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Heat-set gel formed from easily accessible gelators of succinamic acid derivative (SAD) and primary alkyl amine (R-NH₂)

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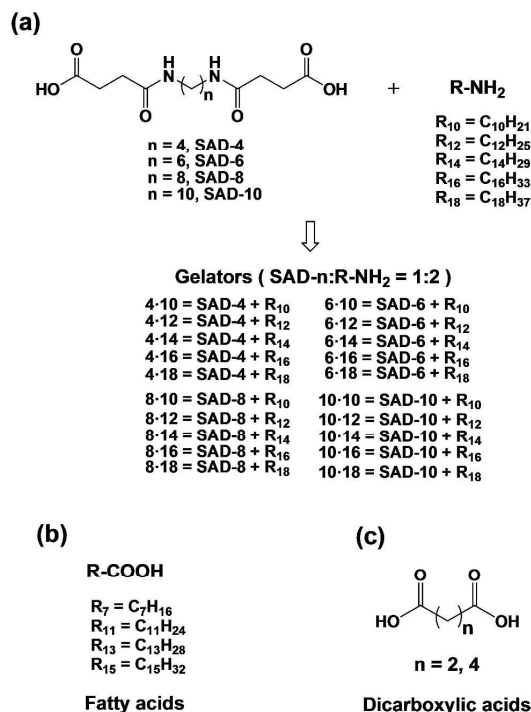
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Currently, design and construction of an intelligent stimuli-responsive gel system is still a significant challenge. We present here a new gel system from which the formation of heat-set gel, conventional gel and irreversible heat-set gel can be achieved in aromatic solvents. This gel system is based on two-component gelators containing a succinamic acid derivative (SAD) and a primary alkyl amine (R-NH₂). Increase of temperature to 85 °C, a rarely reported reversible heat-set gel (gel formation with the increase of temperature) is afforded. Addition of fatty acid to the two-component gelators, a conventional gel (gel formation with the decrease of temperature) is formed. When the fatty acid is replaced with dicarboxylic acid, a new heat-set gel is generated, which is irreversible and thermally super-stable. X-ray diffraction analysis reveals that the formation of reversible heat-set gel relies on electrostatic interactions, hydrogen bonds, and hydrophobic interactions. This two-component gelators shows a perfect gel system for formation of diverse gels including heat-set gel, conventional gel and irreversible heat-set gel. The tunable strategy demonstrated in this letter may provide a new way for creation of more functional gels in gel science.

1. Introduction

As one kind of “smart” soft materials, the self-assembled supramolecular gels formed by low molecular weight organic gelators (LMWGs) have attracted much attention in material science.¹ They are stabilized by weak intermolecular non-covalent interactions such as hydrogen bond, π - π stacking interaction, and hydrophobic interactions. The dynamic and reversible nature of the weak non-covalent interactions in the self-assembled supramolecular gels endows the gels with multi-response to external stimuli, such as temperature,² redox reactions,³ light,⁴ sound,⁵ and so on. Among supramolecular gels, conventional gel, formed by undergoing a process containing one heating step for gelator dissolution and the other cooling step for gel formation, is the most studied and reported.^{2,6} The reversible transitions between gel and sol are usually realized by increasing or decreasing the system temperature. Heat-set gel, formed by low molecular weight organic gelators, firstly reported in 2004, can be described as the reverse conventional gel.⁷ With the increase of temperature, the gel gradually generates and then with the decrease of temperature, the gel gradually transmits to solution, showing reverse processes to conventional gel. As there is few assembly rule to follow, to date, the reported heat-set gels, especially these assembled from LMWGs are very limited.⁸ However, heat-set gels have currently attracted considerable interest, due to their great potential applications in fields of catalysis,⁷ thermo-responsive materials,⁹ bio-medicine¹⁰ and so on. Besides conventional gel and heat-set gel, irreversible heat-set gel formed by LMWGs has also attracted considerable attention.¹¹ This gel usually exhibits high thermal stability. Once formed, this gel is thermally unresponsive in a broad temperature range. It is well-known that the types of gels are greatly dependent on the gelators, as gelators show different gelling performances. To produce more gel materials, unearth diverse gels from one gel system is much desired. However, to the best of our knowledge, there is no gelator(s) based on which different types of gels such as conventional gel, heat-set gel, and so on can be respectively formed.

Multi-component supramolecular gels, containing more than one compound as gelators, now exhibit an increasingly important role in designing new supramolecular gel materials.^{12,13} The advantage of multi-component gels over



Scheme 1 Structures of gelators. (a) SAD and R-NH₂; (b) fatty acids. (c) dicarboxylic acids.

one-component gels is that the structures and properties of resulted gel materials can be tuned by changing the ratio of the components or by exchanging one of the components¹³. It has been reported that some amide compounds can be served as good gelators^{6,14}, and some others without gel abilities can also gelate liquids by adding suitable counterparts¹⁵. In this paper, we report that an unprecedented two-component gel system based on a succinamic acid derivative (SAD) and a primary alkyl amine (R-NH₂) (Scheme 1), can be used for assembling different types of supramolecular gels, including heat-set gel, conventional gel and irreversible heat-set gel. Increase of the temperature, a reversible heat-set gel is formed. Addition of fatty acid to the two-component gelators, a conventional gel with fiber-like microstructure is generated. When the fatty acid

is replaced with dicarboxylic acid, a new heat-set gel with sheet-like microstructure is afforded, which is irreversible and thermally super-stable.

2. Experiment Section

2.1 Materials

Succinic anhydride ($\geq 99.5\%$) and 1,6-hexanediamine ($\geq 99\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). 1,8-Diaminooctane ($\geq 98\%$) and 1,10-Decanediamine ($\geq 97\%$) were purchased from Tokyu Chemical Industry Co., Ltd. Other chemicals were obtained from J&K Scientific Co., Ltd (Shanghai) and used without further purification. All the organic solvents were obtained from Tianjin Damao Chemical Reagent Factory (China).

2.2 Gelation tests

Gelation tests for SAD and R-NH₂ in organic solution were investigated by a typical tube inversion method¹⁶. SAD and R-NH₂ (molar ratio of 1:2) were mixed in an organic solvent (1 mL) in a sealed scintillation vial with a cap and the mixture was sonicated until the solid dissolved. The resulting solution was heated and gel was gradually generated. Once formed, the gel was stationary and the scintillation vial can be inverted without deformation of the gel. Gelation tests for SAD and R-NH₂ with fatty acid or dicarboxylic acid in organic solution were carried out by a similar procedure.

2.3 Characterization

Mass spectra were recorded with a Bruker Dalton Esquire 3000 plus LC-MS apparatus. ¹H NMR spectra were recorded on a Bruker AM 400 spectrometer. Fourier transform infrared (FT-IR) spectra were recorded in the 4000 to 400 cm⁻¹ region using KBr pellets and a Nicolet AVATAR 360. All data were collected for 128 interferograms with a resolution of 4 cm⁻¹. Small-angle X-ray powder diffraction (SA-XRD) patterns of dried organogel were collected on a Bruker D8 Focus diffractometer using the Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The methods for production of dried organogel were shown in ESI†. Single-crystal data were collected on a Bruker Smart APEX II diffractometer, with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Scanning electron microscope (SEM) measurements were

carried out on FEI Quanta 450. Differential scanning calorimetry (DSC) measurements were conducted on Setaram μ DSC7-Evo instrument (heating rate, 1.0 °C·min⁻¹).

Rheological characterization was performed using a stress-controlled rheometer (HAAKE RheoStress 6000) with a parallel plate type geometry (plate diameter, 3.5 cm). The rheometer equipped with a solvent trap for protecting the sample from evaporation. Temperature dependences of the storage shear moduli (G') and the loss shear moduli (G'') were investigated by heating the sample at a rate of 0.1 °C·s⁻¹. The viscoelastic moduli were monitored under small-amplitude oscillatory shear at an applied frequency of 1 Hz and stress of 0.1 Pa.

3. Results and Discussion

3.1 Gel formation and transformation

A series of SAD were synthesized and characterized by satisfactory ¹H NMR, IR, MS and melting-point measurements (Scheme S1 in ESI†). The gelation tests for single component of SAD (SAD-4, SAD-6, SAD-8, SAD-10) or R-NH₂ (R₁₀, R₁₂, R₁₄, R₁₆, R₁₈), as well as two components of SAD and R-NH₂ in different molar ratio were carried out in the solvents used in the experiments. It has been found that any single component has no gelation ability in all tested solvents (Tables S1 and S2 in ESI†). However, two components of SAD and R-NH₂ in molar ratio of 1:2 exhibit rarely observed heat-set gelation ability. The results summarized in Table S3-S6 (ESI†) clearly show that in aromatic solvents such as tetralin, benzene, nitrobenzene, and so on, SAD and R-NH₂ with a molar ratio of 1:2 can generate stable gels with the increase of temperature, and the gels will transform to a solution within several minutes when cooled to room temperature, showing a reversible sol-gel process (Fig. 1a and b). This gelation process is repeatable. In non-aromatic solvents, SAD and R-NH₂ can not exhibit gelation behavior and thus can not form any gel. The quite different result reveals that solvent properties are important parameters in the process of the heat-set gelation. Additionally, it has been found that for a certain SAD-n, a primary alkyl amine with suitable length of tail chain is needed to form heat-set gel in aromatic solvent. The longer of the carbon chain in

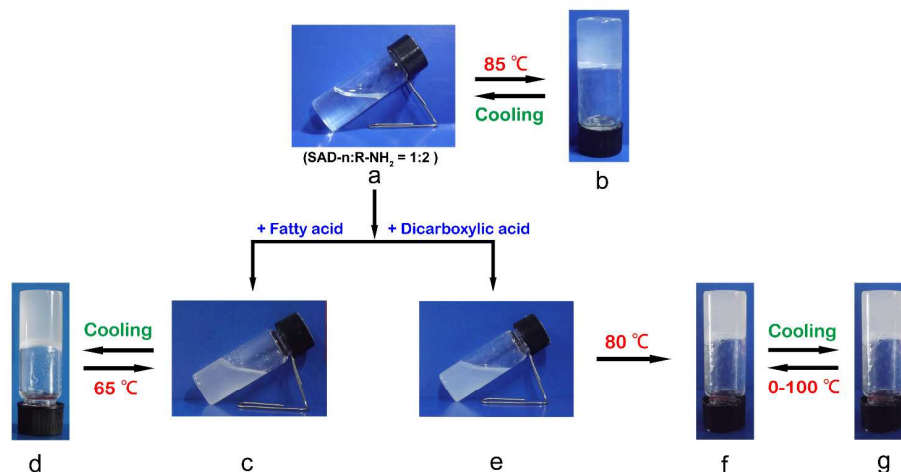


Fig.1 Optical images of gel formation and transformation. (a) and (b), heat-set gel, SAD-6 and R₁₄-NH₂ (6:14) in 1:2 molar ratio in tetralin (1.88 wt.%). (c) and (d), conventional gel, SAD-6, R₁₄-NH₂ and dodecanic acid in 1:2:3 molar ratio in tetralin (3.35 wt.%). (e), (f) and (g), irreversible heat-set gel, SAD-6, R₁₄-NH₂ and SAD-6 in 1:2:1 molar ratio in tetralin (2.66 wt.%).

SAD-n, the longer of alkyl chain in R-NH₂ is needed. For instance, **4-10** and **4-12** show gelation (Table S3 in ESI[†]), while **4-14**, **4-16** and **4-18** show no gelation. **6-12** and **6-14** exhibit gelation, while **6-10**, **6-16** and **6-18** exhibit no gelation. These observations indicate that matched lengths of alkyl chain of two-component gelators (both SAD and R-NH₂) are very important for their gelation ability. Differential scanning calorimetry (DSC) measurements for gel of **6-14** in tetralin (1.88 wt.%) show an exothermic peak ($\Delta H = -113.8$ J/g) between 65 and 85 °C, indicating that the gel formation is an exothermic process (Fig. S1 in ESI[†]), which is perfectly consistent with the typical characteristic of heat-set gel⁷. The second and the third runs of scanning show similar DSC curves to that of the first run, elucidating that the gel of **6-14** possesses well reversible behavior in gel-sol transformation.

The gelation properties of SAD and R-NH₂ in molar ratio of 1:1 and 1:3 have also been investigated. We have found that SAD and R-NH₂ in 1:3 shows similar gelation abilities to that in 1:2, indicating excessive R-NH₂ does not affect the formation of heat-set gel. SAD and R-NH₂ in 1:1 also exhibits heat-set gelation behavior. Surprisingly, the resulted heat-set gel is irreversible and thermally super-stable, suggesting excessive SAD affects the property of the heat-set gel.

Considering that the gelation behavior of two-components of SAD and R-NH₂ is sensitive to organic acids, we added different types of organic acids including fatty acids and dicarboxylic acids to this two-component system to tune the assembly structures and properties of this heat-set gel. These fatty acids and dicarboxylic acids used here can not gelate any solvents tested in the experiments (Table S7 in ESI[†]). However, when fatty acid such as dodecanoic acid, tetradecanoic acid and so on is added to the two-component gelators, the reversible heat-set gel transforms to a reversible conventional gel (Fig. 1c and d; Table S8 in ESI[†]). In addition, when fatty acid is replaced with dicarboxylic acid such as succinic acid, sebacic acid, SAD-6, SAD-10 and so on, the reversible heat-set gel transforms to an irreversible heat-set gel (Table S9 in ESI[†]), which shows super-thermo-stability in the temperature range of 0–100 °C (Fig. 1e, f and g). To our knowledge, this irreversible heat-set organogel, showing highly thermal stability, is rarely reported in literatures.¹¹ Therefore, on the basis of the two-component gelators, two rarely reported gels including a reversible heat-set gel and an irreversible heat-set gel, as well as one conventional gel have been formed, which has not been realized in other gel system before this work.

3.2 Rheological properties

The formation of heat-set gel of **6-14** has been traced by rheological technique. The results depicted in Fig. 2a show that with the increase of temperature, the storage shear moduli (G') and loss shear moduli (G'') gradually decrease. G' and G'' reach minimal values, then a cross-over point appears at 67 °C, where G' equals to G'' , affording an indicator for the heat-set gel formation and marking the transition from primarily viscous (solution) to elastic properties (gel).^{7,17} In the temperature range of 67–87 °C, G' is perfectly accordant with G'' , corresponding to the process of the heat-set gel formation. Upon further heated above 87 °C, G' increases and exceeds G'' , indicating the full formation of the heat-set gels. Rheological study for gel of **6-14** with dodecanoic acid shows that with the increase of the temperature, the overall variation tendency of G' and G'' decrease, indicating the gradual transformation from gel to solution. When the temperature reaches 93 °C, a cross-over

point where G' equals to G'' appears, marking the transition from primarily elastic to viscous properties. Upon further heating, G'' increases and exceeds G' , indicating that more and more gel transforms to solution (Fig. 2b). These observations clearly show that after addition of dodecanoic acid to the gel of **6-14**, the heat-set gel has really transformed to conventional gel. It should be noted that these curves are slightly different from those of standard conventional gels, of which G' and G'' usually continuously decrease with the increase of the temperature. The slightly increase of G' and G'' for gel of **6-14** with dodecanoic acid from 34 to 56 °C may be ascribed to the gelator

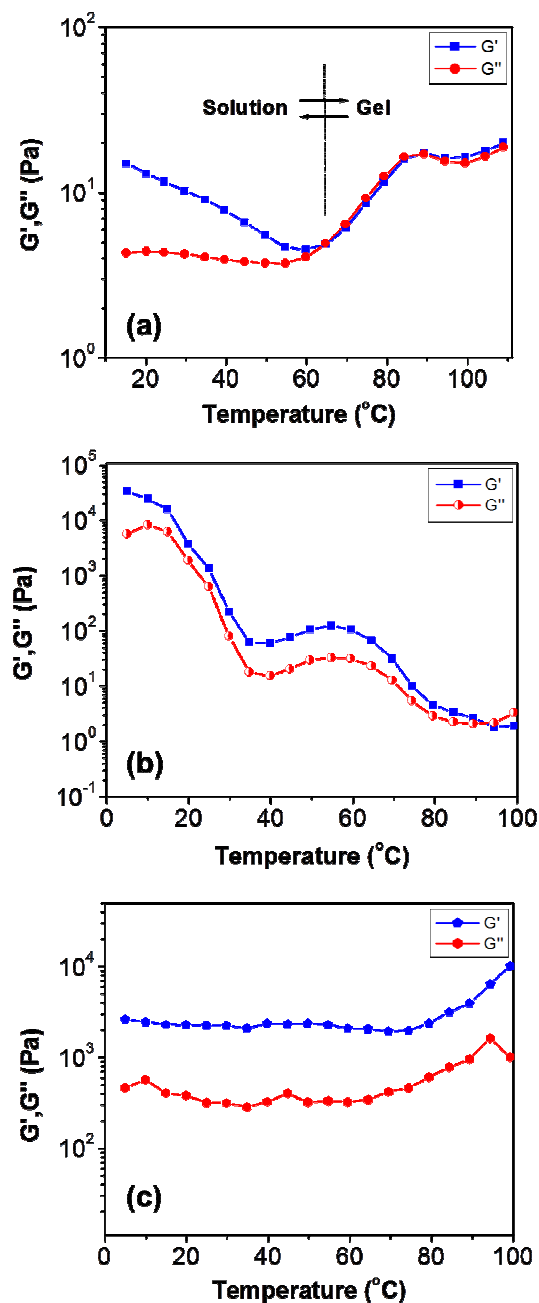


Fig.2 Temperature dependence of the storage modulus (G') and the loss modulus (G''). (a) composite of **6-14** in 1:2 molar ratio in tetralin at a frequency of 1 Hz and stress of 0.1 Pa. (b) gel of **6-14** with dodecanoic acid in 1:2:3 molar ratio at a frequency of 1 Hz and stress of 0.1 Pa. (c) gel of **6-14** with SAD-6 in 1:2:1 molar ratio at a frequency of 1 Hz and stress of 0.1 Pa.

rearrangement. The gel of **6-14** with SAD-6 has also been investigated by rheological measurement. As shown in Fig. 2c, both G' and G'' almost keep constant from room temperature to 80 °C, above which both G' and G'' slightly increase, which demonstrates that the resulted gel possesses highly thermal stability, and the reversible heat-set gel of **6-14** has really transformed to an irreversible heat-set gel after addition of SAD-6.

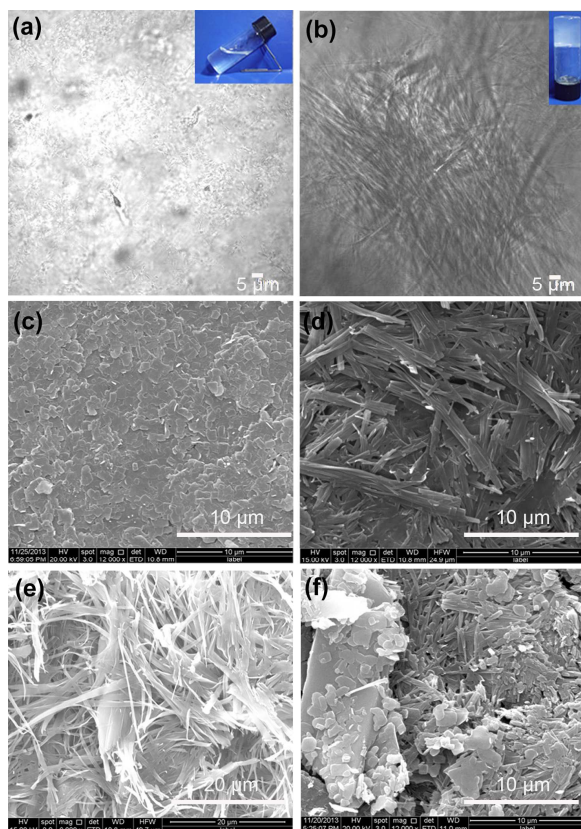


Fig. 3 OM and SEM images of composites/gels. (a) OM image of **6-14** composite mixed at room temperature ($\times 1000$). (b) OM image of **6-14** composite heated at 85 °C ($\times 1000$). (c) SEM image of **6-14** composite dried at room temperature. (d) SEM image of **6-14** composite dried at 85 °C in a vacuum oven. (e) SEM image of xerogel of **6-14** with dodecanoic acid. (f), SEM image of xerogel of **6-14** with SAD-6.

3.3 Morphologies and microstructures

Optical micrograph (OM) and scanning electron microscopy (SEM) have been conducted to investigate the morphologies and microstructures of gels. A typical OM for **6-14** composite in tetralin 1.88 wt.% shows that at room temperature, no obvious assembly structure has been observed (Fig. 3a), whereas at high temperature, fibrous nanoassemblies corresponding to the heat-set gel have been clearly observed (Fig. 3b). SEM measurements reveals that composite of **6-14** mixed and dried at room temperature assumes uniform aggregation structure (Fig. 3c), while the similar mixture dried at 85 °C (corresponding to xerogel of **6-14**) presents nanofiber shape (Fig. 3d). These observations indicate that heating is assumed to facilitate a break–reorganization of hydrogen bonds of gel system, which led to the morphological transition from

uniform aggregation structure to nanofiber capable of gelling solvents.

Conventional gel transformed from heat-set gel of **6-14** has also been characterized by SEM. Fiber-like microstructure has been clearly observed (Fig. 3e), which suggests that although addition of dodecanoic acid extremely change the property of heat-set gel of **6-14**, the morphologies have not been greatly affected. SEM images for the irreversible heat-set gel transformed from heat-set gel of **6-14** show sheet-like shape (Fig. 3f), which indicates the addition of SAD-6 to gel system of **6-14** not only change the property of heat-set gel of **6-14**, but also change the microstructure of this gel.

3.4 Molecular self-assembly

To reveal the molecular assembly mechanism of gel formation, Fourier transform infrared (FT-IR) and small-angle X-ray powder diffraction (SA-XRD) have been used to characterize these three types of gels. As we known, the bands of -NH and -C=O stretching vibrations for free secondary amides usually appear at 3440 and 1680 cm^{-1} respectively.¹⁸ For heat-set gel of **6-14**, Figure 4a clearly demonstrates that upon gelation, the bands corresponding to stretching vibrations of amide -NH and -C=O of SAD-6 red-shift from 3440 to 3294 cm^{-1} and from 1680 to 1642 cm^{-1} respectively, implying the amide group takes part in the formation of intermolecular hydrogen bonds between neighboring amides in gel.¹⁹ Additionally, the band at 1696 cm^{-1} corresponding to the stretching vibration of -COOH of SAD-6 disappears, and a shoulder peak at 1558 cm^{-1} corresponding to antisymmetric COO⁻ stretching vibrations appears, indicating that in gel all -COOH groups of SAD-6 react with $\text{R}_{14}\text{-NH}_2$ by acid-base interaction to form corresponding salt.¹⁹ Therefore, besides hydrogen bond interactions, the electrostatic interactions between deprotonated SAD-6 anion and protonated $\text{R}_{14}\text{-NH}_2$ cation are also beneficial for the gel assembly. Compared with the heat-set gel of **6-14**, IR spectra of the conventional gel (**6-14** with dodecanoic acid) and the irreversible heat-set gel (**6-14** with SAD-6) clearly show absorption peaks of -COOH groups at 1696 and 1709 cm^{-1} respectively (Fig. S2 in ESI[†]), which indicates that the -COOH groups of dodecanoic acid and SAD-6 have not been completely deprotonated. Moreover, these absorption peaks are different from free -COOH ($\sim 1730 \text{ cm}^{-1}$), revealing that both dodecanoic acid and SAD-6 join in the gel formation by hydrogen bonds.¹⁸ SA-XRD patterns of **6-14** xerogel shown in Fig. S3 (ESI[†]) reveal that the d -spacing values of the heat-set gel are of 44.571 Å (001), 22.449 Å (002), 14.855 Å (003), 11.165 Å (004) and 5.590 Å (008), with the 2θ are of 1.98°, 3.93°, 5.95°, 7.91° and 15.84°, respectively. These observations indicate that the xerogel fibers are formed from lamella structures with a long spacing of 44.571 Å. This value is larger than the length of L_1 ($L_1 = \text{R}_{14}\text{-NH}_2 + \text{SAD-6} = 40.317 \text{ Å}$; Evaluated molecular length by optimized CPK model), but smaller than L_2 ($L_2 = \text{R}_{14}\text{-NH}_2 + \text{SAD-6} + \text{R}_{14}\text{-NH}_2 = 59.472 \text{ Å}$), suggesting that the lamella structure in the gel aggregates leans toward one side, rather than arranging on the flat position horizontally (Fig. 4b). The similar results are obtained in **4-12**, **6-12**, **8-14** and **10-16** (Fig. S4 in ESI[†]).

The molecular interactions between SAD-6 and $\text{R}_{14}\text{-NH}_2$ in heat-set gel have been further investigated by single crystal X-ray diffraction. Crystallized in mixed solution of ethanol and distilled water ($v/v = 1:1$), crystals of SAD-6 and $\text{R}_{14}\text{-NH}_2$ composite suitable for X-ray diffraction analysis have been obtained (ESI[†]). The result reveals that in this composite, there

are three types of molecular interactions between SAD-6 and R_{14} -NH₂, including electrostatic interactions, hydrogen bonds, and hydrophobic interactions. As clearly shown in Fig. S5 (ESI[†]), the electrostatic interactions are generated between deprotonated SAD-6 anions and protonated R_{14} -NH₂ cations. Due to the IR spectra of the xerogel is similar to that of the crystal (Fig. S6 in ESI[†]), the reaction between SAD-6 and R_{14} -NH₂ is drove by acid-base interaction, leading the formation of the corresponding salt, which is consistent with the IR result. The hydrogen bond interactions are formed between SAD-6 anions, as well as between SAD-6 anion and R_{14} -NH₂ cation. As shown in (Fig. S5 in ESI[†]), the imino of amide in one SAD-6 anion donates H atom to the carbonyl O atom of amide in the other SAD-6 anion, generating N(1)-H(1)···O(3) hydrogen bond, rely on which adjacent SAD-6 anions are connected together along the *a* axis. Additionally, the protonated amino group of R_{14} -NH₂ cation donates H atoms to the carboxylic O1 and O2 atoms of SAD-6 anion, forming N(2)-H(2)···O(1) and N(2)-H(2)···O(2) hydrogen bonds, depend on which R_{14} -NH₂ cations are linked together with SAD-6 anions. Based on the electrostatic interactions and intermolecular hydrogen bonds, a supermolecular layer assembled by acid-base complex of SAD-6 anion and R_{14} -NH₂ cation is generated (Fig. 4b). These layers are further connected together by hydrophobic interactions between alkyl chains of R_{14} -NH₂ cations, resulting in a 3D supramolecular structure (Fig. S7 in ESI[†]). The thick of the layer measured from the crystal structure is about 44.271(3) Å, which is much close to 44.571 Å, the long spacing of heat-set gel of **6-14**. This result illustrates that the assembly mode of SAD-6 and R_{14} -NH₂ in heat-set gel is consistent with that in the crystal. SA-XRD shows that the peaks in the small angle of the measured diffraction pattern of xerogel closely match to those simulated from the single-crystal diffraction data (Fig. 4c), which further indicates the lamella structure in the gel aggregate is consistent with the layer structure in the crystal. These observations reveal that the molecular assembly of SAD-6 and R_{14} -NH₂ in the lamella structure of gel also depends on the electrostatic interaction, intermolecular hydrogen bonds, and hydrophobic interactions, as presented in the crystal structure.

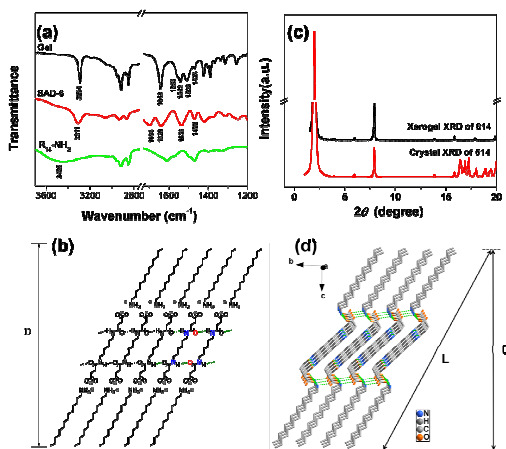


Fig.4 Molecular self-assembly. (a), FT-IR spectra of the heat-set gel of **6-14** (1.88 wt.%), SAD-6 and R_{14} -NH₂. (b) Proposed local microstructure of aggregates in heat-set gel of **6-14**. (c) SA-XRD patterns of the **6-14** xerogel and simulated XRD pattern from the crystal data of **6-14** composite. (d) 3D crystal structure of **6-14** composite.

4. Conclusion

In summary, a reversible heat-set gel has been formed from SAD and R-NH₂. Interestingly, by addition of fatty acid and dicarboxylic acid, this heat-set gel can be successfully adjusted to conventional gel and irreversible heat-set gel, respectively. Structural investigations reveal that the molecular assembly of the heat-set gel depends on electrostatic interaction, intermolecular hydrogen bonds, and hydrophobic interactions. The reversible heat-set gel and the irreversible heat-set gel, rarely reported but greatly desired currently, may find wide range of applications as new thermo-responsive materials.

Acknowledgments

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† Electronic supplementary information (ESI)

available: Synthesis and characterization of succinamic acid derivatives, method for obtaining xerogels for powder XRD, the detailed experiment for crystal growth, Tables S1-S9, and Figures S1-S7. See DOI: 10.1039/xxxxxx.

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TOC graphic for

Heat-set gel formed from easily accessible gelators of succinamic acid derivative (SAD) and primary alkyl amine (R-NH₂)

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We report here a gel system based on two-component gelators containing a succinamic acid derivative (SAD) and a primary alkyl amine (R-NH₂), from which the formation of heat-set gel, conventional gel and irreversible heat-set gel can be achieved in aromatic solvents.

