

Research Article

Preparation and Characterization of Binary Organogels via Some Azobenzene Amino Derivatives and Different Fatty Acids: Self-Assembly and Nanostructures

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In present work the gelation behaviors of binary organogels composed of azobenzene amino derivatives and fatty acids with different alkyl chains in various organic solvents were designed and investigated. Their gelation behaviors in 20 solvents were tested as new binary organic gelators. It showed that the length of alkyl substituent chains and azobenzene segment have played a crucial role in the gelation behavior of all gelator mixtures in various organic solvents. Longer alkyl chains in molecular skeletons in present gelators are favorable for the gelation of organic solvents. Morphological studies revealed that the gelator molecules self-assemble into different aggregates from lamella, wrinkle, to belt with change of solvents. Spectral studies indicated that there existed different H-bond formation and hydrophobic force, depending on different substituent chains in molecular skeletons. The present work may also give new perspectives for designing new binary organogelators and soft materials.

1. Introduction

In recent years, organogels have been attracting more attention as one class of important soft materials, in which organic solvents are immobilized by gelators [1–4]. Although gels are widely found in polymer systems, there has recently been an increasing interest in low-molecular-mass organic gelators (LMOGs) [5–8]. In recent years, physical gelation of organic solvents by LMOGs has become one of the hot areas in the soft matter research due to their scientific values and many potential applications in the biomedical field, including tissue engineering, controlled drug release, and medical implants [9–12]. The gels based on LMOGs are usually considered as supramolecular gels, in which the gelator molecules self-assemble into three-dimensional networks in which the solvent is trapped via various noncovalent interactions, such as hydrogen bonding, π - π stacking, van der Waals interaction, dipole-dipole interaction, coordination, solvophobic interaction, and host-guest interaction [13–16]. Such organogels

have some advantages over polymer gels: the molecular structure of the gelator is defined and the gel process is usually reversible. Such properties make it possible to design various functional gel systems and produce more complicated and defined, as well as controllable, nanostructures [17–20].

In our reported work, the gelation properties of some cholesterol imide derivatives consisting of cholesteryl units and photoresponsive azobenzene substituent groups have been investigated [21]. We found that a subtle change in the headgroup 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 [22]. 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. Furthermore, in another relative research work, the gelation behaviors of some new azobenzene imide derivatives

with different alkyl substituent chains and headgroups of azobenzene residues were investigated [23]. The experimental results indicated that more alkyl chains in molecular skeletons in synthesized imide gelators were favorable for the gelation of organic solvents.

As a continuous research work, herein, we have designed and prepared new binary organogels composed of aminoazobenzene derivatives and fatty acids with different alkyl chains. We have found that some of present mixtures of acid/amine compounds 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 in gelators on the microstructures of such organogels in detail and found different kinds of hydrogen bond interactions.

2. Experiments

2.1. Materials. The starting materials, 4-aminoazobenzene, 2-aminoazotoluene, stearic acid, palmitic acid, tetradecanoic acid, and dodecanoic acid, were purchased from Alfa Aesar Tianjin Chemicals, Aldrich Chemicals, and TCI Shanghai Chemicals, respectively. Other used reagents were all for analysis purity from Beijing Chemicals and were distilled before use.

2.2. Gelation Test. All mixed organogels were prepared according to a simple procedure. Firstly, these fatty acid and amine derivatives 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 heated in a water bath 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 a "PS." Critical gelation concentration refers to the minimum concentration of the gelator for gel formation.

2.3. Measurements. Firstly, the xerogel was prepared by a vacuum pump for 12–24 h. The dried sample thus obtained was attached to copper foil, glass, and CaF₂ slice for morphological and spectral investigation, respectively. Before SEM measurement, the samples were coated on copper foil fixed by conductive adhesive tape and shielded by gold. SEM pictures of the xerogel were taken on a Hitachi S-4800 field emission scanning electron microscopy with the accelerating voltage of 5–15 kV. Transmission FT-IR spectra of the xerogel were obtained by Nicolet is/10 FT-IR spectrophotometer from Thermo Fisher Scientific Inc. by average 32 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. The scan rate was 0.5°/min.

3. Results and Discussions

3.1. Gelation Behaviors of These Binary Mixtures. The gelation performances of all binary mixtures in 20 solvents are tested. The experimental data showed that the binary mixtures of fatty acids with different alkyl chains and 4-aminoazobenzene/2-aminoazotoluene could form organogels in special organic solvents, as listed in Table 1. The binary mixtures of fatty acids with different carbon numbers (18, 16, 14, and 12) and 4-aminoazobenzene are denoted as C18-Azo, C16-Azo, C14-Azo, and C12-Azo, respectively. Similarly, the binary mixtures of these acids and 2-aminoazotoluene are denoted as C18-Azo-Me, C16-Azo-Me, C14-Azo-Me, and C12-Azo-Me, respectively. Firstly, for the mixtures containing 4-aminoazobenzene, C18-Azo, C16-Azo, and C14-Azo can form organogel in ethanolamine, while C12-Azo do not form any organogel in present solvents. In addition, it is interesting to note that C16-Azo can form another organogel in nitrobenzene. However, for the mixtures containing 2-aminoazotoluene, only C18-Azo-Me and C16-Azo-Me can form gel in ethanolamine, respectively. Their photographs of all as-made organogels in different solvents were shown in Figure 1. The present research results indicated that length change of alkyl chains can have a profound effect upon the gelation abilities of these studied mixtures. It seemed that longer alkyl chains in molecular skeletons in present mixture gelators are more favorable for the present mixtures, which was similar to the recent reports [21, 22].

3.2. Morphological Investigation of Organogels. Many researchers have reported that a gelator molecule constructs nanoscale superstructures such as fibers, ribbons, and sheets in a supramolecular gel [23, 24]. To obtain a visual insight into the gel nanostructures, the typical organized structures of these organogels were studied by SEM technique, as shown in Figure 2. From the present diverse images, it can be obviously observed that the nanostructures of all xerogels from ethanolamine and nitrobenzene are significantly different from each other, and the morphologies of the aggregates change from lamella, wrinkle, to belt with change of solvents and mixtures. In addition, more rod-like or belt-like aggregates with different sizes were prepared in gels of C16-Azo in nitrobenzene. In addition, it is interesting to note that these belt aggregates showed a tendency to aggregate together due to highly directional intermolecular interactions and/or solvent evaporation. The difference of morphologies can be mainly due to the different strengths of the intermolecular hydrophobic force between alkyl chains of fatty acids, which have played an important role in regulating the intermolecular orderly staking and formation of special aggregates.

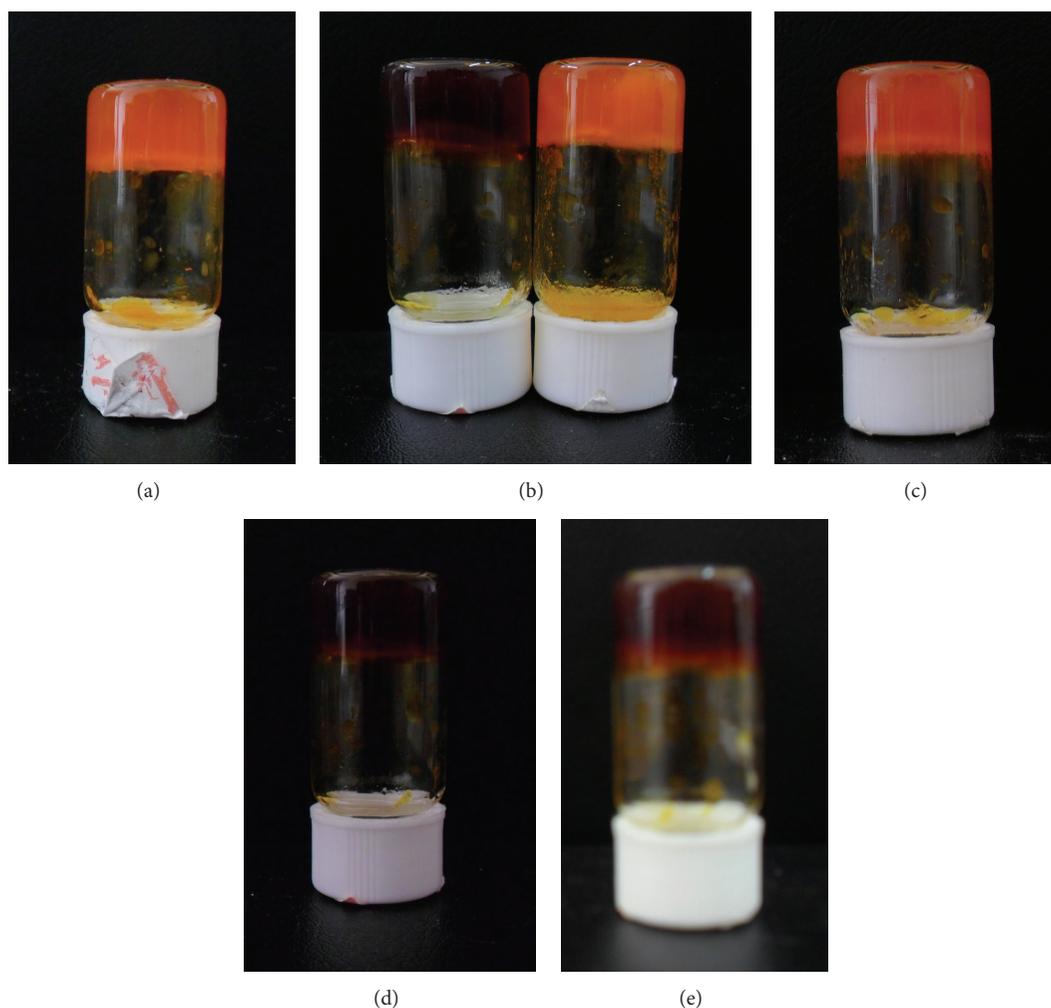


FIGURE 1: Photographs of as-made organogels: (a) C18-Azo; (b) C16-Azo; (c) C14-Azo; (d) C18-Azo-Me; (e) C16-Azo-Me, respectively.

3.3. Spectral Investigation of Organogels. In addition, in order to further investigate the orderly stacking of xerogels nanostructures, XRD of all xerogels from gels were measured, as shown in Figure 3. Firstly, the curves of C16-Azo xerogels from ethanolamine and nitrobenzene show similar strong peaks in the angle region (2θ values, 3.56, 7.18, 10.90, 18.28, and 21.94°) corresponding to d values of 2.48, 1.23, 0.81, 0.49, and 0.41 nm, respectively. In addition, for the curves of C14-Azo and C18-Azo xerogels from ethanolamine, weaker peaks appeared, suggesting more disordered structures in the gels. However, as for the curves of C18-Azo-Me and C16-Azo-Me from ethanolamine, the minimum 2θ values are 3.20 and 3.32°, corresponding to d values of 2.76 and 2.66 nm, respectively. The difference of values between C16-Azo and C16-Azo-Me can be mainly assigned to the change of substituent groups linked to azobenzene segment in the molecular skeleton, which affected the assembly modes in the 3D stacking of organogels [22]. The XRD results described above demonstrated again that the many factors, such as chain length and substituent group, had great effect 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 [25–27]. At present, in order to further clarify this and investigate the effect of many factors on assembly, we have measured the FT-IR spectra of all xerogels, as shown in Figure 4. Firstly, C18-Azo xerogel was taken as examples, as shown in Figure 4(a). Some main peaks were observed at 3354, 3224, 2918, 2850, 1724, 1633, and 1470 cm^{-1} , respectively, which can be assigned to the N–H and O–H stretching, methylene stretching, carbonyl group band, amide I band, and methylene scissoring, respectively [28–31]. These bands indicated the formation of hydrogen bonding interactions between intermolecular amino and carboxylic acid groups in the gel state, which can regulate the stacking of the gelator molecules to self-assemble into ordered structures. Similar spectra were observed for other xerogels.

Considering the XRD results described above and the hydrogen bonding nature of these binary mixtures as confirmed by FT-IR measurements, a possible assembly mode for present xerogels was proposed and schematically shown in Figure 5. As for C18-Azo xerogel containing longer alkyl

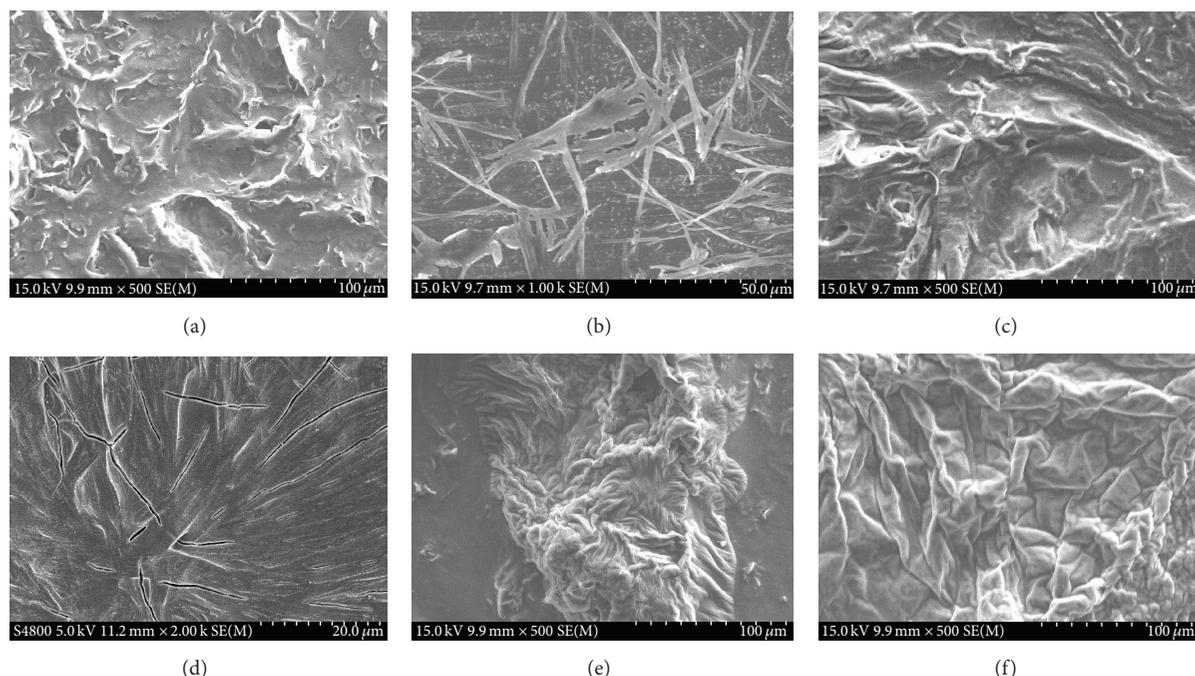


FIGURE 2: SEM images of xerogels: (a) and ((c)–(f)): C18-Azo, C16-Azo, C14-Azo, C18-Azo-Me, and C16-Azo-Me in ethanolamine, respectively; (b) C16-Azo in nitrobenzene.

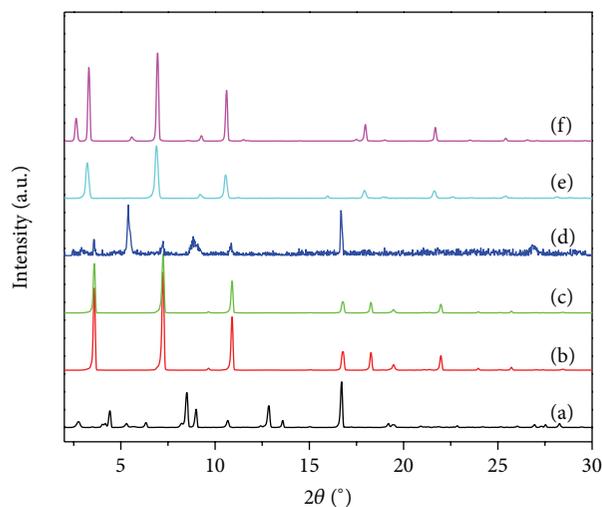


FIGURE 3: X-ray diffraction patterns of xerogels: (a) and ((c)–(f)): C18-Azo, C16-Azo, C14-Azo, C18-Azo-Me, and C16-Azo-Me in ethanolamine, respectively; (b) C16-Azo in nitrobenzene.

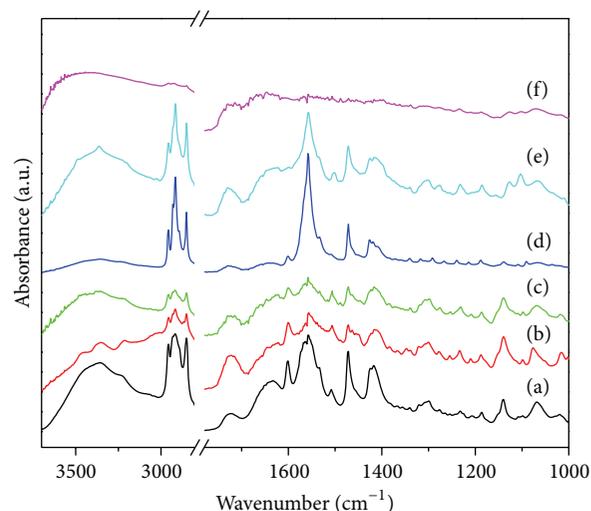


FIGURE 4: FT-IR spectra of xerogels: (a) and ((c)–(f)): C18-Azo, C16-Azo, C14-Azo, C18-Azo-Me, and C16-Azo-Me in ethanolamine, respectively; (b) C16-Azo in nitrobenzene.

chain, due to the hydrophobic force of methylene chains, after the intermolecular hydrogen bonding and orderly stacking, the nanostructures of supramolecular assembly were obtained. For the binary mixture C12-Azo with shorter alkyl chain, the intermolecular interaction is not enough to connect the repeating units with each other, so no gels were formed.

4. Conclusion

In summary, the gelation behaviors of binary organogels composed of azobenzene amino derivatives and fatty acids with different alkyl chains in various organic solvents were investigated. The experimental results indicated that their gelation behaviors solvents can be regulated by changing length of alkyl substituent chains and azobenzene segment.

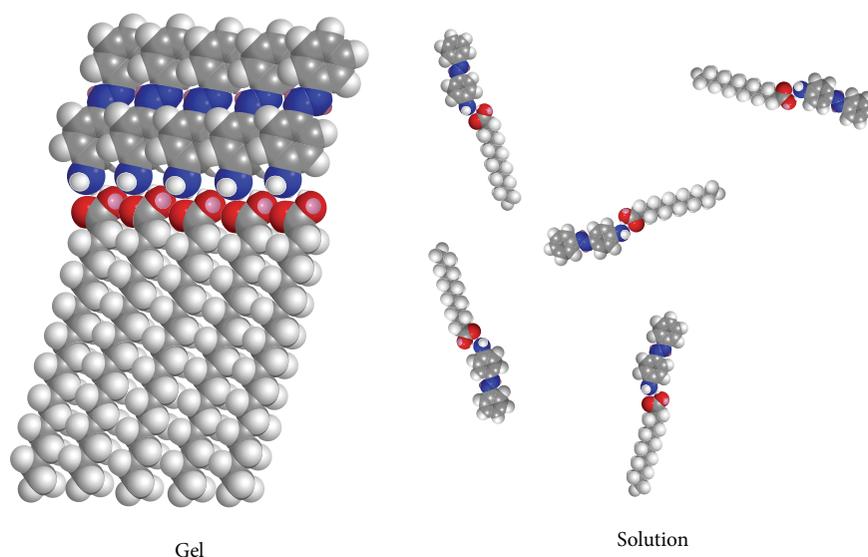


FIGURE 5: Assembly modes for C18-Azo in organogel and C12-Azo in solution.

TABLE I: Gelation behaviors of these binary organogels.

Solvents	C18-Azo	C16-Azo	C14-Azo	C12-Azo	C18-Azo-Me	C16-Azo-Me	C14-Azo-Me	C12-Azo-Me
Acetone	S	S	S	S	S	S	S	S
Aniline	PS	PS	S	PS	PS	S	PS	S
n-Hexane	S	PS	PS	PS	S	PS	PS	S
Toluene	PS	S	S	S	PS	S	S	S
Pyridine	S	S	S	S	S	S	S	S
Isopropanol	S	S	S	S	S	S	S	S
Cyclopentanone	PS	S	S	PS	S	S	S	S
Cyclohexanone	S	S	S	S	S	S	S	S
Nitrobenzene	PS	G (2.0)	PS	PS	PS	S	S	S
n-Butanol	S	S	S	S	S	S	S	S
Ethanolamine	G (2.5)	G (2.0)	G (2.0)	S	G (2.5)	G (2.0)	S	S
n-Butyl acrylate	PS	S	S	PS	PS	S	S	S
1,4-Dioxane	S	S	S	S	S	S	S	S
Petroleum ether	S	PS	PS	S	S	PS	PS	PS
Ethyl acetate	S	S	S	PS	S	S	S	S
Dichloromethane	PS	PS	S	PS	S	S	S	S
THF	S	S	S	S	S	S	S	S
DMF	PS	S	S	PS	PS	S	S	S
DMSO	S	S	S	S	S	PS	S	S
Benzene	S	S	S	PS	S	PS	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).

Longer alkyl chains in molecular skeletons in present gelators are favorable for the gelation of organic solvents. For the mixtures containing 4-aminoazobenzene, only C12-Azo cannot form any organogel in present solvents. While for the mixtures containing 2-aminoazotoluene, only C18-Azo-Me and C16-Azo-Me can form gel in ethanolamine, respectively. Morphological studies revealed that the gelator molecules self-assemble into different aggregates from lamella, wrinkle,

to belt with change of solvents. Spectral studies indicated that there existed different H-bond formation and hydrophobic force, depending on different 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 some insight to design and character new organogelators and soft materials.

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.

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