Research Article

Self-Assembly and Soft Material Preparation of Binary Organogels via Aminobenzimidazole/Benzothiazole and Acids with Different Alkyl Substituent Chains

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The gelation behaviors of binary organogels composed of aminobenzimidazole/benzothiazole derivatives and benzoic acid with single-/multialkyl substituent chain in various organic solvents were designed and investigated. Their gelation behaviors in 20 solvents were tested as new binary organic gelators. This showed that the number and length of alkyl substituent chains and benzimidazole/benzothiazole segment have played a crucial role in the gelation behavior of all gelator mixtures in various organic solvents. More alkyl chains in molecular skeletons in present gelators are favorable for the gelation of organic solvents. The length of alkyl substituent chains has also played an important role in changing the gelation behaviors and assembly states. Morphological studies revealed that the gelator molecules self-assemble into different aggregates from wrinkle, lamella, belt, to fiber with change of solvents. Spectral studies indicated that there existed different H-bond formation and hydrophobic force, depending on benzimidazole/benzothiazole segment and alkyl substituent chains in molecular skeletons. The prepared nanostructured materials have wide perspectives and many potential applications in nanoscience and material fields due to their scientific values. The present work may also give new clues for designing new binary organogelators and soft materials.

1. Introduction

Organogels, which are various three-dimensional (3D) aggregates with micrometer-scale lengths and nanometer-scale diameters immobilizing the flow of liquids, have been known for potential applications on materials, drug delivery, agents, and sensors as well as water purification in recent years [1–9]. The driving forces responsible for gel formations are specific or noncovalent interactions such as the dipole-dipole interaction, van der Waals forces, hydrogen bonding, π - π stacking, and host-guest interaction [10–15]. In particular, complementary hydrogen bonding patterns play a very important role in forming both mono- and multicomponent

architectures, and their application in the fabrication of organogels has been attempted [16–23]. The reversibility as a crucial feature of supramolecular materials enables these smart gels to be superior to conventional ones and brings accessibility for designing new functional materials [24–30].

Benzimidazole/benzothiazole groups, as versatile units, of which one ring is a benzene ring and one is a five-membered ring with N or S elements, have been widely chosen for designing new amphiphiles because of their unique directional self-association through π - π stacking and van der Waals interactions in the process of supramolecular assembly [31–33]. For example, some benzimidazole and benzothiazole

TABLE 1: Gelation behaviors via acids with single-alkyl substituent chains.

Solvents	S-PC12	S-PC14	S-PC16	S-PC18	N-PC12	N-PC14	N-PC16	N-PC18
Aniline	PS	PS	G (2.0)	PS	PS	PS	PS	PS
Benzene	S	S	PS	PS	PS	PS	PS	I
Acetone	S	PS	I	PS	PS	PS	PS	I
n-Hexane	PS	PS	PS	PS	PS	PS	PS	I
Toluene	S	S	PS	PS	PS	PS	PS	PS
Pyridine	S	S	S	S	S	S	PS	PS
Cyclopentanone	S	S	I	PS	S	S	PS	I
Cyclohexanone	S	S	PS	PS	S	S	PS	I
Nitrobenzene	PS	PS	G (2.0)	G (2.5)	PS	PS	PS	PS
n-Butanol	PS	PS	I	PS	PS	PS	PS	PS
Ethanolamine	PS	G (1.5)	PS	G (2.5)	PS	G (2.0)	PS	G (2.5)
n-Butyl acrylate	S	S	I	PS	PS	PS	PS	I
1,4-Dioxane	S	S	PS	PS	PS	PS	I	PS
Petroleum ether	PS	PS	PS	S	PS	PS	PS	I
Ethyl acetate	PS	PS	PS	PS	PS	PS	PS	I
Chloroform	S	S	PS	PS	PS	PS	PS	PS
Dichloromethane	S	S	S	PS	PS	PS	PS	I
THF	S	S	S	S	PS	PS	PS	PS
DMF	PS	PS	PS	PS	PS	PS	PS	PS
DMSO	S	S	S	S	S	S	S	S

DMF: dimethylformamide; THF: tetrahydrofuran; DMSO: dimethyl sulfoxide; S: solution; PS: partially soluble; G: gel; I: insoluble; for gels, the critical gelation concentrations at room temperature are shown in parentheses (% w/v).

derivatives formed chiral assembly films through a cooperative stereoregular π - π stacking of the functional groups together with the long alkyl chains in a helical sense [31]. Therein the relationship between the chirality of assembly films and the molecular structures of amphiphiles as well as their H-bond or coordination behaviors was discussed. In our reported work, the gelation properties of some cholesterol imide derivatives consisting of cholesteryl units and photoresponsive azobenzene substituent groups have been investigated [34]. We found that a subtle change in the head-group of azobenzene segment can produce a dramatic change in the gelation behavior of both compounds. In addition, the gelation properties of bolaform and trigonal cholesteryl derivatives with different aromatic spacers have been characterized [35]. Therein we have investigated the spacer effect on the microstructures of such organogels and found that various kinds of hydrogen bond interactions among the molecules play an important role in the formation of gels.

As a continuous research work, herein, we have designed and prepared new binary organogels composed of aminobenzimidazole/benzothiazole derivatives and benzoic acid with different alkyl substituent chains. In present benzoic acid derivatives, the long alkyl chains were symmetrically attached to the benzene rings to form single or three substituent states. We have found that some of present mixtures could form different organogels in various organic solvents. Morphological characterization of the organogels revealed different structures of the aggregates in the gels. We have investigated the effect of alkyl substituent chains and benzimidazole/benzothiazole residues in gelators on the microstructures of

such organogels and found different kinds of hydrogen bond interactions between intermolecular assembly units.

2. Experiments

2.1. Reagents. All materials, 2-aminobenzimidazole, 2-aminobenzothiazole, methyl 3,4,5-trihydroxybenzoate, 4-hydroxybenzenecarboxylic acid, 1-bromooctadecane, 1-bromohexadecane, 1-bromotetradecane, and 1-bromododecane, were purchased from Alfa Aesar Tianjin Chemicals, Aldrich Chemicals, and TCI Shanghai Chemicals, respectively. Other used reagents shown in Table 1 were all of analysis purity from Beijing Chemicals and were distilled before use. Deionized water was used in all cases. 4-Alkyloxy-benzoic acid and 3,4,5-tris(alkyloxy)benzoic acid with different alkyl substituent chains were synthesized in our laboratory according to previous report [36] and confirmed by ^1H NMR. The molecular structures of present used acids/amine compounds were shown in Figure 1.

2.2. Gel Preparation. At present 16 kinds of binary mixtures were tested to prepare possible organogels according to a simple procedure. Firstly, these acid/amine compounds were mixed with 1:1 molar ratio according to the number matching of intermolecular carboxylic acid and amine group, 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 ultrasonicated in a sonic bath for 15 min in order to obtain good dispersion. After that, the solution was heated in a water

FIGURE 1: Molecular structures of present used acids/amine compounds.

bath at a temperature of 80°C for 15 min. Then, the solution was cooled to room temperature in air and the test bottle was inverted to see if a gel was formed. At this stage, G, S, PS, and I were denoted to characterize the states of binary mixtures, indicating gel, solution, a few precipitate, and insoluble systems, respectively. Critical gelation concentration refers to the minimum concentration of the gelator for gel formation.

2.3. Instruments and Characterization. These prepared organogels under the critical gelation concentration were dried by a vacuum pump for more than 12 h to remove solvents and form xerogels. Then, the obtained xerogel samples were attached to different substrates, such as mica, copper foil, glass, and CaF₂ slice, for morphological and spectral investigations, respectively. AFM data were measured by using Nanoscope VIII Multimode Scanning Probe Microscope (Veeco Instrument, USA) with silicon cantilever probes. All AFM images were shown in the height mode without any image processing except flattening. SEM images of the xerogels were measured on a Hitachi S-4800 field emission

scanning electron microscope with the accelerating voltage of 5–15 kV. For SEM measurement, the samples were coated on copper foil fixed by conductive adhesive tape and shielded by gold nanoparticles. The XRD was measured by using a Rigaku D/max 2550PC diffractometer (Rigaku Inc., Tokyo, Japan) with CuK α radiation wavelength of 0.1542 nm under a voltage of 40 kV and a current of 200 mA. FT-IR spectra were obtained by Nicolet is/10 FT-IR spectrophotometer from Thermo Fisher Scientific Inc. by an average of 32 scans and at a resolution of 4 cm⁻¹.

3. Results and Discussion

3.1. Gelation Behaviors. The gelation performances of all binary mixtures in 20 solvents are tested. The experimental data showed that the binary mixtures of 4-alkoxybenzoic acid with single-alkyl substituent chain and 2-aminobenzimidazole/2-aminobenzothiazole could form organogels in special organic solvents, as listed in Table 1. The binary mixtures of 4-alkoxybenzoic acid with methylene numbers

FIGURE 2: Photographs of as-made organogels: (a) S-PC14 and S-PC18 in ethanolamine, S-PC16 and S-PC18 in nitrobenzene, and S-PC16 in aniline (from left to right, resp., the following is the same); (b) N-PC14 and N-PC18 in ethanolamine; (c) S-TriC14 and S-TriC16 in aniline, S-TriC18 in aniline and nitrobenzene, 1,4-dioxane, and DMF; (d) N-TriC18 from DMF, n-butyl acrylate, nitrobenzene, 1,4-dioxane, and aniline.

of 12, 14, 16, and 18 and 2-aminobenzothiazole are denoted by S-PC12, S-PC14, S-PC16, and S-PC18, respectively. Similarly, the binary mixtures of present acids with single-alkyl substituent chain and 2-aminobenzimidazole are denoted by N-PC12, N-PC14, N-PC16, and N-PC18, respectively. Firstly, for the mixtures with 2-aminobenzothiazole, S-PC12 does not form any organogel in present solvents. For the case of S-PC14, only one gel in ethanolamine was prepared. With the increment of the methylene numbers to 16 and 18, S-PC16 and S-PC18 can form gel in 2 solvents, respectively. However, for the mixtures with 2-aminobenzimidazole, only N-PC14 and N-PC18 can form gel in ethanolamine, respectively. The photographs of all formed organogels in different solvents were shown in Figure 2. In addition, the binary mixtures of 3,4,5-tris(alkyloxy)benzoic acid with multialkyl substituent chain and 2-aminobenzimidazole/2-aminobenzothiazole could form organogels in special organic solvents, as listed in Table 2. The binary mixtures of 3,4,5-tris(alkyloxy)benzoic acid with methylene numbers of 12, 14, 16, and 18 and 2-aminobenzothiazole are denoted by S-TriC12, S-TriC14, S-TriC16, and S-TriC18, respectively. Similarly, the binary mixtures of present acids with three alkyl substituent chains and 2-aminobenzimidazole are denoted by N-TriC12,

N-TriC14, N-TriC16, and N-TriC18, respectively. Firstly, for the mixtures with 2-aminobenzothiazole, S-TriC12 does not form any organogel in present solvents. For the case of S-TriC14 and S-TriC16, only one gel in aniline was prepared. With the increment of the methylene number to 18, S-TriC18 can form gel in 4 solvents, including aniline, nitrobenzene, 1,4-dioxane, and DMF. However, for the mixtures with 2-aminobenzimidazole, only N-TriC18 can form gel in 5 solvents, including aniline, nitrobenzene, n-butyl acrylate, 1,4-dioxane, and DMF. The present data indicated that change of alkyl substituent chains can have a profound effect upon the gelation abilities of these studied mixtures. It seemed that more alkyl chains in molecular skeletons in present mixture gelators are more favorable for the present mixtures. In addition, the length of alkyl chains in acids for intermolecular stacking in the gel formation process is also obvious for all cases. The reasons for the strengthening of the gelation behaviors can be assigned to the change of the spatial conformation and assembly modes of the gelators due to intermolecular hydrogen bonding of the gelators [37, 38], which may increase the ability of the gelator molecules to self-assemble into ordered structures, a necessity for forming organized assembly structures.

TABLE 2: Gelation behaviors via acids with multialkyl substituent chains.

Solvents	S-TriC12	S-TriC14	S-TriC16	S-TriC18	N-TriC12	N-TriC14	N-TriC16	N-TriC18
Aniline	PS	G (1.5)	G (2.0)	G (2.5)	PS	PS	PS	G (2.5)
Benzene	S	S	S	PS	S	PS	PS	I
Acetone	S	PS	I	PS	PS	PS	PS	I
n-Hexane	S	PS	PS	PS	PS	PS	PS	I
Toluene	S	S	S	S	S	PS	PS	PS
Pyridine	S	S	S	S	S	S	S	S
Cyclopentanone	S	S	PS	PS	S	S	PS	I
Cyclohexanone	S	S	PS	PS	S	PS	PS	I
Nitrobenzene	S	S	PS	G (2.0)	PS	PS	PS	G (2.5)
n-Butanol	S	S	PS	PS	S	PS	PS	S
Ethanolamine	PS	PS	PS	PS	PS	PS	PS	PS
n-Butyl acrylate	S	S	S	PS	S	PS	PS	G (2.0)
1,4-Dioxane	S	S	PS	G (2.5)	S	PS	PS	G (2.5)
Petroleum ether	PS	PS	PS	PS	S	PS	I	I
Ethyl acetate	S	S	I	PS	PS	PS	PS	PS
Chloroform	S	S	S	S	S	S	PS	S
Dichloromethane	S	S	S	S	S	S	PS	I
THF	S	S	S	S	S	S	S	PS
DMF	S	PS	PS	G (2.0)	S	PS	PS	G (2.0)
DMSO	S	S	S	S	S	S	S	S

DMF: dimethylformamide; THF: tetrahydrofuran; DMSO: dimethyl sulfoxide; S: solution; PS: partially soluble; G: gel; I: insoluble; for gels, the critical gelation concentrations at room temperature are shown in parentheses (% w/v).

3.2. Morphological Investigation. Many researchers have reported that a gelator molecule constructs nanoscale superstructures such as nanofibers, nanoribbons, and nanosheets in a supramolecular gel [39, 40]. To obtain a visual insight into the gel microstructures, the typical nanostructures of these gels were studied by SEM technique, as shown in Figures 3-4. From the present diverse images, it can be easily investigated that the microstructures of the xerogels of all mixtures in different solvents are significantly different from each other, and the morphologies of the aggregates change from wrinkle, lamella, belt, to fiber with change of solvents. In addition, more wrinkle-like aggregates with different sizes were prepared in gels of S-TriC18 and N-TriC18 with three alkyl substituent chains in molecular skeletons. Furthermore, the xerogels of S-PC18, S-TriC18, and N-TriC18 in nitrobenzene, with S-PC18 and N-PC18 in ethanolamine, were characterized by AFM, as shown in Figure 5. From the images, it is interesting to note that these big wrinkle or belt aggregates were composed of many little rod-like or needle-like nanodomains by stacking of the present gelator mixtures. The morphologies of the aggregates shown in the SEM and AFM images may be rationalized by considering a commonly accepted idea that highly directional intermolecular interactions, such as hydrogen bonding or π - π interactions, favor formation of organized belt or fiber micro-/nanostructures [41, 42]. The differences of morphologies between molecules with single-/multialkyl substituent chains can be mainly due to the different strengths of the intermolecular hydrophobic force between alkyl substituent chains, which have played

an important role in regulating the intermolecular orderly staking and formation of special aggregates.

3.3. Spectral Investigation. In addition, in order to further investigate the orderly stacking of xerogels nanostructures, XRD patterns of all xerogels from gels were measured. Firstly, the data of S-TriC14, S-TriC16, and S-TriC18 were taken as an example, as shown in Figure 6. The curves of S-TriC18 xerogels from 4 solvents show similar peaks in the angle region (2θ values, 4.52, 6.04, 12.14, 19.86, and 22.56°) corresponding to d values of 1.96, 1.46, 0.73, 0.45, and 0.39 nm, respectively. As for the curves of S-TriC14 and S-TriC16 in aniline, the minimum 2θ values are 4.94 and 5.14°, corresponding to d values of 1.79 and 1.72 nm, respectively. The decrement of values can be mainly assigned to the length change of methylene chains in the stacking units. In addition, other factors, such as the number of alkyl substituent chains and benzimidazole/benzothiazole segment, were also investigated. The curves of S-PC18, S-TriC18, and N-TriC18 in nitrobenzene were shown in Figure 7. While S-PC18 with single-alkyl substituent chains in molecular skeleton showed the minimum 2θ value of 5.4°, it changed to 4.38 and 4.46° for S-TriC18 and N-TriC18 with three alkyl substituent chains in molecular skeleton. The corresponding d values are 1.64, 2.02, and 1.98 nm, respectively. The results indicated that more alkyl substituent chains in molecular skeleton were favorable for the intermolecular organized assembly [43, 44]. Furthermore, the curves of S-PC18 and N-PC18 in ethanolamine were also measured to investigate the effects of benzimidazole/benzothiazole segments. Main

FIGURE 3: SEM images of xerogels: (a) S-PC14 in ethanolamine; (b)-(c) S-PC16 in aniline and nitrobenzene; (d)-(e) S-PC18 in nitrobenzene and ethanolamine; (f)-(g) N-PC14 and N-PC18 in ethanolamine.

peaks were observed at 5.68 and 6.02° for S-PC18 and N-PC18, respectively. The corresponding d values are 1.56 and 1.47 nm, respectively. The XRD results described above demonstrated again that the factors had great effects on the assembly modes of these gelator mixtures.

It is well known that hydrogen bonding plays an important role in the self-assembly process of organogels [45, 46]. At present, we have measured the FT-IR spectra of xerogels of all compounds in order to further clarify this and investigate the effect of other factors on assembly. Firstly, S-TriC14, S-TriC16, and S-TriC18 were taken as examples, as shown in Figure 8. As for spectra of S-TriC18 xerogels, some main peaks were observed at 3146 , 2918 , 2848 , 1679 , and 1467 cm^{-1} , respectively, which can be assigned to the N-H stretching, methylene stretching, amide I band, and methylene scissoring, respectively [47]. These bands indicate H-bond formation between intermolecular amide and carboxylic acid groups in the gel state. In addition, the spectra of xerogels of S-PC18, S-TriC18, and N-TriC18 in nitrobenzene were also compared. As shown in Figure 9, one observed change is that the peaks assigned to carbonyl group shifted from 1709

to 1679 cm^{-1} , respectively. Another change is that the peaks assigned to N-H stretching shifted from 3392 to 3340 cm^{-1} , respectively. This implied that there were differences in the strength of the intermolecular hydrogen-bond interactions in these xerogels. The present data further verified that the number of alkyl substituent groups in molecular skeletons can regulate the stacking of the gelator molecules to self-assemble into ordered structures by distinct intermolecular hydrogen bonding.

3.4. Discussion. Considering the XRD results described earlier and the hydrogen bonding nature of the organized packing of these binary mixtures as confirmed by FT-IR measurements, a possible packing mode of S-TriC18 was proposed and schematically shown in Figure 10. As for xerogels of S-TriC18, due to the near position of S element in benzothiazole ring, after the intermolecular hydrogen bonding and orderly stacking, the repeating unit with length of about 2 nm was obtained. The obtained experimental value was about 2.02 nm, which was in well accordance with the calculation results. Meanwhile, it should be noted that this

FIGURE 4: SEM images of xerogels: (a)–(b) S-TriCl₄ and S-TriCl₆ in aniline; (c)–(f) S-TriCl₈ in aniline, nitrobenzene, 1,4-Dioxane, and DMF; (g)–(k) N-TriCl₈ from DMF, n-butyl acrylate, nitrobenzene, 1,4-dioxane, and aniline.

phenomenon is similar to the results of our recent reports [41, 45, 47]. Therein, functionalized imide derivatives with the substituent groups of azobenzene, luminol, and benzimidazole/benzothiazole residue can have a profound effect upon the gelation abilities and the as-formed nanostructures of the studied compounds. For present binary gelators, the experimental data showed that the number and length of alkyl substituent chains and benzimidazole/benzothiazole segment have played a crucial role in the gelation behavior

of all gelator mixtures in various organic solvents. More alkyl chains in molecular skeletons in present gelators are favorable for the gelation of organic solvents. The length of alkyl substituent chains has also played an important role in changing the gelation behaviors and assembly states. In addition, it seemed that these gels from binary mixtures showed more variable nanostructures than those based on imide derivatives. Now, the drug release behaviors generated by the present xerogels in the mixture of Congo Red are under

FIGURE 5: AFM images of xerogels: S-PC18, S-TriC18, and N-TriC18 in nitrobenzene ((a)–(c), resp.); S-PC18 and N-PC18 in ethanolamine ((d) and (e), resp.).

FIGURE 6: X-ray diffraction patterns of xerogels: (A)–(B) S-TriC14 and S-TriC16 in aniline; (C)–(F) S-TriC18 in aniline, nitrobenzene, 1,4-dioxane, and DMF, respectively.

investigation to display the relationship between the molecular structures, as-formed nanostructures, and properties.

4. Conclusion

In summary, the gelation behaviors of binary mixtures of alkyloxybenzoic acid with single-/multialkyl substituent chains and aminobenzimidazole/benzothiazole derivatives in various organic solvents were investigated. The experimental results indicated that their gelation behaviors can be regulated by changing number and length of alkyl substituent chains and benzimidazole/benzothiazole segment. The numbers of alkyl substituent chains linked to benzene rings in these acid derivatives have a profound effect upon the gelation abilities of these studied gelator mixtures. More alkyl chains in molecular skeletons in present gelators are favorable for the gelation of organic solvents. The length of alkyl substituent chains has also played an important role in changing

FIGURE 7: X-ray diffraction patterns of xerogels: (a) S-PC18, S-TriC18, and N-TriC18 in nitrobenzene ((A)–(C), resp.); (b) S-PC18 and N-PC18 in ethanolamine ((A)–(B), resp.).

FIGURE 8: FT-IR spectra of xerogels: (A)–(B) S-TriC14 and S-TriC16 in aniline; (C)–(F) S-TriC18 in aniline, nitrobenzene, 1,4-dioxane, and DMF, respectively.

FIGURE 9: FT-IR spectra of xerogels: (a) S-PC18, S-TriC18, and N-TriC18 in nitrobenzene ((A)–(C), resp.); (b) S-PC18 and N-PC18 in ethanolamine ((A)–(B), resp.).

FIGURE 10: A reasonable self-assembly mode for S-TriC18 organogels.

the gelation behaviors and assembly states. Morphological studies revealed that the gelator molecules self-assemble into different aggregates from wrinkle, lamella, belt, to fiber with change of solvents. Spectral studies indicated that there existed different H-bond formation and hydrophobic force, depending on benzimidazole/benzothiazole segment and alkyl substituent chains in molecular skeletons. The prepared nanostructured materials have wide perspectives and many potential applications in nanoscience and material fields due to their scientific values. The present work might also give some insights into design and characterize new organogelators and soft materials.

Conflict of Interests

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

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