Terephthaloyl Derivatives as New Gelators; Excellent Gelation Ability and Remarkable Increase of Gel Strength by Adding Polymers

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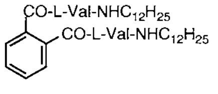
(Received February 25, 1999; CL-990125)

New gelators based on benzenedicarboxylic acid were synthesized, and their gelation abilities were clarified. *N,N'*-Terephthaloyl-bis(L-valylaminooctadecane) was especially an excellent gelator to harden a wide variety of organic fluids. The strength of gel markedly increased with addition of commercially available polymers.

Very rarely dilute binary solutions of organic compounds can form physical gels instead of crystals on cooling process. Such low molecular compounds to harden organic liquids, called "gelators", have received considerable attention during the last decade.[1,2] Gelators are of academic interest in supramolecular chemistry due to the fact that the gelation occurs as a result of cooperating noncovalent interactions. Meanwhile, gelators are characterized by good solubility upon heating and inducement of smooth gelation of organic fluids at the low concentration; therefore, they will have a wide range of possible applications e.g., as hardeners of issued crude oil on the sea and used cooking oil in family kitchen, as medicinal materials for drug-delivery system, as cosmetics, and as artificial gelling additives for food. We have developed a dozen of gelators so far,[3] and a few gelators were actually used for the quasi-solidification of liquid crystals[4] and the preparation of organogel electrolytes for solar cells[5] by our coworkers. When developing new gelators, it is important to consider whether they can be prepared from available starting materials by simple procedures. Now, we focus on phthalic acid, isophthalic acid, and terephthalic acid, which are important industrial intermediates, to develop new gelators. In this communication, we report new gelators based on benzenedicarboxylic acids and improvement of gel strength by adding polymers. Poly(*N*-vinylpyrrolidone), poly(ethylene glycol), and poly(styrene) are referred to as PVP, PEG, and PSt.



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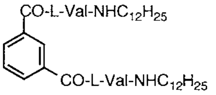

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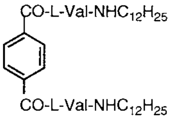

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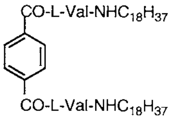

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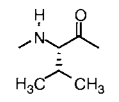

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L-Valine-containing benzenedicarbonyl derivatives (**1**-**4**) were prepared from benzenedicarbonyl chlorides and L-valylaminoalkanes in a yield of 80-95%.[6] The photograph of the gels prepared by **3** are shown in Figure 1. The gels were completely transparent like the toluene gel (Figure 1a) or translucent like the 1-propanol gel (Figure 1b) and the cyclohexanone gel (Figure 1d). Figure 1c and Figure 1e show the PVP-containing 1-propanol gel and the PSt-containing cyclohexanone gel, respectively. It is noteworthy that the gel of polymer solution by **3** is visually no different from the gel without polymer. To our knowledge, this is the first time the polymer solutions were hardened by using gelator.

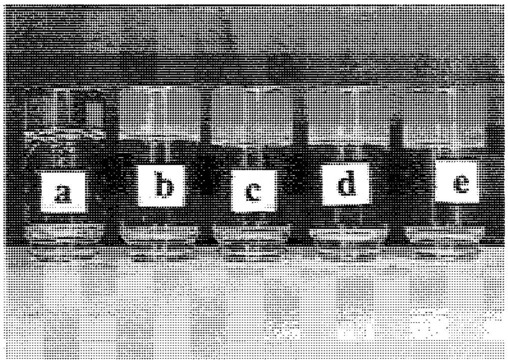

Figure 1. Photograph of various gels. (a) Gel from toluene (10 cm^3) and gelator **3** (50 mg). (b) Gel from 1-propanol (10 cm^3) and gelator **3** (50 mg). (c) Gel from 1-propanol (10 cm^3), gelator **3** (50 mg), and PVP (1.00 g). (d) Gel from cyclohexanone (10 cm^3) and gelator **3** (70 mg). (e) Gel from cyclohexanone (10 cm^3), gelator **3** (70 mg), and PSt (1.00 g).

The results of gelation tests[7] toward typical organic fluids are summarized in Table 1, where the fluids are placed in order of high dielectric constants except for silicone and soybean oils. Gelators **3** and **4** based on terephthalic acid exhibited strong gelation abilities as compared to **1** from phthalic acid and **2** from isophthalic acid. Gelator **1** did not form gel in polar solvents with high dielectric constants; while gelators **3** and **4** were able

Table 1. Gelation test of gelators based on benzenedicarboxylic acids (**1**-**4**) toward typical organic fluids at 25 °C[a]

Fluid	**1**	**2**	**3**	**4**
DMSO	soln.	4	3	3
N,N-dimethylacetamide	soln.	soln.	cryst.	6
DMF	soln.	soln.	cryst.	5
ethanol	soln.	soln.	3	7
1-propanol	soln.	10	6	7
2-butanone	soln.	8	3	5
pyridine	cryst.	cryst.	cryst.	9
THF	soln.	7	3	6
chloroform	soln.	6	4	17
benzene	10	5	7	24
tetrachloromethane	vf	8	5	15
cyclohexane	vf	insol.	8	20
kerosene	5	6	4	8
silicone oil	1	1	2	1
soybean oil	3	4	2	2

[a]soln. = isotropic solution at a glance; cryst. = crystallization; vf = viscous fluid; insol. = almost insoluble. Values mean minimum gel concentration (g dm^{-3}; gelator/fluid) at 25 °C.

to gel up nitrobenzene, 2-propanol, cyclohexanone, chlorobenzene, 1,4-dioxane, toluene, light oil, and salad oil in addition to the fluids in Table 1. It is should be mentioned that gelation ability strongly depends on amino acid segment; for example, gel fails to form when the L-valine segment of **3** is converted to glycine, L-alanine, L-leucine, and L-phenylalanine. It is also important to note that the racemate of **3** containing D,L-valine residue does not gel up any fluids at all.

It was clarified by FT-IR spectroscopy that hydrogen bonding is one of driving forces for gelation. In addition to the hydrogen bonding, which is of primary importance for gelation, there are; (1) steric effect of amino acid residue, (2) hydrophobic interaction of the tail alkyl chains, and (3) direction of two substituents around the benzene ring. Because the strong gelation ability was found exclusively in terephthaloyl derivatives with L-valine or L-isoleucine segment. Moreover, N,N'-terephthaloyl-bis(L-valylaminohexane) does not form gels, and the gelation abilities of **1** and **2**, which were based on phthalic acid and isophthalic acid, are inferior to that of **3**.

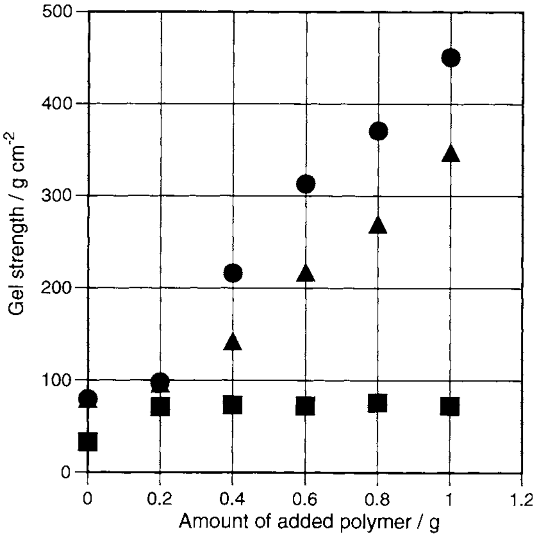

Figure 2. Effect of added polymer on gel strength. (●); Gel from 1-propanol (10 cm^3), gelator **3** (50 mg), and PEG. (▲); Gel from 1-propanol (10 cm^3), gelator **3** (50 mg), and PVP. (■); Gel from cyclohexanone (10 cm^3), gelator **3** (70 mg), and PSt.

We have reported that organogel electrolytes are readily made by physical gelation of high polar solvent containing supporting electrolyte.[8] Considering the practical use of gels, the strength of gel would be one important factor. Actually, the gel strength increases with increasing gelator concentration;[8] however, the improvement of strength by gelator concentration is limited by the solubility of gelators. Recently we found that polymer solutions were gelled by gelators and the gel strength was markedly increased by addition of polymers. Figure 2 shows the effect of added polymer on gel strength.[9] The addition of PEG (1.00 g) raised the strength of gel from 1-propanol (10 cm^3) and gelator **3** (50 mg) from 80 g cm^{-2} to 451 g cm^{-2}. Although the strength of cyclohexanone gel is not appreciably improved by the addition of PSt, the strength of 1-propanol gel is obviously enlarged by PEG or PVP. At the present time, we have not determined why the addition of PEG and PVP raises the gel strength while that of PSt does not. From the fact that there is no difference in optical appearances between the gel without polymer (Figure 1b and 1d) and the gel with polymer (Figure 1c and 1e), it seems that the polymer is dissolving homogeneously in the gel. In order to study the microscopic environment of the polymer solution fixed in the three-dimensional networks of gelator, the gel electrolytes containing $(n\text{-Bu})_4NClO_4$ was prepared and the ionic conductivity was measured. The log σ for the gel electrolyte prepared from 1-propanpl (10 cm^3), **3** (50 mg), and $(n\text{-Bu})_4NClO_4$ (342 mg; 0.10 M) was −3.45, while the log σ for the gel electrolyte from 1-propanpl (10 cm^3), **3** (50 mg), PVP (0.50 g), and $(n\text{-Bu})_4NClO_4$ (342 mg; 0.10 M) was −3.49. Moreover, the log σ for the gel electrolyte from 1-propanpl (10 cm^3), **3** (50 mg), PVP (1.00 g), and $(n\text{-Bu})_4NClO_4$ (342 mg; 0.10 M) was −3.60. It is clear that the addition of PVP hardly interferes with the ionic mobility of ion species. The slight decrease of the log σ by addition of 1.00 g of polymer can be attributed to the relatively low mobility of carrier ions in the high viscosity of polymer solution in the microscopic domain.

In conclusion, new gelators which can gel various fluids were synthesized from terephthalic acid. It is the first knowledge that the strength of gel increases markedly when the polymer-containing solution is gelled by low molecular weight gelator.

This work was supported by Grant-in-Aid for COE Research (10CE2003) and a grant (No. 09450347) from the Ministry of Education, Science, Sports and Culture of Japan.

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6 A typical procedure for **4**: L-valylaminooctadecane (7.37 g, 0.02 mol) was added to a solution of terephthaloyl chloride (2.00 g, 0.01 mol) in THF (200 cm^3). The solution was cooled by an ice bath, and triethylamine (3.07 cm^3, 0.022 mol) was added. The resulting mixture was stirred at room temperature for several hours and then heated for 5 min on a heating mantle. After evaporating, methanol was added to the residue, and insoluble matter was filtered off. The crude product was dissolved in hot DMF (300 cm^3) and filtered. Water (1 dm^3) was added to the filtrate, and then the precipitated matter was filtered off, washed with water, dried. Gelator **4** was obtained in a yield of 7.98 g (92%).

7 Gelation tests were carried out in a test tube with screw cap (inside diameter; 14 mm). A weighed sample was mixed with an organic fluid (2.0 cm^3) in a test tube and the mixture was heated until the solid was dissolved. The resulting solution was cooled at 25 °C for 2 h and then the gelation was checked. When upon inversion there was no fluid running down the walls of the tube, we judged it "gel". When the samples caused gelation, we quantitatively evaluated the gelation ability by minimum gel concentrations which are the minimum concentrations of gelators necessary for gelation at 25 °C.

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9 The strength of gels was measured and evaluated as the strength necessary to sink a cylinder bar (10 mm in diameter) 4 mm deep in the gel with a Sun Science RHEO TEX SD-305.