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Covalent Cross-Linked Polymer Gels with Reversible Sol−Gel Transition and Self-Healing Properties

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Introduction. Covalent and reversible noncovalent interactions are two basic cross-linking forces to form three-dimensional networks in polymer gels. Accordingly, polymer gels can be defined as chemical gels or physical gels, respectively.[1−3] The networks based on covalent bonds in chemical gels are stable under ambient conditions owing to their robust and irreversible natures of the covalent bonds. Although a chemical gel can dramatically change its volume by swelling or deswelling its permanent network in response to stimuli, it cannot be transformed into its starting polymer (monomer) solution.[4−6] In contrast, the supramolecular networks based on noncovalent interactions in physical gels are susceptible to the external environment. It is easy for a physical gel to perform a sol−gel transition in response to temperature, pH and solvent.[7,8] In this sense, a physical gel is smarter than a chemical gel. Integrating the stimuli-responsibility of the physical gels and stability of the chemical gels into a single system to yield a robust but smart gel is still a challenge.

Dynamic covalent chemistry[9] offers an appealing prospect of constructing such materials. It employs reversible covalent bonds instead of noncovalent interactions to prepare products. By adjusting the thermodynamic controlled reactions involving such reversible covalent bonds, distribution or constitution of the products and their properties can be tuned. Consequently, the products are smart as supramolecular entities in response to external stimuli, but they are more stable than the supramolecular ones due to the strong nature of the reversible covalent bonds.[10−12] As one of the dynamic covalent bonds, acylhydrazone bond has been successfully used by Lehn and co-workers to prepare dynamic covalent polymers. Polyacylhydrazones, the so-called dynamers,[10,11] could exchange their components with outside monomers and incorporated them into the original polymers.[13,14] Taking advantage of this exchange, the mechanical properties[15] or the color and fluorescence[16] of the original dynamers can be modified. Very recently, glycodynamers bearing side saccharide moieties were reported by the same group.[17] All these dynamers were linear or branched, however, cross-linked networks based on acylhydrazone bonds and their dynamic properties in a gel have not been reported so far.

Herein, we report a strategy of constructing novel reversible polymer gels based on dynamic covalent chemistry. As shown in Scheme 1, by condensation of acylhydrazines at the two ends of a poly(ethylene oxide) (PEO) (A_2) with aldehyde groups in tris[(4-formylphenoxy)methyl]ethane (B_3), a network with acylhydrazone bonds as cross-links is generated. Acylhydrazone bonds are covalent in nature and, therefore, the polymer network should be stable under normal conditions as that of conventional covalent gels. But more importantly, acylhydrazone formation displays reversibility under mild conditions with acid catalysis, breaking down the network and regenerating the starting reagents. By adjusting the acidity of the system, this chemical gel reveals reversible sol−gel phase transitions. Moreover, the chemical gel possesses self-healing property based on the reversible breaking and regenerating of acylhydrazone bonds.

Results and Discussion. Bis-acylhydrazine functionalized PEO polymer (A_2) was synthesized by modification of HO-PEO−OH (M_n = 2000) through three steps as shown in Figure S1. The degree of acylhydrazine functionality was close to 100% as determined by ^{1}H NMR and MALDI-TOF mass spectroscopy (Figure S2−S6). The preparation method for tris[(4-formylphenoxy) methyl]ethane (B_3) was also shown in Figure S1. Gelation conditions of A_2 and B_3 in DMF was explored at first. Acidic catalyst was necessary for the gelation because acylhydrazone formation was very slow at neutral conditions while a catalytic amount of acid drastically accelerated the reaction as reported in the literature.[13] When A_2 (0.02 mmol, 45.4 mg) and B_3 (0.0134 mmol, 5.8 mg) were mixed in 0.4 mL of DMF (gelator concentration 12 wt %) at room temperature, no gel was formed in 20 days. However, after the apparent pH of the solution was adjusted to 6−7 by adding 5 μL of glacial acetic acid (the concentration in solution 1.25% v/v), gelation occurred in 16 h. The gelation time was proved to be highly catalyst concentration dependent and closely related with gelator concentration as well (Table S1). A solution containing 3.0 wt % gelators with 60 μL of acetic acid in 0.4 mL DMF could not form a gel in 20 days, illustrating the fact that the lowest gelator concentration to form a gel was between 3.0−6.0 wt %. Viscosity (η) vs time of a mixture (gelator concentration 12 wt %, acetic acid concentration 15% v/v) during gelating process was recorded as shown in Figure S7a. Comparing with a sample without acetic acid catalyst, a sharp viscosity increase was observed at 18 min and a gel was formed in 30 min by visual observation. The dynamic moduli of the gelation process were also monitored (Figure S7b), and the point of storage modulus (G') intersecting loss modulus (G'') was found at 610 s, indicating formation of a network at that time. The rheological spectra of G' and G'' of the gel, as depicted in Figure 1a, show that G' (average 6.4 × 10^3 Pa) exceeds G'' (average 13 Pa) by about 2 orders of magnitude, and G' is independent of oscillatory frequency, exhibiting a plateau in a wide frequency region; these are the characteristics for a strong polymer gel with covalent cross-linked networks.[18] The robustness of this gel was also tested by "table-top" rheology method as shown in Figure S8. The gel (gelator concentration 6 wt %, acetic acid concentration 15% v/v) could be lifted by tweezers (Figure S8a) and deformed under pressure of a cylindrical iron block (Figure S8, parts d and e). Once the iron block was removed from the gel surface, the

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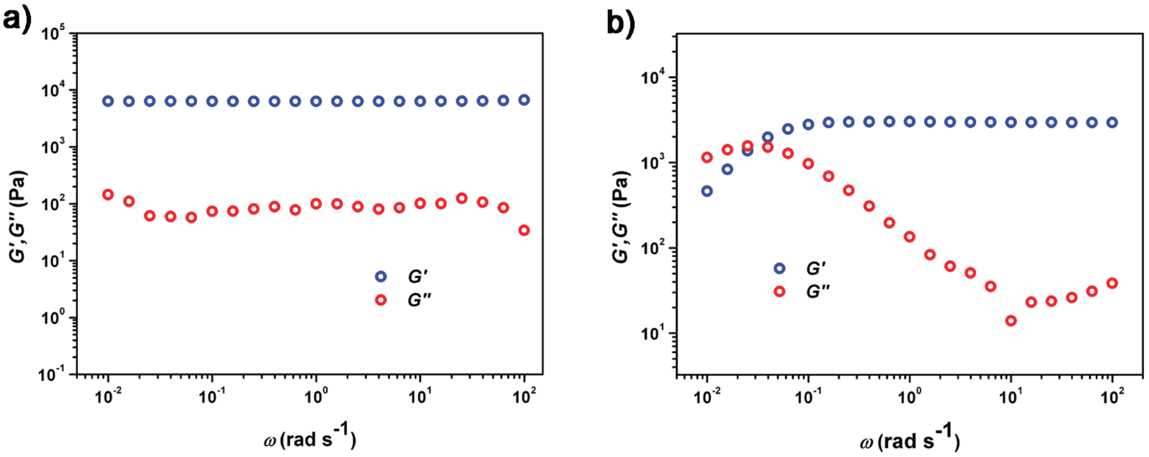
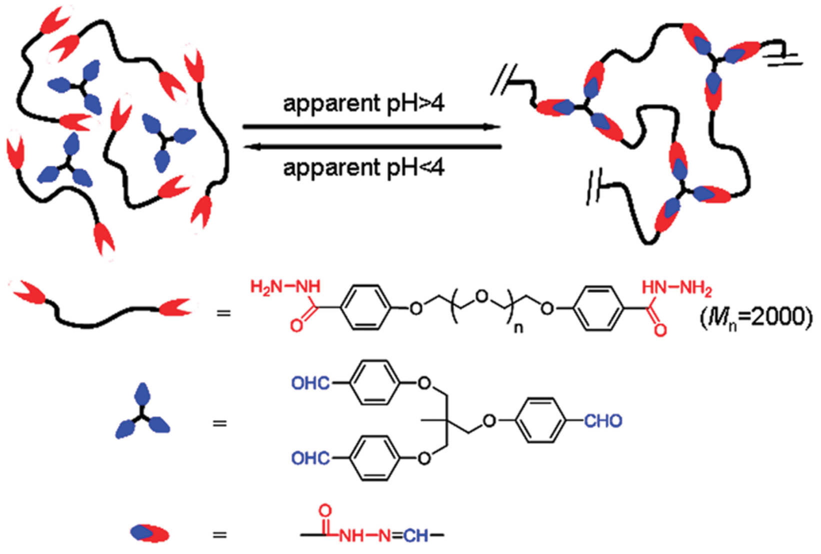


Figure 1. (a) Storage modulus (G') and loss modulus (G'') vs angular frequency (ω) of the polymer gel (gelator concentration 12 wt %, acetic acid concentration 15% v/v) at 25 °C after aging 17 h; (b) storage modulus (G') and loss modulus (G'') vs angular frequency (ω) of the gel after three sol−gel transition cycles.

Scheme 1. Construction of Covalent Cross-Linked Polymer Gel Based on Reversible Covalent Acylhydrazone Bond



deformed gel recovered its original shape immediately without any visible damage (Figure S8, parts f and g).

As expected, the novel gel revealed interesting sol−gel phase transition ability in response to acidity change. The gel used was prepared in 0.5 mL DMF with gelator concentration 12 wt % and acetic acid concentration 15% v/v (apparent pH ~5). After the gel aged overnight, 5 μL of hydrochloric acid (~37%) was added on the gel surface. The gel completely decomposed into a sol in 1.5 h with a final apparent pH 3−4. When 8 μL triethylamine (equivalent to hydrochloric acid) was added, the sol transformed into the gel in 20 s. The phase transition process is shown in Figure 2a and was repeated for eight circles. Along with the increasing cycles of the phase transition, the time of decomposing and reforming gel became longer, 2.25 h and 2 min, respectively for the fifth cycle. Double volume of hydrochloric acid was needed to decompose the gel completely after the fifth cycle while apparent pH of the sol almost kept constant. During the repeated transition cycles, white salts of HCl and triethylamine gradually appeared due to its low solubility in DMF, turning the gel opaque (Figure 2b). G' and G'' of the gel after 3 transition cycles were detected as shown in Figure 1b. The G' became lower than the G'' at low ω, indicating the gel deviated from the original one. Actually, the gel formed after eight transition cycles was not as stable as the original one, and about 0.05 mL of liquid was observed on the surface of the gel (volume 0.5 mL) after storage at room temperature for 3 days. More cycles of sol−gel phase transition were not tried, but the present results showed that the gel was more tolerable to high ionic strength than some of the reported peptide molecular gels.[19]

The dynamic polymer gels formed as well in other solvents like ethanol, DMSO and CH_2Cl_2 (Figure S9). Because of limited solubility of B_3 in ethanol, the resulted gel was not as transparent as the others. In the mixture of water and DMF (1/1 v/v), the gel formed in 3 h without acid catalyst. These results show that gelation of the A_2 and B_3 components is less solvent polarity dependent in comparison with the dendritic two-component gelator system based on hydrogen bonds reported by Smith and coworkes.[20] They proved that apolar, non-hydrogen-bonding solvents were the preferred solvent environment for the formation of the two-component supramolecular gel, and no gel formed in methanol, pyridine and dichloromethane.[21,22] In response to solvents dilution, the present dynamic gel behaved as a chemical gel. When immersed in pure DMF (1.5 mL), a piece of gel (0.34 g;

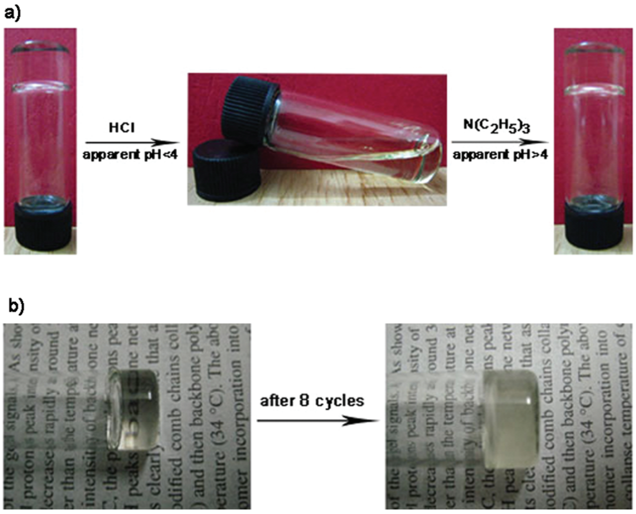


Figure 2. (a) Sol−gel phase transition of the covalent dynamic polymer gel (gelator concentration 12 wt % and acetic acid concentration 15% v/v in 0.5 mL DMF) in response to alteration of acidity at room temperature. (b) Appearance of the original gel (left) and the gel after eight transition cycles (right).

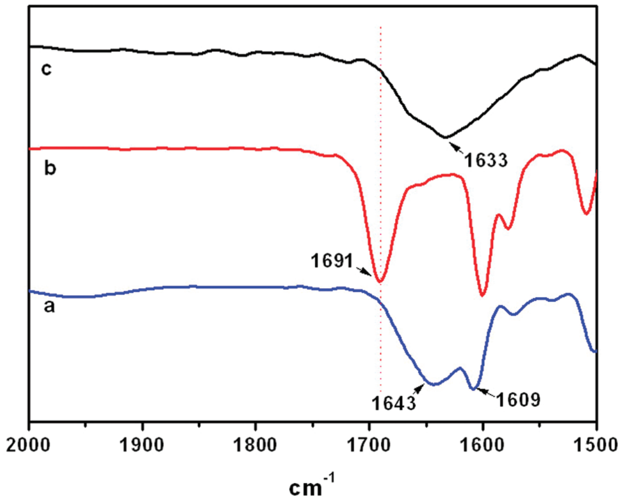


Figure 3. IR spectra of A_2 (curve a), B_3 (curve b), and the gel formed in CH_2Cl_2 after drying (curve c).

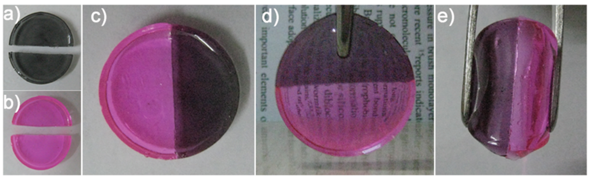


Figure 4. Self-healing properties of the covalent dynamic polymer gels (gelator concentration 12 wt %, acetic acid concentration 15% v/v in 1.5 mL DMF): (a) cracked gel containing carbon black (0.8 mg/mL); (b) cracked gel containing rhodamine B (0.067 mg/mL); (c) merged bicolor gel by simply putting half a and half b together in an original container for 7 h without any outside intervention at ambient temperature; (d) merged bicolor gel lifted by tweezers; (e) merged bicolor gel squeezed by tweezers. The boundary line for the two halves is clear but the gels have merged together as a whole.

gelator concentration 12 wt %,) absorbed 0.22 g DMF in 6 h at ambient temperature (ca. 20 °C). This amount reached to a maximum value of 0.25 g in 24 h and then kept constant. So, the gel swelled rather than dissolved in the solution. When the gel containing CH_2Cl_2 solvent was dried, it became hard and lost most of its elasticity. But the dry gel could regain its original shape and elasticity and became soft after swelling in solvent.

IR spectra (Figure 3) of A_2, B_3 and the dried gel proved the occurrence of condensation reaction between acylhydrazine and aldehyde groups in the gel. The absorption from aldehyde groups of B_3 on curve *b* at 1691 cm^{-1} became invisible on the curve *c* of the gel, while a new peak appeared around 1633 cm^{-1} on curve *c*, indicating the formation of the acylhydrazone bonds. These results further proved that the gel is a chemical gel. The reversible nature of the covalent acylhydrazone bonds gave dynamic characteristics to the gel, making it perform sol−gel phase transition easily like a molecular gel.[7,8] Although acylhydrazone bonds have been used in preparing hydrogels before,[23,24] their dynamic nature was used for the first time to construct a covalent dynamic polymer gel here.

The covalent dynamic polymer gels possess interesting self-healing ability. As depicted in Figure 4, two pieces of cracked gel plates with dark (carbon black) and red (rhodamine B) colors can merge autonomously into a whole piece by simply putting them together and keeping contact for 7 h without any outside intervention. The joint between the two colored parts in the merged gel was strong enough to sustain vigorous squeeze by the tweezers although the boundary line was clear in the gel (Figure 4, parts c−e). When the merged bicolor gel was cut into separated pieces along the boundary again and then put them together closely as before, the self-healing process occurred once again, proving this process could be repeated and effective. The mechanism of this self-healing property should be related with the equilibrium of acylhydrazone bond formation.[11] In the as-prepared gel with captured solvents and catalytic acid, there are small amounts of free A_2 and B_3 in equilibrium with the formed polymer networks. The free monomers may diffuse and cross the interface of two plates and reform the acylhydrazone bonds in the networks, i.e. merge the two plates into a whole piece. Detailed analysis on the self-healing process and the properties of the healed gels in relation with the dynamic reaction is in progress. It is noteworthy that the self-healing process in the current gel can occur autonomously without any external intervention which differs from the self-repairing polymer materials that need external treatments.[25,26] This behavior is much like that of a thermoreversible rubber based on supramolecular chemistry reported by Leibler and co-workers.[27]

Conclusion. In present work, novel covalent dynamic gels based on reversible acylhydrazone bonds were prepared by condensation of bis(acylhydrazine) functionalized PEO (A_2) and tris[(4-formylphenoxy)methyl]ethane (B_3) in several organic solvents catalyzed by acetic acid at ambient temperature. These gels were covalent cross-linked and revealed typical properties of chemical gels. However, they can be switched into their starting polymer (monomer) solution by lowering acidity and turned back to gel state by adding base. The sol−gel phase transitions can be reversibly performed for several cycles in a similar way of a supramolecular gel. Furthermore, the gel revealed interesting self-healing property which occurred autonomously without any outside intervention. Employing this dynamic character, it is possible to reshape a strong chemical gel (Figure S10) and regenerate the used gel. The present discovery indicates that dynamic polymer gels may have a broad application as smart soft materials.

Experimental Section. *Typical Procedure for Preparation of the Polymer Gels.* Predetermined amount of bis-acylhydrazine functionalized PEO polymer (A_2) and equivalent tris[(4-formylphenoxy) methyl]ethane (B_3) were mixed in a certain amount of DMF to form a homogeneous solution in a container. After catalyst of acetic acid was added and mixed homogenously, the solution was sealed in the container and placed at ambient temperature without stirring until a gel was formed.

"Table-Top" Rheology Test. A plate gel (gelator concentration 6 wt %, acetic acid concentration 15% v/v) with 36 mm in diameter and 6 mm in thickness was prepared and aged overnight in a container. After the plate gel was transferred from the container on the surface of a piece of glass (Figure S8, parts a−c), a cylindrical iron block (158 g, 22 mm in diameter at bottom) was put on the gel to test the deformation of the gel (Figure S8, parts d and e). When the iron block was removed from the gel surface, the deformed gel recovered its original shape (Figure S8, parts f and g). All pictures were taken with a digital camera, Canon SD800 IS.

Self-Healing Experiment. Polymer gel plates (gelators concentration 12 wt %, acetic acid concentration 15% v/v in 1.5 mL of DMF) were prepared in a round bottle with a bottom of 30 mm in diameter. For preparing the black gel plate, carbon black (0.8 mg/mL) was added, while the red one was obtained by adding rhodamine B (0.067 mg/mL). Each of the gel plates was cut by a blade into two halves. Half of the black plate and half of the red plate were spliced in the original round bottle. The bottle was sealed and placed at room temperature without any other intervention.

Rheology Measurements. Rheology measurements were carried out with a stress controlled rheometer AR-G2 (TA) using a parallel plate of 40 mm diameter at 25 ± 0.1 °C.

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Supporting Information Available: Text giving experimental details on synthesis and full characterization of all of the reported compounds, including figures showing the synthesis reactions, ^{1}H NMR spectra, MALDI−TOF spectra, a plot of viscosity (η) change vs time, and other pictures showing gel properties and a table of gel formation conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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