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Two-component supramolecular organogels formed by maleic N-monoalkylamides and aliphatic amines

Xuzhong Luo *, Zhixing Chen, Wei Xiao, Zengfu Li, Qiong Wang, Jinlian Zhong

Key Laboratory of Jiangxi University for Materials Chemistry, Gannan Normal University, Ganzhou 341000, PR China
Key Laboratory of Organo-pharmaceutical Chemistry of Jiangxi Province, Gannan Normal University, Ganzhou 341000, PR China

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ABSTRACT

The complexes of maleic N-monoalkylamides and aliphatic amines lead to the formation of sheet-like and fiber-shaped aggregates in diverse organic solvents. Their morphologies and microstructures were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), as well as small angle X-ray diffraction (SA-XRD). The results reveal that the alkyl chain lengths of 8–12 carbons for maleic N-monoalkylamides, and 12–18 carbons for aliphatic amines, are suitable for obtaining highly efficient two-component gelators.

1. Introduction

During the past two decades, more and more attention has been paid to the synthesis of supramolecular organogels due to their special properties and potential applications in fields such as drug delivery [1,2], inorganic nanomaterials [3,4], biofilm simulation [5,6], liquid crystallines [7,8], photochemistry [9,10], and electrochemistry [11,12]. It is well known that organogelators, possessing functional groups like hydroxyl, amide, linear alkyl chains, aromatic group, are able to self-assemble into aggregates with diverse morphologies such as fibers, sheets, ribbons through non-covalent interaction including hydrogen bonding, van der Waals force, π–π stacking, coordination interaction, and charge transfer [13–21]. Such aggregates form a three-dimensional network through further cross-linking and immobilizing the solvents and finally result in the formation of organogels. The physical characteristics of organogels can range from those of surfactants in solution to those of polymer solutions. Gels are at the interface between "complex fluids" and phase-separated states of matter. To date, diverse categories of organogels have been prepared and studied, including steroid derivatives [22,23], cholesterols [22,24], amino acids [25,26], carbohydrates [27,28], urea [29,30], organometallics [31], and so on. Recently, some chemists begin to transfer their attention from single component organogels to two-component organogels. Compared with the single component organogels, two-component organogels can build new organogel systems, obtain more new organogels with interesting morphologies and microstructures, and offer the potential of developing more soft materials with highly tunable microscopic and macroscopic properties. George and Weiss reported the complexes of aliphatic amines with carbon dioxide could gelate organic solvents [32,33]. Suzuki and coworkers reported a two-component gelator consisting of L-lysine derivatives and aliphatic acids [34]. The above citations provide ample evidence of the promising features of the two-component approach to achieve gel. However, most of these studies do not provide much structural insight as to how the two components interact to form the gel. It has been know that succinic N-monoalkylamides can form organogels [35], while the structurally related compounds, maleic N-monoalkylamides, do not gelatinize any organic solvents. To further enrich the two-component organogel system with desired functions and observe a well-defined structure–property relationship, herein, we report a new class of two-component organogelators comprised of maleic N-monoalkylamides and aliphatic amines. Their gelation ability, morphologies and microstructures were explored and characterized.

2. Materials and methods

2.1. Synthesis

All starting materials were available from commercial sources and used without further purification. Compounds **1**–**3** (Scheme 1) were synthesized according to the procedure described as follows: A mixture of maleic anhydride and equivalent mol aliphatic amine was dissolved in 50 mL toluene in a round-bottomed

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* Corresponding author. Fax: +86 797 8393670.
E-mail address: luoxuzhong@hotmail.com (X. Luo).

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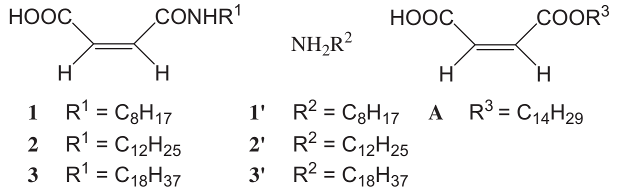

Scheme 1. Chemical structures of maleic N-monoalkylamides, aliphatic amines and tetradecyl hydrogen maleate.

flask equipped with a condenser. After stirring for about 30 min at 80 °C, the toluene was removed by vacuumizing method, and white solid was obtained. Highly pure products of **1**–**3** were gotten after the white solids recrystallized using mixed solvent of ethanol/water (*v*/*v* = 1:1) for four times, respectively. The method for preparing **A** (Scheme 1) is similar to that of **1**–**3**, except using 1-tetradecanol instead of aliphatic amine. Satisfactory ^{1}H NMR, element analysis data were obtained for the corresponding maleic N-monoalkylamides (see Supporting information).

2.2. Gelation test

The gelation ability of nine combinations of **1**–**3** with **1′**–**3′** was investigated by a typical test tube experiment. A weighted sample of maleic N-monoalkylamides and equivalent mol aliphatic amine was mixed in an organic solvent (1 mL) in a sealed test tube and the mixture was heated until the solid dissolved. The resulting solution slowly cooled to room temperature and then the gelation generated. Once formed, the organogel was stationary and the tube can be inverted without deformation of the gel.

The reversible gel–sol transition temperature (T_{gel}) was measured using a classical drop-ball method as described by Takahashi [36]. A locally made steal ball with a diameter of 2 mm was gently laid on the gel surface, and the gel was heated gradually in an oil bath. The temperature at which the ball started to fall down was considered as the T_{gel}.

2.3. SEM measurements

Scanning electron microscope (SEM) measurements were carried out on Philips XL 30W/TMP. A drop of organogel was cast onto glass slides, which was slowly dried in air and then the remained xerogel was subjected to SEM observation.

2.4. FTIR measurements

Fourier transform infrared (FT-IR) spectra were recorded on Nicolet AVATAR 360. All data were collected for 128 interferograms with a resolution of 4 cm^{-1}. CaF_2 substrates and KBr pellet were used for transmission spectra of xerogel and crystal, respectively.

2.5. SA-XRD measurements

Small-angle X-ray diffraction (SA-XRD) patterns of dried organogel were measured on a Bruker D8 Focus diffractometer using the Cu Kα radiation. X-ray was generated with a Cu anode and the Cu Kα beam (λ = 1.5418 Å) was taken out via a graphite monochrometer. The long spacing (*D*) were obtained from the typical peak.

3. Results and discussion

3.1. Gelation test

The gelation test results are shown in Table 1. It was found that only **1** + **2′**, **1** + **3′**, **2** + **2′**, **2** + **3′**, **3** + **2′**, **3** + **3′** showed gelation property, while **1** + **1′**, **2** + **1′**, **3** + **1′** gave no gelation, which may be related with the alkyl chain length of both maleic N-monoalkylamides and aliphatic amines. Aliphatic amine compound **1′**, compared with **2′** and **3′**, has the shortest alkyl chain, which led to the intermolecular interactions among **1′**, maleic N-monoalkylamides and solvent molecule too weak to generate gelation. Therefore, the combinations of **1′** + **1**, **1′** + **2**, **1′** + **3** exhibited no gelation behavior. In addition, although the rest six combinations of **1** + **2′**, **1** + **3′**, **2** + **2′**, **2** + **3′**, **3** + **2′**, **3** + **3′** exhibited gelation, their gelation performances were markedly different. **1** + **3′** and **2** + **2′** are excellent gelators, as they are able to gelate many organic liquids at very low concentrations. For instance, the minimum gel concentration (MGC g/dm^3) of **1** + **3′** for toluene, o-xylene, and cyclohexane are 1.3 g/dm^3, 1.3 g/dm^3, and 1.4 g/dm^3, respectively. **1** + **2′** and **3** + **2′** also display good gelation capacity. However, the MGC of them are slightly higher than that of **1** + **3′** and **2** + **2′**. For **2** + **3′** and **3** + **3′**, although they could gelate many organic liquids, they are still considered as low efficiency gelators due to high MGC in most solvents. Comparing the molecular structures of **1**–**3** with **1′**-**3′**, it can be inferred that as a highly efficient two-component gelator, the suitable length of tail chain is 8 and 12 carbons for mono-chain maleic acid derivatives and 12 and 18 carbons for aliphatic amines. The results may be ascribed to the fact that the proper length of the carbon chain can strengthen the intermolecular interactions among maleic N-monoalkylamides, aliphatic amines, and solvent molecules.

Table 1
The MGC[a] (g/dm^3) of each combination in different organic liquids.

Solvent	**1** + **2′**	**1** + **3′**	**2** + **2′**	**2** + **3′**	**3** + **2′**	**3** + **3′**
Carbon tetrachloride	TG 5.7	CG 3.1	TG 4.9	TG 10.8	OG 7.3	OG 15.1
1,1,2,2-Tetrachloroethane	S	P	S	P	TG 29.4	CG 10.7
Benzene	CG 4.5	CG 1.5	CG 2.1	TG 26.5	TG 13.0	TG 11.8
Toluene	CG 4.2	CG 1.3	CG 2.1	TG 21.3	TG 6.7	TG 10.4
o-Xylene	CG 8.1	CG 1.3	CG 2.2	TG 27.0	TG 7.4	TG 19.2
Mesitylene	TG 8.5	CG 2.1	TG 18.0	TG 30.8	TG 7.3	TG 12.1
Tetralin	TG 8.7	CG 1.6	TG 15.1	TG 22.2	TG 9.7	TG 7.5
Isopropyl ether	P	OG 15.3	OG 11.2	P	P	OG 18.8
Cyclohexane	OG 3.9	CG 1.4	OG 11.2	OG 16.9	OG 7.3	OG 20.0

OG: opaque gel; TG: translucent gel; CG: clear transparent gel; S: solution; P: precipitate.

[a] Total concentration of two components (molar ratio = 1:1) for each combination.

Table 2
The gelation capacities of combinations with different CH_2 length.

Total CH_2 length	**1** + **2′**	**1** + **3′**	**2** + **2′**	**2** + **3′**	**3** + **2′**	**3** + **3′**
20	Good	–	–	–	–	–
24	–	–	Excellent	–	–	–
26	–	Excellent	–	–	–	–
30	–	–	–	Good	Low	–
36	–	–	–	–	–	Low