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## Gelation Behavior and Polymerization Reactivity of 7,7,8, 8-Tetrakis (2-phenoxyethoxycarbonyl) quinodimethane

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### ABSTRACT

Organogels composed of tetrakis (2-phenoxyethoxycarbonyl) quinodimethane (PhOEtCQ) and various organic solvents, such as ethanol, isopropyl alcohol and mixture solvents of chloroform or benzene and hexane, were prepared, and the gelation behavior and polymerization reactivity were investigated. The SEM image of xerogel prepared by freeze-drying of benzene/hexane-gel showed the highly entangled network structures composed of fibers. The photo-polymerization of PhOEtCQ by UV irradiation proceeded in the gel state, but not in crystalline or solution state.

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## INTRODUCTION

In recent years, supramolecular gel, which is formed from low molecular weight compounds by non-covalent interactions such as hydrogen bonds, van der Waals interaction and  $\pi$ - $\pi$  stacking, have attracted much interest as high functional and stimuli-responsive materials for wide range of applications. Previously, we investigated the crystal structures and solid-state polymerization reactivities of 7,7,8,8-tetrakis(alkoxy-carbonyl) quinodimethanes with various alkyl groups (RCQ), and reported that the solid-state polymerization of certain RCQs are topochemical polymerization, which proceeds with no movement of the center of gravity of monomer molecules and with retaining the crystallographic position and symmetry of the monomer crystals (Itoh *et al.*, 2002). More recently, we found that the solid-state polymerization of cocrystals composed of RCQ and 7,7,8,8-tetracyanoquinodimethane also proceeds topochemically, and gave the highly crystalline alternating copolymer (Itoh *et al.*, 2011). In a series of those studies on solid-state polymerization of RCQs, we found that the hot ethanol solution of 7,7,8,8-tetrakis(2-phenoxyethoxycarbonyl)quinodimethane (PhOEtCQ) gelate when the solution was cooled to room temperature. However, the gelation mechanism of PhOEtCQ was not clarified. In this work, we investigated the gelation behavior of PhOEtCQ in detail, and also researched polymerization reactivity of PhOEtCQ in various physical states such as gel, crystal and solution.

### Experimental Section:

#### 1. Synthesis of PhOEtCQ

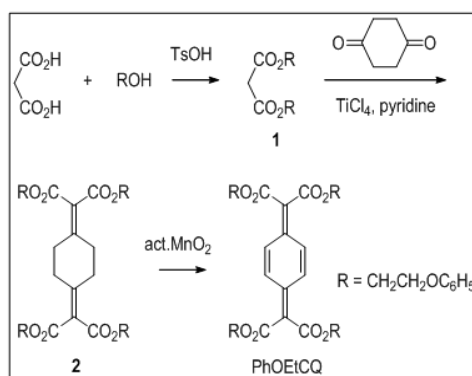
PhOEtCQ was synthesized by the same procedure reported previously for RCQs (Figure 1) (Itoh *et al.*, 2002).

*Di(2-phenoxyethyl) malonate (1)*: colorless plates by recrystallization from the mixture solvent of chloroform, ether and hexane (74% yield); mp 47.5-48.0 °C; IR (KBr,  $\text{cm}^{-1}$ )  $\nu$  = 3061, 2961 (C-H), 1720 (C=O), 1500 (C=C), 1247, 1186 (C-O-C); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 7.28 (t,  $J$  = 8.10 Hz, 4H), 6.97 (t,  $J$  = 7.29 Hz, 2H), 6.90 (d,  $J$  = 7.29 Hz, 4H), 4.49 (t,  $J$  = 4.86 Hz, 4H), 4.16 (t,  $J$  = 5.40 Hz, 4H), 3.48 (s, 2H); <sup>13</sup>C NMR (67.5 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 166.3 (C=O), 158.3 (Ar), 129.5 (Ar), 121.2 (Ar), 114.6 (Ar), 65.5 (CH<sub>2</sub>), 63.8 (CH<sub>2</sub>), 41.2 (CH<sub>2</sub>).

*1,4-Bis[di(2-phenoxyethoxycarbonyl)methylene]-cyclohexanone (2)*: white powder by recrystallization from the mixture solvent of chloroform, ether and hexane (57% yield); mp 45.5-46.5 °C; IR (KBr,  $\text{cm}^{-1}$ )  $\nu$  = 3060, 2961 (C-H), 1725 (C=O), 1498 (C=C), 1247, 1185 (C-O-C); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 7.26 (t,  $J$  = 8.91 Hz, 8H), 6.94 (t,  $J$  = 7.02 Hz, 4H), 6.82 (d,  $J$  = 7.83 Hz, 8H), 4.47 (m, 8H), 4.12 (m, 8H), 2.75 (s, 8H); <sup>13</sup>C NMR

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(67.5 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 166.1 (C=O), 159.3 (>C=), 158.2 (Ar), 129.4 (Ar), 122.6 (=C<), 121.1 (Ar), 114.5 (Ar), 65.3 (CH<sub>2</sub>), 63.6 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>).



**Fig. 1:** Synthetic rout of PhOEtcQ.

*PhOEtcQ*: pale yellow needles by recrystallization from acetonitrile (46% yield); mp 113-114 °C; IR (KBr, cm<sup>-1</sup>)  $\nu$  = 3099, 2951 (C-H), 1722 (C=O), 1597, 1499 (C=C), 1244 (C-O-C); <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 7.47 (s, 4H), 7.26 (t,  $J$  = 7.29 Hz, 8H), 6.96 (t,  $J$  = 7.02 Hz, 4H), 6.86 (d,  $J$  = 7.56 Hz, 8H), 4.55 (t,  $J$  = 4.86 Hz, 8H), 4.15 (t,  $J$  = 4.59 Hz, 8H); <sup>13</sup>C NMR (67.5 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm) 164.3 (C=O), 158.2 (Ar), 139.6 (>C=), 130.2 (C=C), 129.5 (Ar), 125.4 (=C<), 121.2 (Ar), 114.6 (Ar), 65.4 (CH<sub>2</sub>), 63.9 (CH<sub>2</sub>).

## 2. Preparation of Gels:

PhOEtcQ and an appropriate solvent were placed in screw-capped test tube, and heating until PhOEtcQ was dissolved. Then the solution was allowed to cool to room temperature. The formation of gels was evaluated by tube inversion.

## 3. Measurement of Sol-Gel Transition Temperature (T<sub>g</sub>):

The sol-gel transition temperature (gel-destruction temperature; T<sub>g</sub>) was determined by the dropping-ball method. A glass ball weighing 0.17 g was placed on the gel in a test tube, and then the test tube was heated in an oil bath. The T<sub>g</sub> was noted when the ball sank in the gel completely.

## 4. Photopolymerization:

Photopolymerization was carried out under UV irradiation by using a high-pressure mercury lamp (400W) at 30 °C. The conversion was determined by GPC measurement of reaction mixture, and calculated from the ratio of peak areas due to reaction product and unreacted monomer.

# RESULT AND DISCUSSION

## 1. Gelation Behavior:

The gelation properties of PhOEtcQ was investigated in various organic solvents such as ethanol, isopropyl alcohol, chloroform, benzene, and the mixture solvents of hexane and chloroform or benzene, and the results are summarized in Table 1. The gels formed with alcohols were opaque gel and showed low CGC (critical gelation concentration) values. Ethanol-gel was too fragile to determine the sol-gel transition temperature (gel-destruction temperature; T<sub>g</sub>). On the other hand, isopropyl alcohol-gel showed the highest T<sub>g</sub> at 63 °C. Although chloroform or benzene, which is good solvent for PhOEtcQ, did not yield gels, the transparent gels were obtained by the mixing with hexane. The increase in the ratio of hexane in benzene/hexane-gel led the decrease of CGC and the increase of T<sub>g</sub>.

**Table 1:** Gelation properties of PhOEtcQ in selected organic solvents.

Solvent <sup>a)</sup>	State <sup>b)</sup>	CGC <sup>c)</sup> / gL <sup>-1</sup>	T <sub>g</sub> <sup>d)</sup> / °C
EtOH	O	3	nd <sup>e)</sup>
IPA	O	4	63
CHCl <sub>3</sub> /Hex = 1/0 <sup>f)</sup>	X	—	—
1/1	X	—	—
1/2	T	15	53
Bz/Hex = 1/0	X	—	—
1/1	T	10	48
1/2	T	6	51
1/3	T	4	58

<sup>a)</sup> EtOH: ethanol, IPA: isopropyl alcohol, Hex: hexane, Bz: benzene.

<sup>b)</sup> O = opaque gel, X = solution, T = transparent gel.

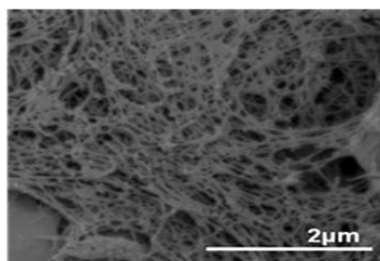
<sup>c)</sup> CGC: critical gelation concentration.

<sup>d)</sup> Tg: sol-gel transition temperature.

<sup>e)</sup> Not determined.

<sup>f)</sup> Ratio of mixture solvents in volume/volume.

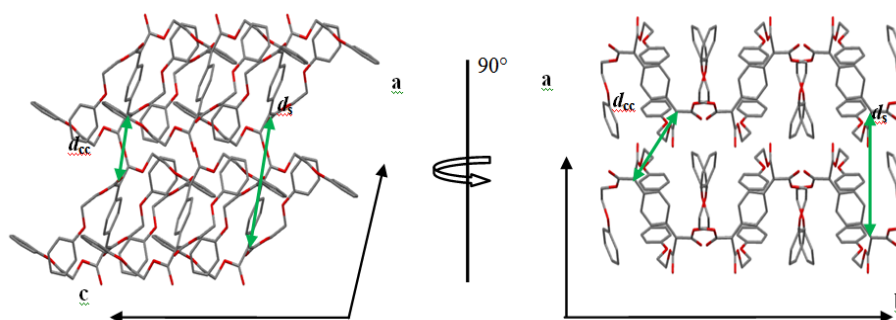
To investigate the morphology of the gel, freeze-dried gels were subjected to scanning electron microscopy (SEM) measurement. The SEM image of xerogel prepared from benzene/hexane(1/1)-gel showed the highly entangled network structures composed of fibers of about 40 nm width (Figure 2). This observation suggests that PhOEtCQ formed fibrous aggregate by interaction between monomers, and gelled by intertwining of the aggregate.



**Fig. 2:** SEM images of xerogel prepared from benzene/hexane(1/1)-gel.

### 2. Crystal Structure Analysis:

The results of X-ray crystal structure analysis of single crystal of PhOEtCQ, which prepared by recrystallization from chloroform/hexane solution, is shown in Figure 3. The crystal of PhOEtCQ belongs to the space group  $P2_1/c$  (No. 14) and has a monoclinic unit cell with  $a = 8.5807(2)$ ,  $b = 18.0867(4)$ ,  $c = 12.8447(3)$  Å and  $\beta = 102.9529(13)^\circ$  in which two molecules are included. PhOEtCQ molecules form a one-dimensional column along the crystallographic  $a$  axis, and the distances between equivalent atoms ( $d_s$ ) and between the reacting exomethylene carbon atoms ( $d_{cc}$ ) in the adjacent molecules were 8.57 and 5.99 Å, respectively. The latter value is about 1.5 times longer than those observed in topochemically polymerizable RCQs (about 4 Å) (Itoh *et al.*, 2002). This suggests that the solid-state polymerization of PhOEtCQ crystal does not proceed.



**Fig. 3:** Crystal structure of PhOEtCQ (omitted hydrogen atoms).

### 3. Photopolymerization:

Photopolymerization of PhOEtCQ were carried out in various physical states, that is gel state obtained from benzene/hexane(1/1), xerogel state prepared by freeze-drying of benzene/hexane(1/1)-gel, crystalline state prepared by recrystallization from  $\text{CHCl}_3$ /hexane(1/1) solution, and solution state in  $\text{CHCl}_3$ , under UV irradiation at 30 °C. The results are summarized in Table 2. Photopolymerization of gel state under UV irradiation proceeded in good conversion. Although xerogel and solution states also gave the oligomer in very low yield, no polymerization occurred in crystalline state, as suggested from X-ray crystal structure analysis. These results strongly suggest that PhOEtCQ molecules in the gel state formed fibrous aggregate by  $\pi$ - $\pi$  stacking of the quinodimethane rings with polymerizable distance, in contrast to the crystalline state in which PhOEtCQ molecules are not stacked.

**Table 2:** Photopolymerization of PhOEtCQ in various physical states.

State (Solvent <sup>a)</sup> )	Conc. / gL <sup>-1</sup>	Conv. <sup>b)</sup> / %	$M_n$ <sup>b)</sup>
Gel (Bz/Hex = 1/1)	10	51	1,100
Xerogel (Bz/Hex = 1/1)	—	13	700
Crystalline ( $\text{CHCl}_3$ /Hex = 1/1)	—	0	—
Solution ( $\text{CHCl}_3$ )	10	9	600

<sup>a)</sup> Bz: benzene, Hex: hexane.

<sup>b)</sup> Calculated from GPC measurement of reaction mixture.

**Conclusion:**

The gelation behavior and polymerization reactivity of organogel composed of PhOEtCQ and various organic solvents were investigated. PhOEtCQ gelled various kinds of organic solvents including ethanol, isopropyl alcohol and mixture solvents of hexane and benzene or chloroform. Alcohols gave the opaque gels, while the transparent gels were obtained from mixture solvents of hexane and benzene or chloroform. The SEM image of xerogel prepared by freeze-drying of benzene/hexane(1/1)-gel showed network structure of entangled fibers. Photopolymerization of PhOEtCQ by UV irradiation successfully proceeded in only gel state, suggesting the formation of fibrous aggregate by  $\pi$ - $\pi$  stacking of the quinodimethane rings in gel.

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