

# Poly[2]catenane Gels Based on Sequential Assembly of Small Molecules

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## Abstract

Polycatenane gels have attracted extensive attention due to their high degree of freedom and mobility. However, the synthesis of poly[2]catenane gels reported to date all rely on the polymer as the backbone. Herein, we prepared poly[2]catenane gels based on entirely sequential assembly of small molecules. Monomer M1 with two unclosed rings was first prepared, which self-assembled to form supramolecular polymers (SPs) via hydrogen bonding and  $\pi$ - $\pi$  interactions. Upon adding small molecule monomers M2 and M3 with aldehyde groups, ring closing of SPs occurred due to the amino groups in the SPs reacted with M2 to form imine bonds. In addition, M3, which has twice the number of aldehyde groups as M2, enabled SPs to ring-close, causing the proceeding of crosslinking process at the same time. Thus linear SPs were transformed into poly[2]catenane gel networks. Due to the presence of hydrogen bonds in the poly[2]catenane gel, the gel also possessed stimulus responsiveness and self-healing properties.

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Poly[2]catenane Gels Based on Sequential Assembly of Small Molecules

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## Keywords

Poly[2]catenane | Gel | Dynamic covalent bond | Non-covalent bond | Self-assembly | Stimuli-responsiveness

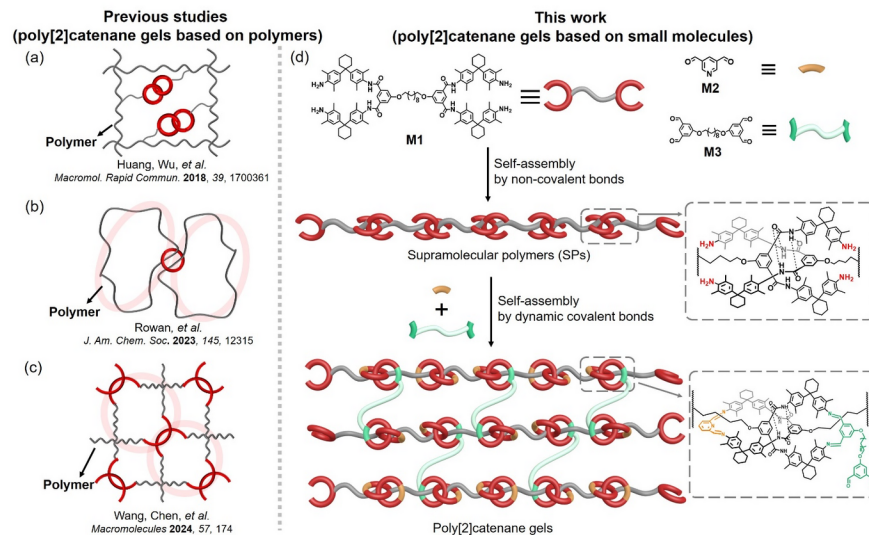
## Comprehensive Summary

Polycatenane gels have attracted extensive attention due to their high degree of freedom and mobility. However, the synthesis

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Background and Originality Content Catenanes are compounds composed of two or more mechanical interlocked macrocycles.<sup>[1-3]</sup> By introducing the catenanes structures into polymers, polycatenanes with chain-like mechanically interlocked structures can be obtained.<sup>[4]</sup> Since catenanes are highly free and mobile, polycatenanes possess greater flexibility and strength caused by different chain conformations compared to con-

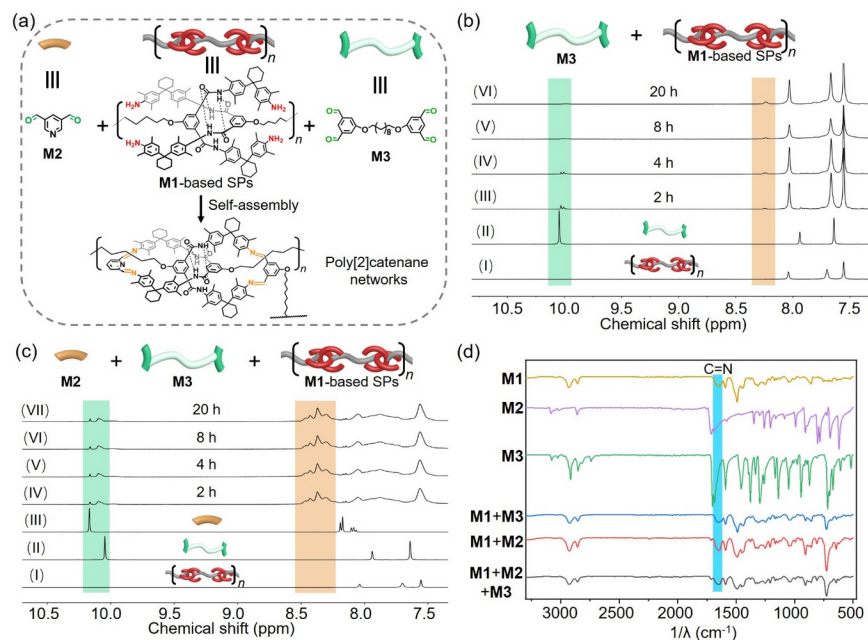
ventional polymers.<sup>[5-8]</sup> The categories of polycatenanes could be divided into a number of subclasses as follow,<sup>[9-15]</sup> depending on the location and connection of the catenane subunits: main-chain polycatenanes obtained by introducing difunctionalized catenanes into the linear polymer main chains or by interlocking a plurality of rings two by two; side-chain polycatenanes obtained by introducing monofunctional catenanes into the linear polymer side chains; polycatenanes based on cyclic polymers formed by two large or one large ring hanging with small rings; Unlike the above types of polycatenanes, polycatenane networks are composed of multiple interlocked rings or of catenanes and polymers, showing solid-like properties different from most of the liquid polycatenanes. Liquid polycatenanes are mostly used for theoretical research and are difficult to be widely used as macroscopic solid materials. Through the linear crosslinking, polycatenanes could be converted from liquid to gels and thus be widely used.<sup>[16]</sup> The above-mentioned polycatenanes networks formed by multiple interlocked rings are also a kind of crosslinked networks, while their structures are complex making it difficult to recognize the exact structure.<sup>[12]</sup> In recent years, many kinds of poly[2]catenane networks have been developed. For example, As shown in Scheme 1a, Huang, Wu and coworkers prepared a poly[2]catenane gel by the “click” reaction between bisvinyl [2]catenanes and poly(ethylene glycol) derivatives containing thiol groups.<sup>[17]</sup> Rowan and coworkers designed a series of poly[2]catenane gels with different numbers of interlocked units by using doubly threaded pseudo[3]rotaxane crosslinkers and covalent crosslinkers (Scheme 1b).<sup>[18]</sup> Besides, Wang, Chen and coworkers designed a poly[2]catenane hydrogel prepared by Tetra-PEG chains crosslinked by the recognition of metal ions, which was a reversible coordination interlock structure (Scheme 1c).<sup>[19]</sup> It could be found from the above-reported examples, the gel formation all relies on the polymer as part of the backbone structure. Herein, we prepared a new type of poly[2]catenane gel by entire sequential assembly of small molecules without any polymer structures. Poly[2]catenane gels were prepared based on the monomer **M1**, monomer **M2** (2,6-pyridinedicarbaldehyde) used for ring closing reactions and the crosslinker monomer **M3**, all of which were small molecules. First, **M1** of alkyl chain linking with two isophthaloyl bis(diamine) groups, self-assembled to form linear supramolecular polymers (SPs) through synergistic intramolecular hydrogen bonding and  $\pi$ - $\pi$  interactions at higher concentrations in chloroform. When **M2** and **M3** were simultaneously added to the **M1** solution, the aldehyde groups of **M2** could spontaneously react with the amino groups of **M1** to form dynamic covalent bonds (imine bonds), and ring closing behaviors occurred. The ring-closing behaviors was caused from: since the number of reactive sites of **M3** was twice as many as that of **M2**, the amino groups in supramolecular polymer chains could react with **M3** to form the closed ring. Additionally, **M3** acted as the crosslinker to crosslink linear SPs. Therefore, the simultaneous addition of **M2** and **M3** could transform linear SPs into poly[2]catenane gels. The reaction process of forming imine bonds is spontaneous and stable, and thus, it would not affect the existing non-covalent bonds and disturb the SPs formed by self-assembly. **Scheme 1** Schematic representation of the three types of poly[2]catenane gels: (a) gels formed by cross-linking of catenane modified in the side chains of polymers, (b) gels formed by polymers acting as irregular catenane macrocycles, (c) gels formed by polymers acting as regular catenane macrocycles, (d) gels formed by the self-assembly of small molecules (**M1**, **M2**, **M3**) through non-covalent and dynamic covalent bonds



## Results and Discussion

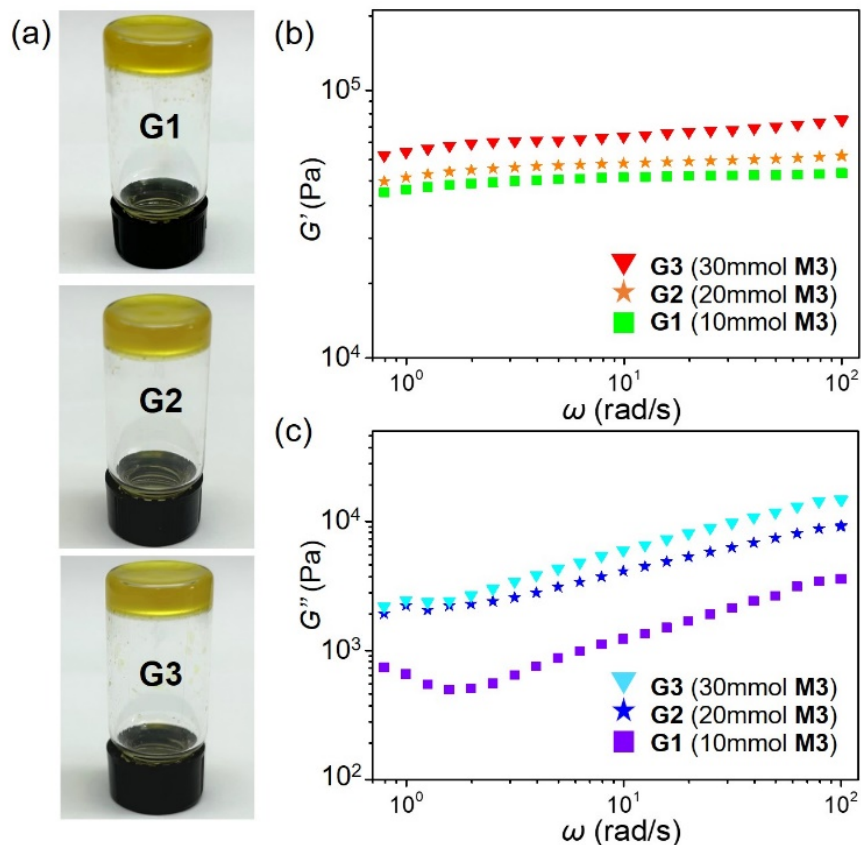
The synthetic routes of monomers **M1** and **M3** are shown in Scheme S1 and the structures were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and high-resolution mass spectrometry analyses (Figure S1–S3, S5–S7). **M2** could be directly by purchased and  $^1\text{H}$  NMR spectra was shown in Figure S4.

In previous work, we had shown that **M1** could self-assemble in chloroform to form SPs.<sup>[20]</sup> To explore the process for adding small molecule **M2** and **M3** into the **M1** solution (Figure 1a), the corresponding  $^1\text{H}$  NMR spectra of the **M3** (Figure S8), and a mixture of **M2** and **M3** (Figure S9) at different time were recorded. As shown in Figure 1b, 0.1 equiv. of **M3** were added to 50 mmol **M1**. Due to the small amount addition of **M3**, SPs were not crosslinked to a high enough degree and therefore formed a network rather than a gel. By comparing the  $^1\text{H}$  NMR spectra of the mixed solution at 2 h, 4 h, 8 h, 20 h, it could be determined that the reaction was essentially complete after 8 h. The peak of the aldehyde group of **M3** at 10.05 ppm was significantly weakened, but the peak did not disappear completely. This was due to the fact that  $\text{H}_2\text{O}$  was generated from the reaction of amine aldehyde condensation causing the hydrolysis of newly formed imine bond, thus leading to incomplete reaction.<sup>[21]</sup> In addition, a new peak appeared in the range of 8.20–8.28 ppm, which also proved that the imine bond were generated through the reaction between the amino groups at the ends of **M1** and the aldehyde groups of **M3**.<sup>[22]</sup>



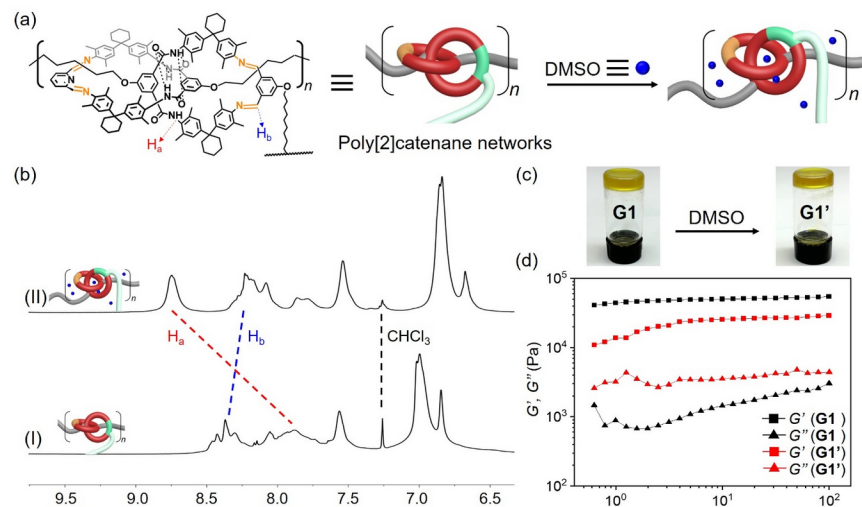
**Figure 1** (a) Schematic representation of the self-assembly of **M1**- based SPs to form Poly[2]catenane networks by adding **M2** and **M3**. (b) <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 298 K) of (I) **M1**, (II) **M3**, a mixture of 50 mmol **M1** and 5 mmol **M3** after (III) 2 h, (IV) 4 h, (V) 8 h, and (VI) 20 h. (c) <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 298 K) of (I) **M1**, (II) **M3**, (III) **M2**, a mixture of 50 mmol **M1**, 5 mmol **M3** and 90 mmol **M2** after (IV) 2 h, (V) 4 h, (VI) 8 h, and (VII) 20 h. (d) FT-IR spectra of **M1**, **M2**, **M3**, the mixture of **M1** (50 mmol) and **M3** (5 mmol), **M1** (50 mmol) and **M2** (90 mmol), **M1** (50 mmol), **M2** (90 mmol) and **M3** (5 mmol). Note that all the mixtures were first dissolved **M1** in solvent for 15 min before the addition of other monomers (**M2**, **M3**) to ensure the formation of SPs first.

As shown in Figure 1c, 0.1 equiv. of **M3** and 1.8 equiv. of **M2** were added into 50 mmol **M1**, this was done in order to keep the amount of aldehyde groups in **M2** and **M3** consistent with the amounts of amino groups in the **M1**-based SPs. The aldehyde peaks of **M2** and **M3** were almost no longer decreasing after 8 h, while at the same time the imide peaks that appeared in the range of 8.20-8.50 ppm were no longer changing. This proved that the reaction between the amino groups of **M2**, **M3** and the **M1**-based SPs promoted to generate imine bonds.<sup>[23]</sup> Infrared spectroscopy (IR) assessments were also conducted on **M1**, **M2**, **M3**, as well as their mixture corresponding **M1** and **M2**, **M1** and **M3**, **M1**, **M2** and **M3**. As shown in Figure 1e, compared to the individual spectra of **M1**, **M2**, and **M3**, it could be found that the vibrational peaks of the spectra of their mixtures were distinctly different: a C=N stretching vibration peak at 1654 cm<sup>-1</sup> was detected in the mixtures. These results also proved that **M1** reacted with **M2** and **M3**.<sup>[24]</sup>



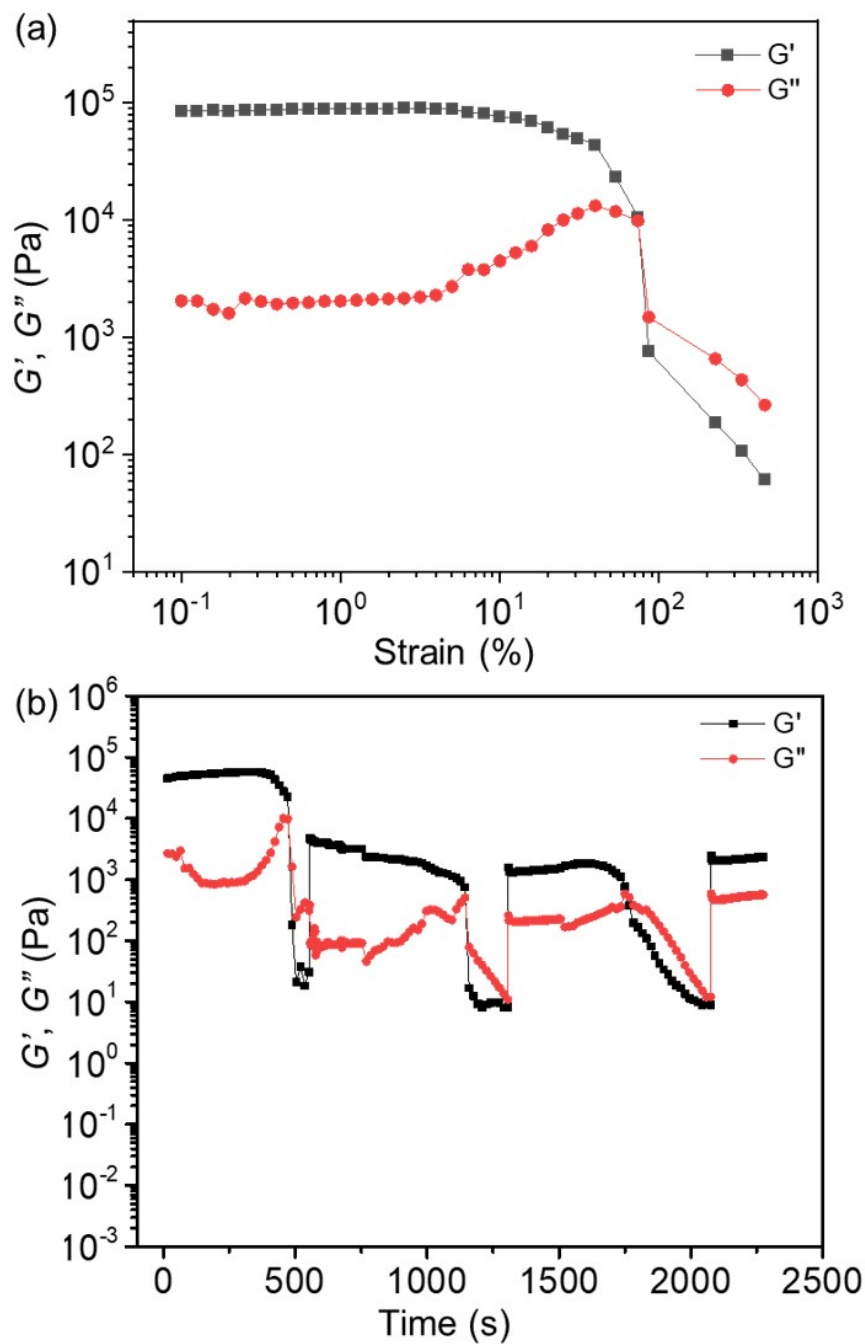
**Figure 2** (a) Photographs, (b) storage modulus ( $G'$ ) and (c) loss modulus ( $G''$ ) with versus scanning frequency ( $\omega$ ) for the gels **G1**, **G2**, and **G3**. (**G1**: adding 10 mmol **M3** and 180 mmol **M2** into 100 mmol **M1**; **G2**: adding 20 mmol **M3** and 160 mmol **M2** into 100 mmol **M1**; **G3**: adding 30 mmol **M3** and 140 mmol **M2** into 100 mmol **M1**)

In order to characterize the formation of poly[2]catenane gels and the changes in the crosslinking degree, we performed linear oscillation sweep experiments on three gels **G1**, **G2**, and **G3** with different crosslinking degrees. Gels **G1**, **G2**, and **G3** were obtained by adding 10 mmol **M3** and 180 mmol **M2** to 100 mmol **M1**, 20 mmol **M3** and 160 mmol **M2** to 100 mmol **M1**, 30 mmol **M3** and 140 mmol **M2** to 100 mmol **M1**, respectively. As shown in Figure 2a, three gels were formed by adding different amounts of **M2** and **M3**. The variation of storage modulus ( $G'$ ) and loss modulus ( $G''$ ) with frequency in chloroform for the fabricated gels was shown in Figure 2b,c. The storage modulus of all three gels was larger than the loss modulus and was independent of the frequency, which proved that the formation of gel states.<sup>[25-26]</sup> Comparing the storage modulus and loss modulus of gels **G1**, **G2**, and **G3**, it could be found that with the addition of **M3**, the storage modulus and loss modulus of gel **G1**, **G2** and **G3** increased significantly: the plateau value of the storage modulus of the gels increased from  $5 \times 10^4$  to  $8 \times 10^4$ , and the value of the loss modulus of the gels rose by one order of magnitude. This indicated that the crosslinking degree increased gradually with the increase of the incorporation amount of **M3** (from 10 mmol **M3** to 30 mmol **M3**).<sup>[27]</sup>



**Figure 3** (a) Schematic representation of poly[2]catenane networks upon addition of DMSO, (b) <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 298 K) of (I) poly[2]catenane networks and (II) the addition of 10% DMSO-*d*<sub>6</sub> (*v* : *v*) into poly[2]catenane networks (poly[2]catenane networks were prepared by adding 5 mmol **M3** and 90 mmol **M2** into 50 mmol **M1**), (c) photographs of **G1** and **G1'** (after adding DMSO to **G1**), where **G1** was prepared by adding 10 mmol **M3** and 180 mmol **M2** to 100 mmol **M1**, (d) storage modulus ( $G'$ ) and loss modulus ( $G''$ ) with versus scanning frequency ( $\omega$ ) for the **G1** and **G1'**.

Since the formation of the poly[2]catenane networks was driven by hydrogen bonding interactions, the solvent response of poly[2]catenane after the addition of DMSO was investigated. As shown in Figure 3a, hydrogen bonding interactions originated from the amide hydrogen in polycatenanes caused the catenanes to be immobilized, whereas the hydrogen bonding was disrupted upon the addition of DMSO. But this would not affect the structure of poly[2]catenane structure. To verify this, the mixture of **M1**, **M2** and **M3** was first obtained by adding 5 mmol **M3** and 90 mmol **M2** into 50 mmol **M1** in chloroform, and then 10% DMSO-*d*<sub>6</sub> was added to the mixture. Besides, the corresponding <sup>1</sup>H NMR spectra of the mixture before and after adding DMSO were performed (Figure 3b, S10). With the addition of DMSO-*d*<sub>6</sub>, it could be found from the spectra that the signal of amide hydrogen H<sub>a</sub> shifted from 7.88 ppm to 8.74 ppm, which indicated that the intramolecular hydrogen bonding was partially disrupted on account of the newly formed hydrogen bonding from the amide hydrogen. The signal peak of the imide hydrogen (H<sub>b</sub>) remained almost unchanged, indicating that the poly[2]catenane structure was not disrupted.<sup>[28]</sup> Next, gel **G1** was obtained by adding 10 mmol **M3** and 180 mmol **M2** to the SPs formed from 100 mmol **M1** in chloroform, and then gel **G1'** was obtained by adding DMSO to **G1** (Figure 3c). As can be seen from the photographs, there was no significant change in the state of the gel before and after the addition of DMSO, which indicated that although the hydrogen bonding was destroyed. But the gel network was not dissolved owing to the existence of poly[2]catenane structure. Meanwhile, the rheological experiments were carried out on the gels **G1**, **G1'** (Figure 3d). The results showed that the storage modulus of **G1** and **G1'** was greater than the loss modulus in a certain frequency range (0.6 to 100 rad/s at a strain of 1%). This indicated that the gel state did not change due to the existence of dynamic covalent bonds. The storage modulus of **G1'** with DMSO addition was smaller than that of **G1**, which was due to the disruption of hydrogen bonds within the gel, thus reducing the rigidity of the gel network and enhancing the mobility.<sup>[29]</sup>



**Figure 4** (a)  $G'$  and  $G''$  values of a gel sample prepared with 180 mmol **M2** and 10 mmol **M3** adding into 100 mmol **M1** during strain sweep from 0.1% to 400%, and (b)  $G'$  and  $G''$  values of the sample during the time sweep at a scan frequency of 10 rad/s, time-dependent strain sweep from 0.1% to 200% and then returned to 1% strain in 200 s. Furthermore, three cycles were performed.

Considering the presence of noncovalent and dynamic covalent bonds in poly[2]catenane gels, the gels were expected to exhibit self-healing properties.<sup>[30]</sup> In order to verify this property, rheological experiments were



performed. First, strain sweep tests were performed on the poly[2]catenane gel prepared from adding 180 mmol **M2** and 10 mmol **M3** added into 100 mmol **M1** (Figure 4a). The results showed that when the strain was less than 80%, the storage modulus of the samples was larger than loss modulus, thus the sample mainly exhibited elastic; whereas, when the strain was larger than 80%, the loss modulus was larger than storage modulus. In this way, the samples mainly exhibited viscous, which was due to the fact that the network of the samples was broken under larger strains. According to the above strain sweep results, the strain greater than the damage of the gel networks (greater than 80%) was further tested. In Figure 4b, during the strain scanning of the sample from 0.1% to 200% strain at scan frequency of 10 rad/s for 550 s, loss modulus was gradually larger than storage modulus, which was leading by the break of the network at higher strains. Subsequently, time sweep experiments were performed for 200 s with a strain of 1% and a scanning frequency of 10 rad/s. It could be observed that storage modulus became larger than loss modulus in a short period of time, which was due to the rapid recovery of networks. Two other cycles of time sweep experiments were performed on the same gel, for which the similar trends were observed. The above test results showed that the poly[2]catenane gels possessed self-healing properties.<sup>[31]</sup> Therefore, it was inferred that the self-healing mechanism of poly[2]catenane gels was due to reversible noncovalent and dynamic covalent bonds. When the gel was subjected to a large strain, the noncovalent and dynamic covalent bonds disintegrated. Without any external strain, the noncovalent and dynamic covalent bonds recombined again resulting in self-healing behavior.

## Conclusions

In conclusion, poly[2]catenane gels were prepared by sequential self-assembly of small molecules. Firstly, monomer **M1**, which consisted of an alkyl chain linking isophthaloyl bis(diamine) groups, was prepared. SPs were formed by self-assembly of **M1** through hydrogen bonding and  $\pi$ - $\pi$  interactions at high concentrations in chloroform. Upon the addition of monomers **M2** and **M3** into SPs, the amino groups in SPs reacted with the aldehyde groups to form imine bonds, which resulted in ring-closing and the crosslinking process of SPs. As a result, the linear SPs were transformed into poly[2]catenane gels with network structures. The formation of the gel was demonstrated by <sup>1</sup>H NMR spectroscopy, infrared spectroscopy, and rheological testing. Furthermore, the experiment results showed that the poly[2]catenane gels also possessed solvent responsiveness and self-healing properties. This work provided a new method for the preparation of poly[2]catenane gels. In addition, it also promoted the development of dynamic polymer materials.

## Supporting Information

The supporting information for this article is available on the WWW under <https://doi.org/10.1002/cjoc.202400xxx>.

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### Entry for the Table of Contents

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**A Poly[2]catenane Gel Based on Small Molecules** Hanwei Zhang,<sup>a</sup> Jinsa Li,<sup>b</sup> Ziqing Hu,<sup>b</sup> and Xiaofan Ji<sup>\*,b</sup> *Chin. J.*  
We reported poly[2]catenane gels prepared by entirely sequential self-assembly of small molecules via noncovalent and dynam

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