Research Article

Investigation of Self-Assembly of Two-Component Organogel System Based on Trigonal Acids and Aminobenzothiazole Derivatives

Youbo Di, Wei Hong, and Jinming Dai

College of Textile Engineering and Art, Taiyuan University of Technology, Taiyuan 030024, China

Correspondence should be addressed to Jinming Dai; jinmingdai12@126.com

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We reported here the gelation behaviors of two-component organogel system based on different acids and aminobenzothiazole derivatives in various organic solvents. Their gelation behaviors in 20 solvents were tested as new organic gelators. It was shown that the molecular skeletons and substituted groups in these compounds played a crucial role in the gelation behavior of the mixtures. Only the binary mixture of 2-aminobenzothiazole and trigonal 1,3,5-benzenetricarboxylic acid with aromatic core could form organogels in ethanol and acetone. Morphological observations reveal that the microstructures of both xerogels showed similar wrinkle-shaped domains composed of sheet-like aggregates with many holes. Spectral studies reveal the hydrogen bonding interaction between the amide of the gelator and lamellar-like structure of the aggregates in both gels. The present investigation is a perspective to provide new clues for the design of new nanomaterials and functional textile materials with special microstructures.

1. Introduction

The self-assembly of small functional molecules into supramolecular structures is a powerful approach to the development of new materials and nanoscale devices [1–4]. The properties of these materials depend not only on the nature of their molecular constituents but also on the precise spatial positioning of the functional groups [5, 6]. As a novel class of self-assembled materials, low-molecular-mass organic gels (LMOGs) have become one of the most active frontiers in recent years because they can organize into regular nanoarchitectures through specific noncovalent interactions including hydrogen bonds, π - π interactions, hydrophobic interactions, and other forces [7–10]. Nowadays, physical gelation of organic solvents by LMOGs has become one of the hot areas in soft matter research due to their scientific values and many potential applications in biomedical field, including multifunctional textile materials, drug release, and implants [11–13]. The noncovalent nature of the three-dimensional networks within the supramolecular gels promises accessibility for designing and constructing new textile materials and other molecular devices [14–17]. In addition, most of

the gelators reported so far are either serendipitous or derivatives from a well-known gelator, and in most cases, a detailed description of the supramolecular aggregates responsible for gel formation is not investigated due to the intrinsic difficulty of analyzing the superstructure within a gel. Recently, Tang and coworkers reported the utilization of the complementary carboxyl and pyridyl groups in preparing a new kind of gelators [18–20]. For example, they described the preliminary result of the hydrogel based on the complex formed from para-hydroxy pyridinium salt of 1,2,4,5-benzene tetracarboxylic acid [18] and investigated the structure-property relation of hydrogels based on pyridinyl amino butanoic acid isomeric compounds [19].

In this study, we reported the gelation behaviors of two-component organogel system based on different acids and aminobenzothiazole derivatives in various organic solvents. Their gelation behaviors in 20 solvents were tested as new organic gelators. We found that the self-assembly of these two-component mixtures can be controlled and directed to form sheet-like supramolecular structures. The detailed morphologies and assembly modes of gels were investigated by scanning electron microscopy (SEM), Fourier transform

TABLE 1: Gelation behaviors at room temperature^a.

Solvents	SC2	SC3	SN3	NC2	NC3	NN3
Cyclopentanone	PS	PS	PS	PS	PS	PS
DMF	S	S	S	S	PS	PS
1,4-Dioxane	PS	I	PS	PS	PS	S
Petroleum ether	I	PS	I	I	I	I
Pyridine	S	S	PS	PS	PS	S
Ethyl acetate	I	PS	PS	I	PS	PS
n-Butanol	I	I	PS	PS	PS	PS
Chloroform	PS	PS	S	S	S	PS
n-Hexane	I	PS	PS	I	PS	PS
Aniline	PS	S	S	PS	S	S
Nitrobenzene	PS	PS	PS	PS	PS	S
n-Butyl acrylate	I	PS	PS	PS	PS	PS
Toluene	I	PS	I	I	I	I
Benzene	I	PS	PS	PS	PS	PS
THF	PS	PS	PS	PS	PS	S
Acetone	PS	G(2.5)	S	PS	S	S
Ethanol	PS	G(2.5)	PS	PS	PS	PS
Ethanolamine	PD	S	S	I	S	PS
Cyclohexanone	PS	PS	S	I	S	PS
DMSO	PS	S	S	PS	S	S

^aS: solution; PS: partially soluble; G: gel; I: insoluble; for gels, the critical gelation concentrations at room temperature are shown in parentheses (%w/v).

infrared spectrometer (FT-IR), and X-ray diffraction (XRD) methods. This report may afford a specific approach to understanding the soft matter and design of new nanomaterials and functional textile materials.

2. Experimental Section

2.1. Reagents and Materials. The starting materials, 2-aminobenzothiazole (98%), 2-aminobenzimidazole (97+%), 1,3,5-benzenetricarboxylic acid (98%), nitrilotriacetic acid (99%), and terephthalic acid (98+%) were purchased from Alfa Aesar China Chemicals, TCI Shanghai Chemicals, and Sigma-Aldrich (Shanghai) Chemicals without further purification. All used 20 kinds of solvents were obtained from Beijing Chemicals in purity analysis with names shown in Table 1.

2.2. Gelation Test. All two-component organogels were prepared according to a simple procedure. Firstly, these acids and amino compounds were mixed according to the number matching of intramolecular carboxylic acid and amino groups, respectively. For example, 1,3,5-benzenetricarboxylic acid was mixed with both amino compounds with the molar ratio of 1 : 3, respectively. Then, a weighted amount of binary mixtures and a measured volume of selected pure organic solvent were placed into a sealed glass bottle, and the solution was heated in a water bath with 75°C for 20 minutes until the solid was dissolved. Then, the solution was cooled to room temperature in air, and the test bottle was inverted to see if

a gel was formed. When the binary mixtures formed a gel by immobilizing the solvent at this stage, it was denoted as “G”. For the systems in which only solution remained until the end of the tests, they were referred to as solution (S). When the binary mixtures formed into a few precipitate in some solvent, it was denoted as “PS”. The system in which the potential gelator of binary mixtures could not be dissolved even at the boiling point of the solvent was designated as an insoluble system (I). Critical gelation concentration (CGC) refers to the minimum concentration of the gelator for gel formation.

2.3. Characterization Technology. Firstly, these xerogels were prepared by a vacuum pump for 12–24 h from the as-formed gels under the critical gelation concentration. Then, the dried samples were attached to different substrates, such as copper foil, glass, KBr, or CaF₂ slice, for morphological and spectral investigation, respectively. Before SEM measurement, the samples were fixed by conductive adhesive tape and shielded by gold. SEM pictures of the xerogels were taken on a Hitachi S-4800 field emission scanning electron microscopy with the accelerating voltage of 2.0 kV. Transmission FT-IR spectra of the xerogels were obtained by a JASCO FT/IR-660 plus spectrophotometer (JASCO Corp., Tokyo, Japan). The measurement results of FT-IR spectra were obtained by average 64 scans and at a resolution of 4 cm⁻¹. The XRD measurement was conducted using a Rigaku D/max 2550PC diffractometer (Rigaku Inc., Tokyo, Japan). The XRD pattern was obtained using CuK α radiation with an incident wavelength of 0.1542 nm under a voltage of 40 kV and a current of 200 mA.

3. Results and Discussion

3.1. Gelation Behaviors. The gelation performances of all binary mixtures in 20 solvents are tested. The binary mixtures of 2-aminobenzothiazole with terephthalic acid, 1,3,5-benzenetricarboxylic acid, and nitrilotriacetic acid are denoted as SC2, SC3, and SN3, respectively. For the binary mixtures of 2-aminobenzimidazole with these acids, NC2, NC3, and NN3 are similarly denoted, respectively. The experimental data showed that only the case of SC3, the binary mixture of 2-aminobenzothiazole and 1,3,5-benzenetricarboxylic acid could form white opaque organogels in ethanol and acetone, as shown in Figure 1. At the same time, other mixtures were inefficient gelators with the detailed data shown in Table 1. The present experimental results indicated that the change of aromatic/alkyl cores and molecular skeletons in acids and substituted groups in amino derivatives could regulate the gelling abilities of these binary mixtures. It is reported that C3-symmetrical molecules are highly suitable building blocks for the formation of mesophases as well as cylindrically shaped fiber [21, 22]. In the present case, the C3-symmetric molecular structures and aromatic cores in acids seemed to be more favorable for the gelation of organic solvents than the case with other molecular structures. In addition, the substituted group of benzothiazole showed better gelation properties than benzimidazole part. The reason for the influence of molecular structures on the gelation behaviors could be proposed to the change of the spatial

FIGURE 1: Photographs of SC3 organogels from ethanol (a) and acetone (b), respectively.

conformation and assembly mode of the gelators, which decreased the ability of the gelator molecules to self-assemble into ordered structures, a necessity for forming organized network structures. Furthermore, it should be noted that the organogels of SC3 only form in ethanol and acetone rather than in present other solvents due to the complexed conditions, such as different hydrogen bonding and π - π interactions, as well as other intermolecular forces between gelators and solvents molecules. So the formation of gels in present system is a cooperative result of many factors.

3.2. Morphological Investigation. To obtain a visual insight into the gel microstructures, the typical nanostructures of these gels were studied by SEM technique, as shown in Figure 2. Many researchers have reported that a gelator molecule constructs nanoscale superstructures such as nanofibers, nanoribbons, and nanosheets in a supramolecular gel [23, 24]. From the present both images, it can be easily investigated that the microstructures of the xerogels of SC3 gels from ethanol and acetone showed similar wrinkle-shaped domains composed of sheet-like aggregates with many holes. The similar morphologies suggested similar microstructures and molecular assembly modes for SC3 gels in solvents of ethanol and acetone. The morphologies of the aggregates shown in the SEM images may be also rationalized by considering a commonly accepted idea that highly directional intermolecular interactions, such as hydrogen bonding and/or π - π interactions, favor formation of belt or fiber structures. It should be noted that the addition of aromatic core in 1,3,5-benzenetricarboxylic acid of SC3 provides the gelators more opportunities in adopting conformations of lower energies, which must weaken the hydrogen-bonding

interactions between gelator molecules and result in loss of flexible fine fibrous structure [25].

3.3. Hydrogen Bond Investigation. It is well-known that hydrogen bonding plays an important role in the formation of organogels. At present, in order to further clarify both organogels, we have measured the FT-IR spectra of these binary mixtures in chloroform solution, KBr pellet, and xerogel forms, as shown in Figure 3. As for the spectrum of SC3 in chloroform solution, as shown in Figure 3(a), two main peaks are observed at 3498, 1727, and 1615 cm^{-1} . These bands can be assigned to the N-H stretching, C=O stretching of ester, and amide I band, respectively [26]. The spectrum in KBr pellet is similar to the one above, indicating the obvious characters of functional groups in molecular skeletons. As far as the SC3 xerogels from ethanol or acetone were concerned, these bands shifted to 3396, 1730, and 1628 cm^{-1} , respectively. The shifts of these bands indicated the formation of different hydrogen bonding in the gel state. Compared with the spectra of xerogels from both different solvents, we found that the spectrum of xerogel from ethanol is similar to that from acetone. This implied that there were similar hydrogen bonding interactions in both xerogels, even though they are from very different solvent systems.

3.4. XRD Investigation. Furthermore, the XRD of both binary xerogels from ethanol and acetone is measured, as shown in Figure 4. The curve for SC3 xerogel from ethanol shows main peaks in the angle region (2 values, 5.20°, 11.45°, 16.04°, and 18.41°) corresponding to d values of 1.70 nm, 0.77 nm, 0.55 nm, and 0.48 nm, respectively. In addition, the curve for xerogel in acetone sample shows main peaks in the angle region (2 values, 5.25°, 11.34°, 16.10°, and 18.49°) corresponding to d values of 1.68 nm, 0.78 nm, 0.55 nm, and 0.48 nm, respectively. The corresponding d values in both cases approximately followed a ratio of 1:1/2:1/3:1/4, suggesting a lamellar-like structure of the aggregates in both gels [27]. This data is in well accordance with the results from morphological investigation. In addition, it is noteworthy that the spacing of the first peak in both curves is very close, which demonstrates that the molecular structures have a great effect on the packing mode of the binary mixtures. Considering the XRD results described above and the hydrogen bonding nature of the organized packing of these binary mixtures as confirmed by FT-IR measurements, a possible packing mode of SC3 organogel in ethanol and acetone was proposed and is schematically shown in Figure 5.

4. Conclusions

The gelation behaviors of two-component organogel system based on different acids and aminobenzothiazole derivatives can be regulated by changing molecular skeletons and substituted groups. Only the binary mixture of 2-aminobenzothiazole and 1,3,5-benzenetricarboxylic acid could form organogels in ethanol and acetone. This result

FIGURE 2: SEM images of xerogels of SC3 gels from ethanol (a) and acetone (b), respectively.

FIGURE 3: FT-IR spectra of SC3 in chloroform solution (a), KBr pellet (b), and xerogels from gels in ethanol (c) and acetone (d), respectively.

FIGURE 4: X-ray diffraction patterns of xerogels of SC3 gels from ethanol (a) and acetone (b), respectively.

indicated that the C3-symmetric molecular structures and aromatic cores in acids seemed to be more favorable for the gelation of organic solvents than the case with other molecular structures. In addition, the substituted group of benzothiazole showed better gelation properties than benzimidazole part. The microstructures of the xerogels showed similar wrinkle-shaped domains composed of sheet-like aggregates with many holes. FT-IR and XRD studies reveal the hydrogen bonding interaction between the amide of the gelator and lamellar-like structure of the aggregates in both gels. The present investigation is a perspective to provide new clues for the design of new nanomaterials and functional textile materials with special microstructures.

Conflict of Interests

The authors declare that they have no direct financial relation with the commercial identities mentioned in this paper that might lead to a conflict of interests for any of the authors.

FIGURE 5: A possible assembly mode of SC3 gels from ethanol.

Acknowledgments

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