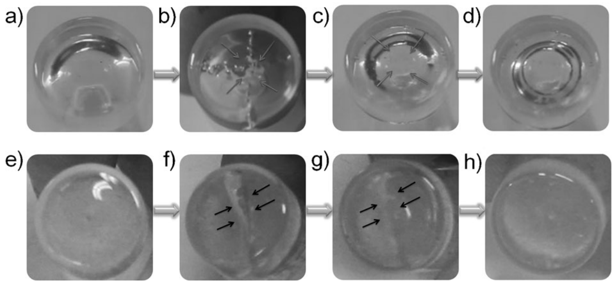

Figure 4. Photographs of a) supramolecular gel **4**, b) after damage, c) after free standing for 2 min, d) after free standing for 4 min and e) supramolecular gel **5**, f) after damage, g) after free standing for 10 min, h) after free standing for 20 min.

Although both gel **4** and gel **5** are self-healing materials, their self-healing mechanisms are quite different owing to their structural differences. For gel **4**, the self-healing properties are inferred to be caused by reversible host–guest

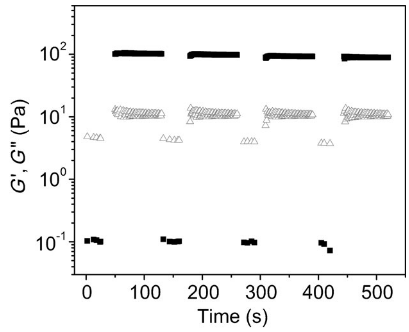

Figure 5. G' (■) and G'' (△) values of gel **5** in continuous step strain measurements. Gel **5** was subject to 10000% strain for 30 s, then back to 1% strain in the linear regime for 100 s, and this process was repeated four times. The scanning frequency was 10 rad/s.

interactions.[13] For gel **5**, it should be pointed out that even though only a few cross-links are formed by the addition of cross-linker **3**, the unthreaded **3** can still interact with DB24C8 by electrostatic and hydrogen-bonding interactions with a two-point binding geometry in a nonthreading manner.[14a,15b] Thus, the formation of supramolecular gel **5** was mainly due to the efficient mechanically interlocked cross-linking of DB24C8 and bisammonium salts, while the breakage of gel **5** under large strains and its fast recovery may be related to the destruction and reformation of electrostatic and hydrogen-bonding interactions between cross-linker **3** and DB24C8 moieties of the polymer; the destruction and reformation of these interactions should be much faster than the threading of the secondary ammonium salt units (**2** or **3**) into DB24C8 cavities, thus giving excellent self-healing properties for gel **5**.

In summary, we prepared supramolecular gels by cross-linking a PMMA polymer with pendent DB24C8 units by using two bisammonium salts with different end groups based on the host–guest interactions of DB24C8 units and secondary ammonium salt moieties. Owing to the intrinsic pH-controllable properties of the host–guest recognition motif, the two gels can both act as degradable materials triggered by pH stimuli. Moreover, the gels exhibit excellent self-healing properties, which not only can be seen visually and directly, but also were fully studied using rheological measurements, showing 100% recovery even under 10000% strain in less than ten seconds for gel **5** over several cycles. The study of pH-responsiveness and self-healing of supramolecular gels will undoubtedly shed light on the properties of supramolecular cross-linked polymers and polymer gel networks acting as adaptive and smart materials; these topics are under investigation in our group.

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Keywords: gels · host–guest systems · molecular recognition · self-assembly · self-healing

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[16] Gel **5** can reform by adding the same amount of solvent to the xerogel.

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[19] It should be noted that the complexation percentages of DB24C8 and DBAS cannot be determined based on proton NMR data owing to the heavy overlap of proton NMR peaks not only for the complexation between **1** and **2**, but also for the complexation between **1** and **3**. Instead, we used viscometry and rheological data to estimate these percentages.[23]

[20] In the measured concentration ranges, no gels formed. Here we use "gel" just for clarity. The lower specific and reduced viscosities were due to the low concentration of the solution. Owing to the significant partial gelation of the samples, we measured the viscosity of polymer **1**, gel **4**, and gel **5** in the polymer concentration ranges 0.31–4.80 mM, 0.28–4.26 mM, and 0.37–1.47 mM, respectively.

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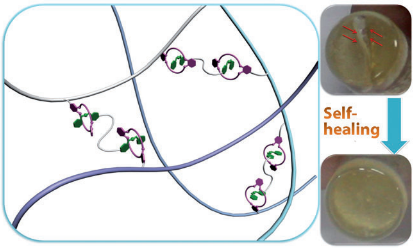
[23] See the Supporting Information for details.

Communications

Supramolecular Chemistry

M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng, F. Huang* ______ ▮▮▮▮–▮▮▮▮

Self-Healing Supramolecular Gels Formed by Crown Ether Based Host–Guest Interactions



Automatic repair: A polymer with pendent dibenzo[24]crown-8 units (purple in picture) was cross-linked by two bisammonium salts (green) to form two supramolecular gels based on host–guest interactions. These two gels are stimuli-responsive materials that respond to changes of the pH value and are also self-healing materials, as can be seen by eye and as evidenced by rheological data.