Remarkable Viscoelasticity of Organic Solvents Containing Trialkyl-1,3,5-benzenetricarboxamides and Their Intermolecular Hydrogen Bonding

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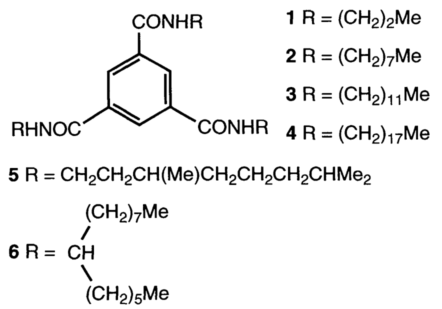
Remarkable rise of viscosity was observed by adding trialkyl-1,3,5-benzenetricarboxamide into organic solvents; the formation of highly viscoelastic solution was discussed by viscosity measurement, FTIR spectroscopy, and X-ray molecular structure in the crystal.

Non-covalent intermolecular forces (hydrogen bonding, electrostatic interaction, van der Waals forces, π–π interaction, etc.) play an essential role in supramolecular chemistry.[1,2] If non-covalent intermolecular interactions should be performed, macromolecule-like phenomena would be observed in the solution. However, investigation of macromolecule-like behavior in solution has rarely been done in the field of supramolecular chemistry. We have been studying low-molecular weight compounds causing thermoreversible physical gelation in organic fluids, whose behavior is governed by intermolecular hydrogen bonding and van der Waals interactions.[3-5] Recently, we encountered the unambiguous behavior of low-molecular weight compounds in organic solvents, indicating the formation of macromolecule-like aggregate. In this communication we report the remarkable rise of viscosity of organic solvents by trialkyl-1,3,5-benzenetricarboxamides and their intermolecular hydrogen bonding as the main driving force on the basis of X-ray crystallography.

We prepared trialkyl-1,3,5-benzenetricarboxamides (**1**-**6**) from 1,3,5-benzenetricarbonyl trichloride and alkylamines with the expectation that intermolecular hydrogen bondings and π–π stacking act for formation of macromolecule-like aggregate. Actually, trioctadecyl-1,3,5-benzenetricarboxamide (**4**) was reported to show discotic liquid crystalline phase[6] and the intermolecular hydrogen bonding was assumed to be driving force for liquid crystal of the related compound.[7] A procedure for studying aggregation behavior is described elsewhere.[3-5] When forming highly viscoelastic solution, it was referred to as "gel-like". When upon inversion there was no fluid running down the walls of the tube, we judged it "gel". The formed "gel" and "gel-like" were completely transparent.



Aggregation behavior of **1**-**6** is summarized in Table 1. No striking phenomenon was observed by adding tripropyl-1,3,5-benzenetricarboxamide **1**, on the contrary, a completely transparent and thermoreversible gel was formed in hexane by tri(3,7-dimethyloctyl)-1,3,5-benzenetricarboxamide **5**. The minimum gel concentration of **5** necessary for gelation at 25 °C was 55 g dm^{-3} (**5**/hexane), corresponding to 8.8 x 10^{-2} M. It is noteworthy that the marked rise of viscosity was observed by adding **2**-**6** to some organic solvents. The indication of "gel-like" in Table 1 shows such a formation of thermoreversible viscoelastic material.

Table 1. Aggregation behavior of **1**-**6** in solvents at 25 °C

Organic solvent	**1**	**2**	**3**	**4**	**5**	**6**
EtOH	a	b	b	c	b	b
2-PrOH	a	b	b	c	b	b
Me_2SO	c	d	c	c	d	c
DMF	c	b	b	c	b	c
Benzene	a	d	d	b	d	c
Toluene	a	d	d	d	d	c
Nitrobenzene	c	c	c	c	c	c
$CHCl_3$	a	b	b	b	b	b
CCl_4	a	d	d	b	d	d
Hexane	a	d	d	c	e	d
Cyclohexane	a	d	d	d	d	d
Kerosene	a	d	d	c	d	d
Silicone oil	c	d	d	d	d	d
Soybean oil	a	d	d	d	b	b

a = Almost insoluble: b = isotropic solution: c = crystallization: d = highly viscous fluid: e = gel.

In Figure 1 is shown the dependence of viscosity on concentration of **3**-**6** in cyclohexane at 20 °C. The viscosity was calculated by corrected density and kinematic viscosity determined using Ubbelohde viscometer. The viscosity of cyclohexane containing **3** at the concentration of 20 g dm^{-3} was 1800 cP and that of **5** (30 g dm^{-3}) was increased to 20000 cP at 20 °C, though the viscosity of cyclohexane was 0.97 cP. The viscosity of toluene containing **2**, **3**, and **4** at the concentration of 30 g dm^{-3} raised to 35 cP, 37 cP, and 5.7 cP; while the viscosity of toluene is 0.6 cP at 20°C. In general, the addition of **2**, **3**, and **5** having appropriate hydrophobic alkyl chain causes the marked rise of viscosity as compared to that of **4** having octadecyl groups. In particular, the addition of **5** having 3,7-dimethyloctyl segments resulted in a remarkable rise of viscosity. These results suggest that hydrophobic interaction among alkyl segments is one of significant factors for the remarkable rise of viscosity.

Considering that the rise of viscosity means the formation of macromolecule-like aggregate, the intermolecular hydrogen bonding between the amides should play an important role in the formation of "gel" and "gel-like". The FTIR spectrum of **3** in cyclohexane of highly viscous fluid is characterized by broad bands at 3240 cm^{-1} assigned to NH hydrogen bonding stretching

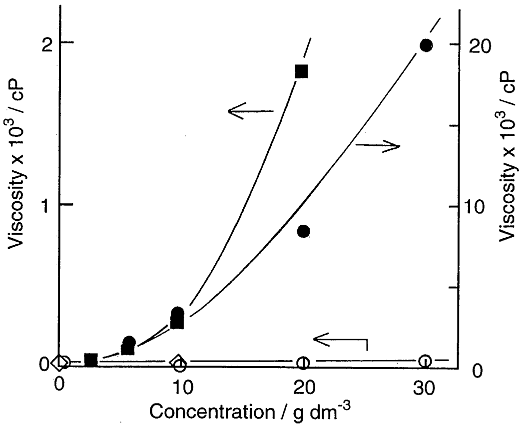


Figure 1. Dependence of viscosity on concentration in cyclohexane at 20 °C: (■); **3**, (○); **4**, (●); **5**, (◇); **6**.

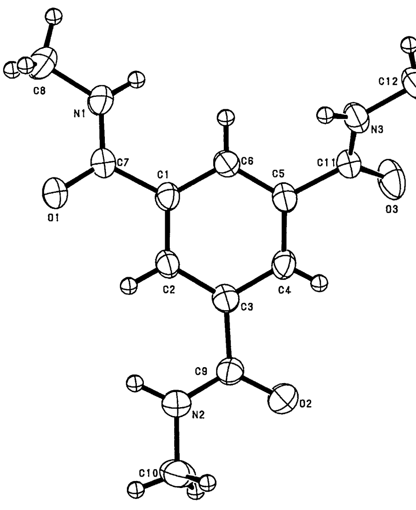


Figure 2. ORTEP drawing of trimethyl-1,3,5-benzenetricarboxamide. Selected conformation angles [°]: N1-C7-C1-C2 -166.9(3), N2-C9-C3-C4 169.1(3), N3-C11-C5-C6 46.1(4).

vibration, and two split bands at 1645 and 1630 cm^{-1} assigned to C=O hydrogen bonding ones. The spectral data suggest that two kinds of intermolecular hydrogen bonding is formed in the gel-like state. The FTIR spectrum of **5** in hexane of gel is essentially similar to that of **3** in cyclohexane of highly viscoelastic fluid. It should be mentioned here that the isotropic chloroform solution of **3** affords bands at 3450 and 1660 cm^{-1} indicative of non-hydrogen bonding stretching vibrations, whereas the solid- state (KBr pellet) of **3** shows bands at 3240 and 1640 cm^{-1} corresponding to hydrogen bonding vibrations.

The form of intermolecular hydrogen bondings for gel and gel-like state is analogized by X-ray crystallographic analysis of the structurally related molecule, trimethyl-1,3,5-benzenetricarboxamide. The molecular structure is shown in Figure 2.[8] The molecular packing is shown in Figure 3. It is found that three intermolecular hydrogen bondings are formed between N-H and C=O of amides; the intermolecular hydrogen bondings of O1-H8 and O3-H4 are formed in the lateral direction and that of O2-H12 is formed between the molecules stacked one upon another in the direction of B-axis. The intermolecular distances of O1-H8, O3-H4, and O2-H12 are 1.91(3), 1.98(4), and 1.95(4) Å.

The molecular packing of single crystal is necessary similar to that of gel or gel-like state at the atomic level, because a crystal, unlike gel or gel-like state, is an entirely static entity. However, with the help of the X-ray analysis of trimethyl-1,3,5-benzenetricarboxamide and FTIR spectra, it may safely said that the macromolecule-like aggregate responsible for gel and gel-like states is held by a favorable backbone orientation enhanced by intermolecular hydrogen bondings. The three bulky alkyl groups of **2**-**6** will prevent their molecular packing as described in Figure 3 and consequently stabilize the metastable gel-like or gel states. We conclude that gel or gel-like state is a special case of supramolecular system. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (No. 277/08246101) from The Ministry of Education, Science, Sports and Culture.

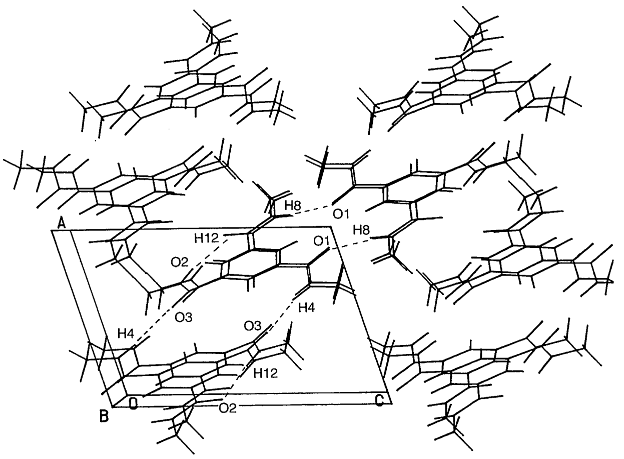


Figure 3. Molecular packing of trimethyl-1,3,5-benzenetricarboxamide.

References and Notes

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8 Crystal data: $C_{12}H_{15}N_3O_3$, *M*r = 249.27, monoclinic, $P2_1$, a = 8.050(1), b = 6.862(1), c = 11.8587(8) Å, β = 107.860(8) °, *V* = 623.5(1) Å^3, $Z = 2$, $D_{calcd} = 1.328$ g cm^{-3}, Mo-*K*α, λ = 0.71069 Å, μ = 0.91 cm^{-1}, *F*(000) = 264, 1214 observed with $I > 3.00\sigma(I)$, 1559 unique reflections at 21 °C, ω -2θ scan. The structure was solved by direct method (MITHRIL) and refined by full-matrix least squares to give R = 0.037, Rw = 0.043.