Gelator and Thickener Derived from Dimethyl 5-Aminoisophthalate

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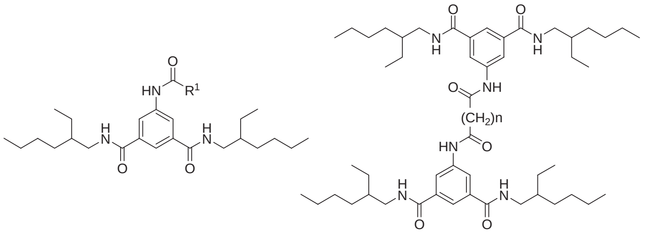
1-Acylamino-3,5-bis(2-ethylhexylaminocarbonyl)benzene derived from dimethyl 5-aminoisophthalate formed a nanoscaled superstructure in organic solvents and acted as gelators or thickeners.

Recently, low molecular weight compounds that self-organize into nanoscaled superstructure such as nanofibers, nanoribbons, nanoparticles, and helical structures have attracted much attention.[1] Compounds which can transform organic liquids into gels are called organogelators.[2,3] When the gelation happens, the gelator molecules self-assemble into macromolecule-like aggregates via noncovalent intermolecular interactions such as hydrogen bonding, π–π stacking, and van der Waals interactions. Actually, electron microscopic studies clearly demonstrate the creation of three-dimensional (3-D) network formed by entanglement of self-assembled nanofibers.[2,3]

During the development of gelators, we have found that derivatives of 5-aminoisophthalic acid act as an effective thickener for some organic solvents instead of gelator. Here thickeners are low molecular weight compounds which can form highly viscous fluids when a small amount of the compounds are added to organic solvents. For instance, aluminium bis(2-ethylhexanoate) is a well-known thickener for printer's ink, paint, or lacquer. However, an extremely limited number of thickeners are reported because of the lack of guideline for the molecular design of thickeners.[4] In this communication, we describe the properties as thickeners and gelators of compounds **1–6**, derived from dimethyl 5-aminoisophthalate.



$R^1 = C_{11}H_{23}$ **1**
$= C_{15}H_{31}$ **2**
$= C_{17}H_{35}$ **3**

n = 8 **4**
=10 **5**
=14 **6**

Figure 1. Formula of **1–6**.

Firstly, dimethyl 5-aminoisophthalate, which is a cheap industrial intermediate, was changed to 1-amino-3,5-bis(2-ethylhexylaminocarbonyl)benzene by reaction with 2-ethylhexylamine. The obtained diamides were converted to **1–6** by using the corresponding acyl chlorides. The behavior of **1–6** in some solvents is listed in Table 1. Dimmer type of compounds **4–6** showed gelation ability against chlorobenzene, nitrobenzene, styrene, and light oil; especially, they could gel up light oil at the concentration less than 0.5 wt %. With increasing concentration of **4**, the strength of the gel increased; for example, the gel strength of chlorobenzene formed by **4** (30 mg/mL) reached 430 g·cm^{-2}.

Table 1. Results of behavior tests of **1–6** at 25 °C

Solvent	1	2	3	4	5	6
Hexane	V.F.	V.F.	V.F.	Insol.	Insol.	Insol.
Cyclohexane	V.F.	V.F.	V.F.	Insol.	Insol.	Insol.
Benzene	V.F.	V.F.	V.F.	G-like	G-like	G-like
Toluene	V.F.	V.F.	V.F.	G-like	G-like	G-like
Chlorobenzene	V.F.	V.F.	V.F.	15	10	10
Nitrobenzene	V.F.	V.F.	V.F.	10	10	10
MMA	V.F.	V.F.	V.F.	C	C	C
Sytrene	V.F.	V.F.	V.F.	10	10	10
Light oil	V.F.	V.F.	V.F.	4	5	5

Values means minimum gel concentration (MGC, mg/mL) necessary for gelation, MMA = methyl methacrylate, V.F. = viscous fluid, G-like = loose gel, C = crystallization, Insol. = almost insoluble.

Though the gels failed to form by compounds **1–3**, we found an interesting property instead of gelation ability in them. Compounds **1–3** have potential for thickeners; namely, we can make highly viscous solutions by adding a small amount of them to solvents. As listed in Table 1, **1–3** acted as thickeners for hexane, cyclohexane, aromatic solvents, methyl methacrylate, styrene, and light oil. For example, **1–3** showed significant thickening effect for toluene; the viscosity of the toluene solution of **3** (15 mg/mL) exhibited over 38500 cP at 20 °C, which is about 70000 times as large as neat toluene. The viscosity of toluene solution of **3** (15 mg/mL) drastically decreased with increasing temperature; the viscosities were 31300 cP (30 °C), 20000 cP (40 °C), and 9200 cP (50 °C), respectively. Figure 2 shows the viscosities of styrene solution of **3** (15 mg/mL) and those of the mixed solution of toluene and MMA (1:1 v/v) of **3**

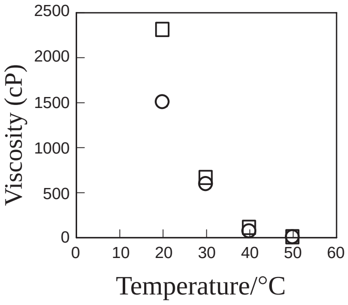


Figure 2. Viscosities of monomer solutions of **3**; (○) Styrene solution of **3** (15 mg/mL), (□) mixed solution of toluene and MMA (1:1 v/v) of **3** (60 mg/mL).

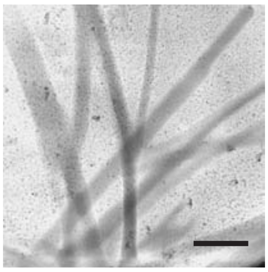


Figure 3. TEM image of sample from highly viscous toluene solution of **3** (15 mg/mL). Scale bar is 200 nm.

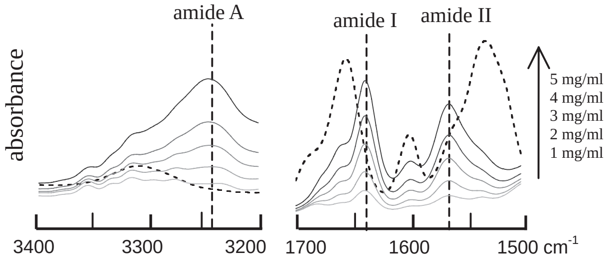


Figure 4. FT-IR spectra of cyclohexane solution (solid line) and chloroform solution (dash line) of **3**.

(60 mg/mL) at several temperatures. The viscosity of styrene was 1500 cP and that of the mixed solution of toluene and MMA was 2300 cP at 20 °C. Considering that the viscosities of pure styrene and MMA are less than 1 cP, the compound **3** should be a good thickener. We would like to emphasize **1**–**3** may be useful thickening agents for studying the Trommosdorff effect (gel effect)[5] in free-radical polymerization of vinyl monomers and controlling molecular weight as well as reaction rate.

Figure 3 shows TEM image of xerogel prepared from viscous toluene solution of **3**. In the high viscous toluene solution, **3** formed the self-assembled nanofibers with a diameter of ca. 50 nm, while a 3-D network was not observed. It is generally known that gelator molecules create a 3-D network so that physical gelation occurs.[2–4] In fact, the TEM images of samples prepared from gels of **4**–**6** demonstrate clear 3-D network structure as well as nanofibers (data not shown). Therefore, thickening properties of **1**–**3** are induced by self-assembly of the molecules into nanofibers, and the gelation abilities of **4**–**6** are caused by the creation of a 3-D network.

More detail studies were carried out using FT-IR spectroscopy. Figure 4 shows the FT-IR spectra of cyclohexane solution and chloroform solution of **3**. It should be mentioned that **3** can't increase the viscosity of $CHCl_3$ at all. The IR bands of $CHCl_3$ solution were observed at 3310 cm^{-1} ($\nu_{N\text{–}H}$, amide A), 1655 cm^{-1} ($\nu_{C=O}$, amide I), and 1540 cm^{-1} ($\delta_{N\text{–}H}$, amide II), attributable to characteristics of non hydrogen bonded amide group. On the contrary, the IR spectra in highly viscous cyclohexane solution showed the hydrogen bonding interaction between the amide groups; the IR bands were observed at 3240 cm^{-1} (amide A), 1639 cm^{-1} (amide I), and 1563 cm^{-1} (amide II). The fact implies that the self-assembly of **3** into nanofibers are formed through intermolecular hydrogen bonding interaction.

It is important to note that the FT-IR spectra of highly viscous solutions were very similar to those of organogels. The FT-IR spectrum of kerosene gel of **4** showed N–H and C=O stretching vibrations at 3246, 1638, and 1561 cm^{-1} for hydrogen bonding. This indicates that the formation of nanofibers through self-assembly, responsible for thickening phenomenon and gelation, proceeds via the same mechanism. What is difference between thickening and gelation? At present we don't know the definite reasons why **1**–**3** act as thickeners, while **4**–**6** function as gelators. It might be due to the lack of ability of formation of three-dimensional network in **1**–**3**.

In summary, we developed new thickeners and gelators derived from dimethyl 5-aminoisophthalate as an industrial intermediate. Compounds **4**–**6** can gel up some organic fluids, while compounds **1**–**3** can act as good thickeners. In particular, **3** has high potential for thickening ordinary solvents, including monomers such as styrene and MMA.

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