Novel Low-molecular-weight Organic Gels : *N,N',N''*-Tristearyltrimesamide/Organic Solvent System

Yoshiaki Yasuda, Eiichi Iishi, Hiroshi Inada, and Yasuhiko Shirota*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

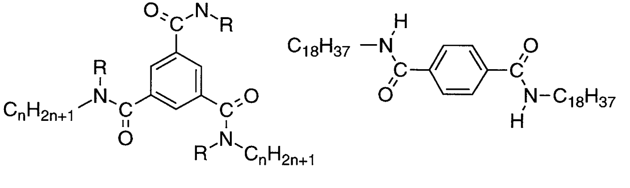
(Received March 29, 1996)

A novel class of low-molecular-weight organic gels has been developed; *N,N',N''*-tristearyltrimesamide (TSTA) forms gels with various organic solvents, immobilizing solvent at a low concentration of TSTA. The gels, which form fibrous bundles leading to three-dimensional networks, exhibit well-defined sol-gel transitions. Both intermolecular hydrogen bonding and intermolecular interactions between long alkyl chains are suggested to be responsible for the formation of gels.

Organic polymer gels have recently attracted great attention in view of both academic interest in *e.g.*, sol-gel and volume phase transitions,[1-3] and practical applications to *e.g.*, actuators.[4,5] On the other hand, few studies have been made of organic gels composed of low-molecular-weight organic compounds, which include cholesterol derivatives, arborols, cyclic dipeptides, and others.[6-12]

Low-molecular-weight organic gels, which we refer to as molecular gels, are of interest as a novel class of organic materials that take a form of solid but contain a liquid inside. Compared with polymer gels, they are expected to exhibit well-defined thermoreversible sol-gel transitions owing to well-defined structures. Developing molecular gels and elucidating their structures, properties and functions are the subjects of interest, opening up a new field in organic materials chemistry. For the development of molecular gels, it is of importance to establish guidelines for molecular design through the study of the correlation between molecular structure and gel-forming property.

We have studied gel-forming properties of *N,N',N''*-tristearyltrimesamide (TSTA) and its analogues, *N,N',N''*-tristearyl-*N,N',N''*-trimethyltrimesamide (MTSTA), *N,N',N''*-trioctyltrimesamide (TOTA), *N,N',N''*-tripropyltrimesamide (TPTA), and *N,N'*-distearylterephthalamide (DSTA). We report here a novel class of molecular gels, showing a guideline for molecular design of gel-forming organic materials.



TSTA: R=H, n=18
MTSTA: $R=CH_3$, n=18
TOTA: R=H, n=8
TPTA: R=H, n=3

DSTA

The compounds TSTA, TOTA, TPTA and DSTA, which have been studied with regard to the formation of liquid crystals,[13] were prepared by the reactions of the corresponding acid chlorides, *i. e.*, trimesoyl chloride or terephthaloyl chloride, with the corresponding aliphatic amines, *i. e.*, stearylamine, n-octylamine, or n-propylamine, in THF. MTSTA was synthesized by the reaction of TSTA with methyl iodide in THF. They were identified by various spectroscopies, mass spectrometry and elemental analysis.

TSTA was found to form gels with a variety of organic solvents such as 1,2-dichloroethane, *N,N*-dimethylformamide, nitrobenzene, *N*-methylformamide, benzonitrile and dimethyl sulfoxide, immobilizing the solvent at a very low concentration of TSTA. The gelation test was carried out as follows. A weighed amount of TSTA was dissolved in an organic solvent (1 ml) by heating in a septum-capped test tube. The resulting solution was then cooled to ca. 20 °C on standing in air and allowed to stand for 5-30 min at that temperature. The gel formation was confirmed by observing that the sample did not flow when the test tube was inverted. Table 1 summarizes minimum concentrations of TSTA required for gel formation with various solvents. Typically, an amount of 5.4 g TSTA incorporates 1000 ml of 1,2-dichloroethane.

Table 1. Minimum concentrations of TSTA for the formation of gels

Solvent	Minimum concentration [g dm^{-3}]	Weight ratio [solvent/TSTA]	Mole ratio [solvent/TSTA]
1,2-dichloroethane	5	230	2230
N, N-dimethylformamide	6	160	2110
nitrobenzene	10	120	940
N-methylformamide	10	100	1630
benzonitrile	22	50	430
dimethyl sulfoxide	41	30	330

The TSTA molecular gels were found to exhibit well-defined, thermoreversible solution - gel (sol-gel) transitions, as measured by differential scanning calorimetry (DSC). Figure 1 shows DSC curves of a TSTA / 1,2-dichloroethane gel. When the gel was

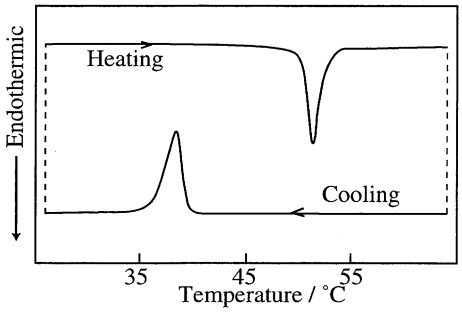


Figure 1. DSC curves of a TSTA / 1,2-dichloroethane gel with a TSTA concentration of 20 g dm^{-3}. Heating and cooling rate : 1 °C min^{-1}.

heated, an endothermic peak due to the phase transition from the gel into a solution was observed. When the resulting solution was cooled, an exothermic peak due to the phase transition from the solution into the gel was observed. The same DSC curves were traced repeatedly by the process of heating and cooling. The transition temperatures from gel to solution and from solution to gel measured from DSC curves are listed in Table 2. The transition temperatures varied depending upon the solvent incorporated in the gels.

Table 2. Sol-Gel transition temperatures of TSTA gels

Solvent	$T_{gel \rightarrow sol}$ [°C]	$T_{sol \rightarrow gel}$ [°C]
1,2-dichloroethane	51	39
nitrobenzene	59	39
N-methylformamide	91	60

As Figure 2 shows, three-dimensional networks of fibrous bundles were observed in the SEM image of xerogels obtained by evaporating the solvent from gels. This is similar to other gels reported.[6-12] It is suggested that the solvent is incorporated among the fibers.

Figure 2. SEM image of a TSTA / 1,2-dichloroethane xerogel.

Like TSTA, MTSTA and TOTA were soluble in various organic solvents; however, MTSTA containing three N-CH_3 groups in place of three N-H groups in TSTA did not form gels. TOTA with a C_8 alkyl chain could incorporate certain solvents such as 1,2-dichloroethane, nitrobenzene and benzonitrile only at two or three orders of magnitude higher concentrations (solvent / TOTA weight ratios: 2.2 to 3.7) relative to those for TSTA. TPTA was insoluble in ordinary organic solvents and did not form gels. DSTA was soluble in nitrobenzene and benzonitrile, but did not form gels with these solvents.

It is indicated that both intermolecular hydrogen bonding and intermolecular interactions between long alkyl chains are responsible for the formation of gels. The intermolecular hydrogen bonding in the TSTA gels was evidenced from infrared absorption spectra. The absorption due to the C=O stretching vibration in TSTA shifted from 1690 cm^{-1} for the dilute solution obtained by heating the gel to a lower frequency 1650 cm^{-1} for the gel. The absorption due to the free N-H stretching vibration at 3450 cm^{-1} observed for the solution also shifted to 3250 cm^{-1} for the gel. It is suggested that the fibrous bundle structures are formed as a result of the intermolecular hydrogen bonding and the intermolecular interactions between long alkyl chains.

The present results suggest that the following molecular characteristics may serve as a guiding principle for molecular design of gel-forming materials. That is, (a) the molecule should have appropriate solubility, being compatible with solvents; and (b) the molecule should have multiple sites for intermolecular hydrogen-bond formation and long alkyl chains for intermolecular interactions to form three dimensional networks.

As reported for polymer gels containing an inorganic salt,[14,15] the TSTA molecular gels containing n-Bu_4NClO_4 (1.0×10^{-1} mol dm^{-3}) were found to function as electrolytes, exhibiting high ionic conductivities (σ) comparable to those of the corresponding solution of n-Bu_4NClO_4 ($\sigma_{25\,°C}$: 1.02×10^{-3} for a 1,2-dichloroethane gel and 1.08×10^{-3} for the solution; 1.56×10^{-3} for a benzonitrile gel and 1.72×10^{-3} S cm^{-1} for the solution), as measured with a vector impedance meter at a frequency range from 20 Hz to 1 MHz.

The present finding of a novel class of gel-forming material TSTA together with the information obtained regarding the structural requirements for gel formation will enable one to design and synthesize further new families of molecules for developing molecular gels.

References and Notes

1 Y. Hirokawa and T. Tanaka, *J. Chem. Phys.*, **81**, 6379 (1984)

2 C. J. Durning and K. N. Morman, Jr., *J. Chem. Phys.*, **98**, 4275 (1993).

3 H. B. Bohidar and S. S. Jena, *J. Chem. Phys.*, **98**, 3568 (1993).

4 Y. Osada, *Adv. Mater.*, **3**, 107(1991).

5 Y. Osada, H. Okuzaki, and H. Hori, *Nature*, **355**, 242 (1992)

6 P. Terech and R. H. Wade, *J. Colloid Interface Sci.*, **125**, 542 (1988)

7 Y. Lin, B. Kachar, and R. G. Weiss, *J. Am. Chem. Soc.*, **111**, 5542 (1989).

8 K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, and S. Shinkai, *J. Am. Chem. Soc.*, **116**, 6664 (1994).

9 G. R. Newkome, C. N. Moorefield, G. R. Baker, R. K. Behera, G. H. Escamillia, and M. J. Saunders, *Angew. Chem. Int. Ed. Engl.*, **31**, 917 (1992).

10 K. Hanabusa, J. Tange, Y. Taguchi, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1993**, 390.

11 K. Hanabusa, T. Miki, Y. Taguchi, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1993**, 1382.

12 K. Hanabusa, Y. Matsumoto, T. Miki, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1994**, 1401.

13 Y. Matsunaga, N. Miyajima, Y. Nakayasu, S. Sakai, and M. Yonenaga, *Bull. Chem. Soc. Jpn.*, **61**, 207 (1988).

14 N. Ozer, F. Tepehan, and N. Bozkurt, *Thin Solid Films*, **219**, 193 (1992).

15 H. Inaba, M. Iwaku, K. Nakase, H. Yasukawa, I. Seo, and N. Oyama, *Electrochim. Acta*, **40**, 227 (1995).