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# Calixarene-Based Gelators of Organic Fluids

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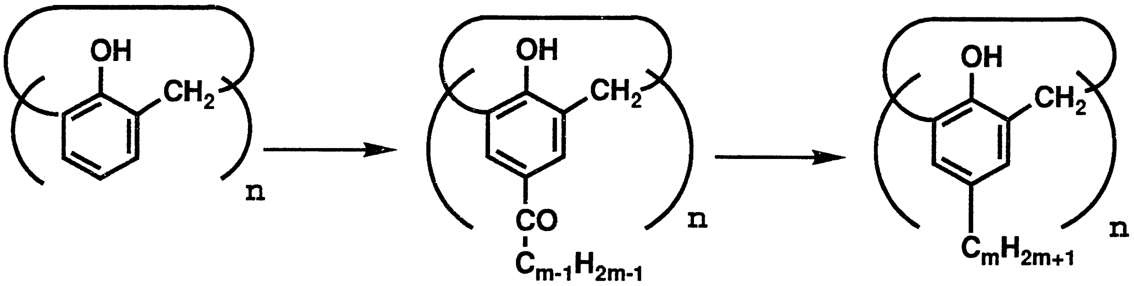
We have found that 5,11,17,23,29,35,41,47-octadodecanoylcalix[8]arene-49,50,51,52,53,54,55,56-octol ($2_8C_{12}$) serves as a novel gelator of organic fluids. The properties and the formation mechanism of the gels were investigated in detail by using spectroscopic, optical microscopic, and thermographic methods.

Calix[n]arenes having long aliphatic chains at p-position have been of increasing concern in host-guest chemistry and Langmuir monolayer formation.$^{1-3)}$ We previously developed a new synthetic route from $1_n$ to $3_nC_m$ via $2_nC_m$.$^{4)}$ In the course of this study, we experienced a surprising finding that the recrystallization of $2_8C_{12}$ from certain solvents results in gels. Recently, new gelators containing cholesterols or condensed aromatic rings are being reported by Lin et al.$^{5,6)}$ To the best of our knowledge, however, the finding is the first example for the gelator derived from macrocycles. We thus considered that the further characterization of this gel would be of great significance not only to understand the gel structure and the gelation mechanism but also to understand the aggregation properties in the Langmuir monolayer system.



$1_n$ $2_nC_m$ $3_nC_m$

The qualitative gelation test was carried out as follows: $2_8C_{12}$ (5.0 mg) was mixed with solvent (0.50 ml) in a septum-capped test tube and the mixture was heated until the solid was dissolved. The solution was cooled to room temperature and then concentrated gradually at room temperature (method A). By this method, the gel formation was observed for n-hexane, n-decane, cyclohexane, n-butanol, n-hexanol, and carbon disulfide (Table 1). Then, the solution was adjusted to 0.10 ml and cooled to -20 °C (method B). By this method, the gel formation was observed for benzene, toluene, and carbon tetrachloride (Table 1).

To determine gelation temperature $T_g$, we set up an inversed test tube containing the gel in a thermo-controlled water bath. We raised the temperature by 1 $°C·min^{-1}$ and measured the temperature where the gel "melts." The results are shown in Fig. 1. It is seen from Fig. 1 that (i) $T_g$ becomes higher with increasing $2_8C_{12}$ concentration, (ii) $T_g$ for n-hexane (35-43 °C) is much higher than those for cyclohexane (16-27 °C) and $CS_2$

Table 1. Organic fluids tested for gelation by $2_8C_{12}$[a)]

| Organic fluid | Room temperature (Method A) | 0 °C (Method B) |
|---|---|---|
| Toluene | S | G |
| Benzene | S | G[b)] |
| Carbon tetrachloride | S | G |
| Chloroform | S -> P | P |
| Dichloromethane | S | S |
| Carbon disulfide | S -> G | G |
| n-Hexane | S -> G | G |
| n-Decane | S -> G | G |
| Cyclohexane | S -> G | G |
| Acetone | I | I |
| Ethyl acetate | S -> P | P |
| Dioxane | S -> P | P |
| THF | S | P |
| Methanol | I | I |
| Ethanol | I | I |
| iso-Propanol | S -> G | G |
| n-Butanol | S -> G | G |
| n-Hexanol | S -> G | G |

a) S, soluble; P, precipitate formed; G, gel formed; I, insoluble.

b) The gel was formed before benzene solvent was solidified.

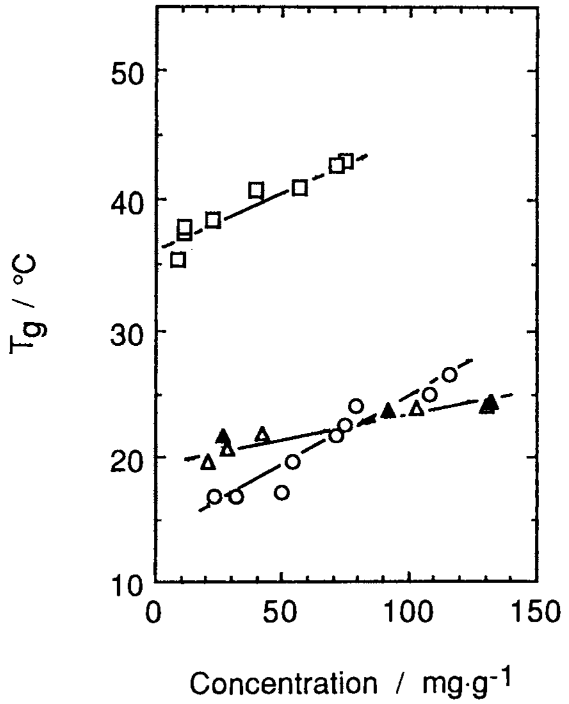


Fig. 1. Gelation temperature ($T_g$, determined by an inversed test tube method) vs. $2_8C_{12}$ concentration: ○ cyclohexane, □ n-hexane, △ $CS_2$, ▲ $CS_2$ ($T_g$, determined by DSC).

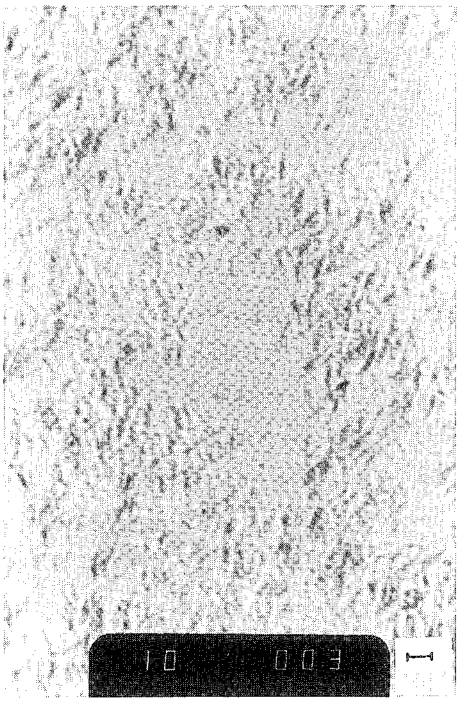


Fig. 2. Optical micrograph of $2_8C_{12}$ in $CS_2$; $[2_8C_{12}]$= 36.4 mg/g of $CS_2$, 10 °C. The bar indicates the 10 μm length.

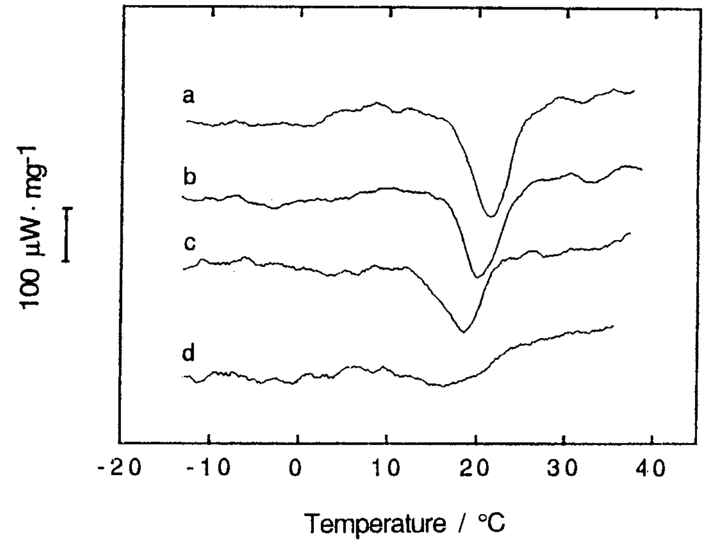


Fig. 3. DSC heating curves of $2_8C_{12}$-$CS_2$. Rate: 2 °C·min$^{-1}$, $2_8C_{12}$ concentration: 40.1 mg·g$^{-1}$. Acetone concentration is (a) 0 mg·g$^{-1}$, (b) 0.91 mg·g$^{-1}$, (c) 8.28 mg·g$^{-1}$, and (d) 20.5 mg·g$^{-1}$.

(18-24 °C), and (iii) the slope (=$dT_g/dC$, °C$(mg\cdot g^{-1})^{-1}$) is in the order of cyclohexane ($dT_g/dC$=0.107) > n-hexane (0.092) > $CS_2$ (0.041). The phase transition from gel to isotropic solution was also detected by DSC. In $CS_2$, for example, an endothermic peak appeared at around 23 °C and the peak shifted to higher temperature region with increasing $2_8C_{12}$ concentration. As plotted in Fig. 1, the phase transition temperatures determined by the DSC measurement show a good agreement with $T_g$ determined by the "melting point" measurement.

Interestingly, the aggregates formed from $2_8C_{12}$ in $CS_2$ could be directly observed by optical microscope (Fig. 2). When the homogeneous solution was cooled below $T_g$, the network formed from fibrillar aggregates with ca. 1 μm diameter appeared. When the gel was heated, the network disappeared at around $T_g$. This observation could be repeated many times. The result clearly shows that the gelation process is reversible.

Why dose $2_8C_{12}$ act as a gelator? The fact that $3_8C_{12}$ (without the carbonyl groups) does not act as a gelator suggests that the driving force for the molecular aggregation is either the C=O···HO- hydrogen-bonding interaction or the C=O···C=O dipole-dipole interaction. We thus measured the IR spectra of $2_8C_{12}$ in various solvents but could not find unequivocal evidence for the formation of the C=O···HO- hydrogen bond. Presumably, the gel network is sufficiently maintained if one C=O or HO group of eight C=O or HO groups is included in the bond formation, so that the spectroscopic detection is rather difficult. Instead, we added a small amount of acetone as an acceptor for the hydrogen bond. As shown in Fig. 3, the DSC peak at $T_g$ gradually disappeared with increasing acetone concentration. We now consider that the C=O···HO- hydrogen bond plays the crucial role for the gel formation although the C=O···C=O dipole-dipole interaction is not yet ruled out.

## References

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