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Super-structures Can Be Constructed in Organogels from Combination of a Boronic-acid-appended Bolaamphiphile with Chiral Diols

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Abstract: A bolaamphiphile bearing two boronic acid groups at the two ends was synthesized. Complexation with chiral diols readily afforded new amphiphiles end-capped with the chiral substituents. Some of them acted as gelators of organic solvents. TEM and SEM observations established that a variety of super-structures are created in the organogels, depending on the solvents and the structure of the end-cap groups.

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The development of new gelators of organic solvents has recently received much attention. They not only gelate various organic solvents but also create novel networks sewn together with fibrous super-structures which can be characterized by SEM pictures of the xerogels.[1-8] The gelators can be classified into two categories according to the difference in the driving force for the molecular aggregation, *viz.* hydrogen-bond-based gelators and nonhydrogen-bond-based gelators. Typical examples of the former group are aliphatic amide derivatives[1-3] and those of the latter group are cholesterol derivatives.[4-6] The structural studies on the fibrous aggregates in the organogels of aliphatic amide derivatives show that they satisfy the complementarity of the intermolecular hydrogen-bonding interactions.[4-6] In particular, when the gelator involves chiral segments, the resultant aggregates frequently create a helical structure.[1] In the preceding literature, however, the examples of such gelators with the helical structures are rather limited in spite of their high potential.[1,9,10] It thus occurred to us that a boronic acid-diol complex,[11] which is readily formed from each component, might be useful to overcome this synthetic difficulty because various chiral diols are already available as synthons. To test this idea we synthesized a bolaamphiphile (**1**) and derived it to chiral diol complexes (**2-4**).[12] We have found that this is a convenient method to provide various chiral gelators and that some of them not only gelate several organic solvents but also create various super-structures (including the helical structure) in organogels.

Compound **1** (mp 206-208 °C) was synthesized from 1, 12-bis(chlorocarbonyl)dodecane and 3-aminophenylboronic acid in 80% yield and identified by IR and ^{1}H NMR spectral evidence and elemental

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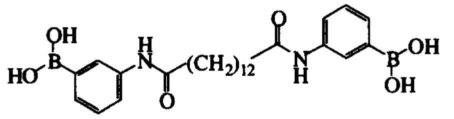
Table 1 Galation test for 1~4 (100 mmol dm^{-3}) in various soluvents [a]

Soluvent	1	2	3	4
Cyclohexane	B	I	B(I)[b]	I
Hexane	B	I	B(I)[b]	I
Benzene	B	I	Gf	G
Toluene	B	I	G(S)[b]	G(G)[b]
Chloroform	I	I	S	S
Dichloromethane	I	B	G(S)[b]	I(S)[b]
Diethyl ether	B	B	B(G)	G(G)[b]
THF	I	I	S	S
1,4-Dioxane	I	I	Rf	Gf
Ethyl acetate	I	I	G(S)[b]	G(S)[b]
Acetone	I	I	S	Gf
Ethanol	B	S	R	G
Methanol	B	B	R	G
Water	I	I	I	I

[a] I: insoluble, B: swelled solid, S: soluble, R: recrystallization, G: gel formed at 25 °C, Gf: gel formed at 5 °C

[b] [Gelator] = 20 mmol dm^{-3}



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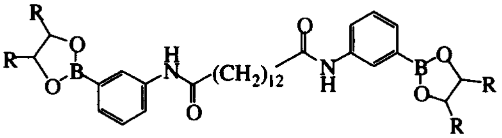

2: R=$COOC_2H_5$ [prepared by the reaction with diethyl (1*R*, 2*R*)-tartarate]
3: R=Me [prepared by the reaction with (1*R*, 2*R*)-2, 3-butanediol]
4: R=Ph [prepared by the reaction with (1*R*, 2*R*)-hydrobenzoin]

analysis. Compounds **2-4** (mp 137-139 °C, 94-96 °C, and 112-113 °C, respectively) were obtained in nearly quantitative yields by refluxing **1** with a corresponding chiral diol in toluene using a Dean-Stark apparatus. They were also identified by the same analytical methods.

The results of the gelation test (by a test-tube-tilting method) are summarized in Table 1. The solution (100 mmol dm^{-3}) was once heated at the reflux temperature and then cooled to 25 °C. G denotes the gel formation at this stage. Gf denotes the gel formation by further cooling to 5 °C. It is seen from Table 1 that neither **1** nor **2** can gelate any solvent tested herein. In contrast, compound **3** can gelate three solvents at 25 °C and one solvent at 5 °C. The diethyl ether solution was gelated only partially. However, **3** was still solubilized homogeneously into these three solvents at 20 mmol dm^{-3} (see marks in the parenthesis: Table 1), suggesting that these gels are formed only under the high gelator concentration and probably not so stable.

On the other hand, compound **4** can gelate eight solvents, indicating that this compound acts as an good gelator. In most cases, white and slightly turbid gels were obtained from both **3** and **4**, but only a **4**-benzene system and a **4**-toluene system afforded translucent, clean gels. The difference suggests that the organogels of **4** have the higher affinity with the solvents and therefore are more stable than those of **3**. The structural difference between **3** and **4** indicates that in **4** two chirally-twisted phenyl groups hamper the formation of tight molecular stacks, which induce the aggregate disorder and eventually facilitate the formation of the stable gels.[6]

The influence of the end-cap groups in **3** and **4** on the super-structures in their organogels was visually estimated by TEM and SEM. As shown in the TEM picture (Fig. 1A), the slightly turbid gel of a **3**-toluene system resulted in left-handed helical, short fibers with an approximate diameter of 50 –100 nm. This structure is considered to be the initial, juvenile aggregate which eventually assembles to the fibrous aggregate characteristic of organogels.[13] As shown in the SEM picture (Fig. 2A), the xerogel of the same system appeared as a well-developed, arborescent-like network and the fibers did not have the helical structure. On the other hand, the translucent gel of a **4**-toluene system resulted in minute fibers with a short diameter of 15-40 nm (Fig. 1B). The presence of the helical structure could not be confirmed because of the

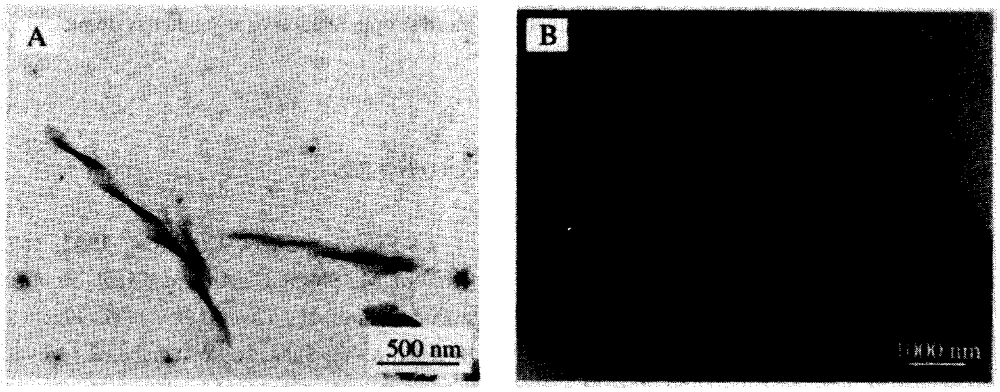

Fig. 1 TEM pictures of (A) **3**-toluene system and (B) **4**-toluene system

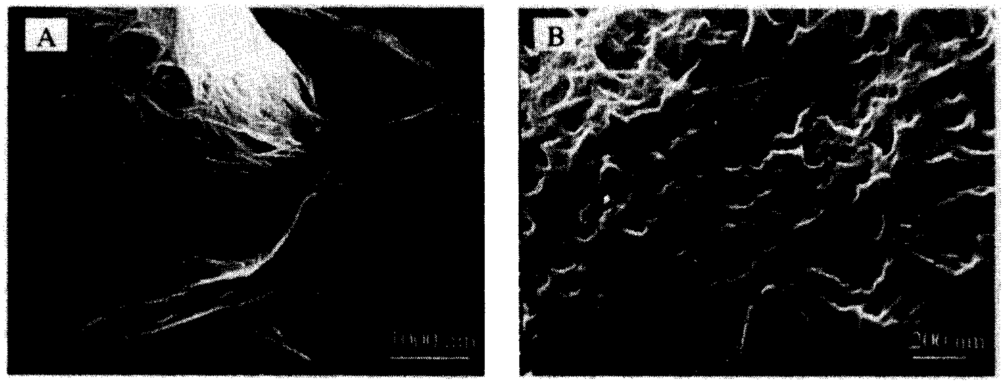

Fig.2 SEM pictures of (A) **3**-toluene system and (B) **4**-toluene system

Table 2 Super-structures as observed by SEM[a]

Solvent	3	4
Benzene	Long fiber (50-100 nm)	Frizzled fibers with lumps (20-35 nm)
Toluene	Long fiber (50-100 nm)	Sponge
Dichlromethane	Long fiber (200-280 nm)	——
Diethyl ether	Long fiber (100-180 nm)	Frizzled fibers with lumps (20-35 nm)
1,4-Dioxane	——	Sponge
Ethyl acetate	Long fiber (100-150 nm)	Frizzled fibers (20-35 nm)
Acetone	——	Frizzled fibers with lumps (15-40 nm)
Ethanol	——	Sponge

The values in the parenthesis denote the fiber diameter.

limitation in the microscope resolution. This implies that **4** cannot create such large crystal–like fibers (as in Fig. 1A) but grows up as minute fibers and the resultant gel becomes apparently translucent. We consider that the two chirally-twisted phenyl groups at the two ends again play a role to obstruct the tight molecular packing. The SEM picture (Fig. 2B) showed the well-developed sponge-like structure. The super-structures of the xerogels observed by SEM are summarized in Table 2. It is clear that a variety of super-structures are created by a change in the solvents and the end-cap groups. In general, **3** tends to afford straight fibers whereas **4** tends to afford frizzled fibers.

In conclusion, the present paper has shown that the aggregate morphologies of bolaamphiphiles in the organogel can be controlled by the chiral diol groups introduced into the chain ends by the boronic acid-diol interaction. This implies that diols (or more in general, sugars) can be regarded as a convenient library source for the creation of various super-structures. We believe that convenience in the synthesis and diversity as shown in this system cannot be attained in a more simple fashion in any other systems.

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