

## Polymerization Reactivity in Solid State of Cocrystals Composed of Tetrakis (alkoxycarbonyl)quinodimethanes and Quinoid Acceptors

<sup>1</sup>T. Fukushima, <sup>1</sup>T. Uno, <sup>2</sup>M. Kubo, <sup>1</sup>T. Itoh, <sup>3</sup>N. Tohnai, and <sup>3</sup>M. Miyata

<sup>1</sup>Graduate School of Engineering, Mie University, 1577 Kurimamachiya-cho, Tsu 514-8507, JAPAN.

<sup>2</sup>Graduate School of Regional Innovation Studies, Mie University, 1577 Kurimamachiya-cho, Tsu 514-8507, JAPAN.

<sup>3</sup>Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita 565-0871, JAPAN.

### ARTICLE INFO

#### Article history:

Received 20 November 2013

Received in revised form 24

January 2014

Accepted 29 January 2014

Available online 25 February 2014

#### Key words:

### ABSTRACT

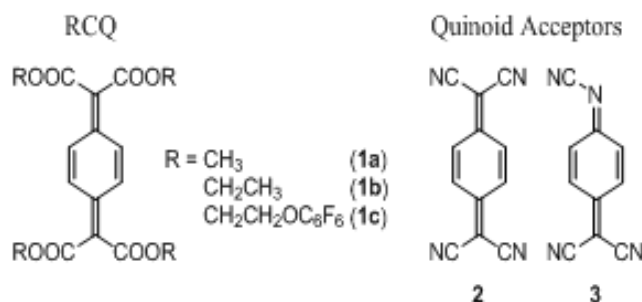
Cocrystals composed of 7,7,8,8-tetrakis (alkoxycarbonyl) quinodimethanes (RCQ) and various quinoid acceptors, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) and *N*,7,7-tricyano-*p*-benzoquinone methide imine (BMI), were prepared and the polymerization reactivities in solid state and crystal structures of those cocrystals were investigated. The solid-state polymerization of RCQ/TCNQ cocrystals and RCQ/BMI cocrystals gave the highly crystalline insoluble copolymers and the amorphous soluble copolymers under UV irradiation, respectively. These differences of polymerization reactivities could explain on the basis of those crystal structures.

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**To Cite This Article:** T. Fukushima, T. Uno, M. Kubo, T. Itoh, N. Tohnai and M. Miyata., Polymerization Reactivity in Solid State of Cocrystals Composed of Tetrakis (alkoxycarbonyl)quinodimethanes and Quinoid Acceptors. *Aust. J. Basic & Appl. Sci.*, 8(4): 516-520, 2014

## INTRODUCTION

Solid-state polymerization is one of polymerization method which produces a crystalline polymer from monomer crystal, and is an environmental-friendly polymerization process. In particular, topochemical polymerization as a specific case of solid-state polymerization has received much attention from a viewpoint of control of polymer structures such as regioselectivity, stereoregularity, and molecular weight, because topochemical polymerization proceeds with no movement of the center of gravity of monomer molecules and with retaining the crystallographic position and symmetry of the monomer crystals. Previously, we reported that the solid-state polymerization of 7,7,8,8-tetrakis(methoxycarbonyl)-quinodimethane (**1a**) proceeds topochemically, and produces highly crystalline polymer (Itoh *et al.*, 2002). More recently, we found that the solid-state polymerization of crystalline charge-transfer complex (*cocrystal*) composed of **1a** and 7,7,8,8-tetracyanoquinodimethane (**2**), which is strongly electron-accepting quinoid compound (quinoid acceptor), also proceeds topochemically, and gave the crystalline alternating copolymer (Itoh *et al.*, 2011). In this work, we prepared the cocrystals composed of three kinds of 7,7,8,8-tetrakis-(alkoxycarbonyl)quinodimethanes with methyl, ethyl and pentafluorophenoxyethyl group (RCQ, **1a-1c**) and various quinoid acceptors, such as **2** and *N*,7,7-tricyanobenzoquinone methide imine (**3**), and investigated the polymerization reactivity in solid state and crystal structure of those cocrystals (Figure 1).



**Fig. 1:** Structures of RCQ and Quinoid Acceptors.

**Experimental Section:****1. Materials:**

Synthesis of **1** and **3** were carried out according to the reported methods (Itoh *et al.*, 2002; Itoh *et al.*, 2011; Iwatsuki *et al.*, 1988). **2** was commercially purchased and purified by recrystallization from acetonitrile.

**2. Preparation of Cocrystals:**

Cocrystals composed of various RCQs and acceptors were obtained by crystallization from a mixture solution of RCQ and acceptor in various organic solvents. The conditions gave a single-crystal of each cocrystal were summarized in Table 1.

**1a/2 Cocrystal:** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2960$  (CH), 2225 (CN), 1747 (C=O), 1434 (C=C), 1264 (C-O), 1223 (C-O); XRD ( $\text{Cu}_{\text{K}\alpha 1}$  / 40 kV / 40 mA,  $2\theta$  (relative intensity %): 6.56 (100), 13.12 (62), 14.60 (15), 15.20 (3), 16.56 (5), 18.80 (3), 19.68 (5), 24.30 (3), 24.40 (3), 26.18 (4), 26.32 (4), 26.78 (4), 28.48 (4), 28.62 (4), 29.26 (3).

**1b/2 Cocrystal:** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2992$  (CH), 2225 (CN), 1718 (C=O), 1698 (C=O), 1576 (C=C), 1252 (C-O), 1222 (C-O); XRD ( $\text{Cu}_{\text{K}\alpha 1}$  / 40 kV / 40 mA,  $2\theta$  (relative intensity %): 7.46 (91), 12.10 (2), 13.08 (12), 14.80 (100), 15.20 (14), 15.64(4), 17.42(7), 22.20 (10), 23.56 (6), 25.02 (11), 25.90 (7), 26.64 (7), 27.72 (3), 29.64 (14), 30.52 (3), 34.80 (3), 35.30 (3), 38.40 (4), 41.28 (4), 44.98 (4).

**1c/2 Cocrystal:** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2960$  (CH), 2225 (CN), 1720 (C=O), 1702 (C=O), 1515 (C=C), 1259 (C-O), 1224 (C-O); XRD ( $\text{Cu}_{\text{K}\alpha 1}$  / 40 kV / 40 mA,  $2\theta$  (relative intensity %): 11.48 (21), 12.54 (11), 13.36 (24), 14.18 (59), 15.29 (38), 16.17 (17), 21.19 (31), 22.00 (29), 22.86 (8), 24.26 (49), 26.32 (100), 27.71 (72).

**1a/3 Cocrystal:** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2957$  (CH), 2226 (CN), 2165 (CN), 1731 (C=O), 1707 (C=O), 1545 (C=C), 1252 (C-O), 1218 (C-O).

**1b/3 Cocrystal:** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2984$  (CH), 2226 (CN), 2165 (CN), 1748 (C=O), 1715 (C=O), 1546 (C=C), 1217 (C-O).

**1c/3 Cocrystal:** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2965$  (CH), 2227 (CN), 2166 (CN), 1732 (C=O), 1706 (C=O), 1581 (C=C), 1222 (C-O); melting point: 94 °C.

**Table 1:** Preparation of Cocrystals Composed of RCQs and Quinoid Acceptors.

[RCQ]/[Acceptor]	Solvent	Cocrystal
1a/2	CH <sub>3</sub> CN	Red Prism
1b/2	CH <sub>3</sub> CN	Red Prism
1c/2	CH <sub>3</sub> CN	Orange Prism
1a/3	CHCl <sub>3</sub> /Hex <sup>a)</sup>	Red Prism
1b/3	DEC <sup>b)</sup> /Hex	Red Prism
1c/3	CHCl <sub>3</sub> /Hex	Orange Plate

<sup>a)</sup> Hexane <sup>b)</sup> Diethyl carbonate

**3. Polymerization:**

Photopolymerization was carried out under UV irradiation with high-pressure mercury lamp (Fuji Glass Work Type HB-400, 400W) at 30 °C. Thermal polymerization was carried out by differential scanning calorimetry (DSC) measurement (Seiko 6220, instrument) at a scan speed of 5 °C / min under nitrogen gas flow.

**Poly(1a/2):** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2961$  (CH), 1747 (C=O), 1435 (C=C), 1266 (C-O), 1200 (C-O); XRD ( $\text{Cu}_{\text{K}\alpha 1}$  / 40 kV / 40 mA,  $2\theta$  (relative intensity %): 7.46 (91), 12.10 (2), 13.08 (12), 14.80 (100), 15.20 (14), 15.64(4), 17.42(7), 22.20 (10), 23.56 (6), 25.02 (11), 25.90 (7), 26.64 (7), 27.72 (3), 29.64 (14), 30.52 (3), 34.80 (3), 35.30 (3), 38.40 (4), 41.28 (4), 44.98 (4); polymerization temperature: 119 °C.

**Poly(1b/2):** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2983$  (CH), 1763 (C=O), 1742 (C=O), 1499 (C=C), 1258 (C-O), 1199 (C-O); XRD ( $\text{Cu}_{\text{K}\alpha 1}$  / 40 kV / 40 mA,  $2\theta$  (relative intensity %): 6.56(100), 13.12 (62), 14.60 (15), 15.20 (3), 16.56 (5), 18.80 (3), 19.68 (5), 23.38 (2), 24.30 (3), 24.40 (3), 26.18 (4), 26.32 (4), 26.78 (4), 28.48 (4), 28.62 (4), 29.26 (3); polymerization temperature: 107 °C.

**Poly(1c/2):** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2960$  (CH), 1745 (C=O), 1515 (C=C), 1243 (C-O), 1191 (C-O); XRD ( $\text{Cu}_{\text{K}\alpha 1}$  / 40 kV / 40 mA,  $2\theta$  (relative intensity %): 11.10 (6), 14.71 (100), 20.56 (13), 26.44 (31), 27.08 (31), 27.09 (19), 29.68 (16); polymerization temperature: 111 °C.

**Poly(1a/3):** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2958$  (CH), 2226 (CN), 2137 (CN), 1743 (C=O), 1508 (C=C), 1266 (C-O), 1201 (C-O); polymerization temperature: 152 °C.

**Poly(1b/3):** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2922$  (CH), 2226 (CN), 2137 (CN), 1746 (C=O), 1509 (C=C), 1261 (C-O); polymerization temperature: 100 °C.

**Poly(1c/3):** IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 2955$  (CH), 2228 (CN), 2134 (CN), 1748 (C=O), 1515 (C=C), 1263 (C-O).

**RESULT AND DISCUSSION****1. Preparation of Cocrystals:**

The preparation of cocrystals composed of RCQ (**1a-1c**) and various quinoid acceptors were investigated by crystallization of the mixture solution of RCQ and quinoid acceptor using various organic solvent systems, and the results are summarized in Table 1. All of the obtained cocrystals were red or orange prism.

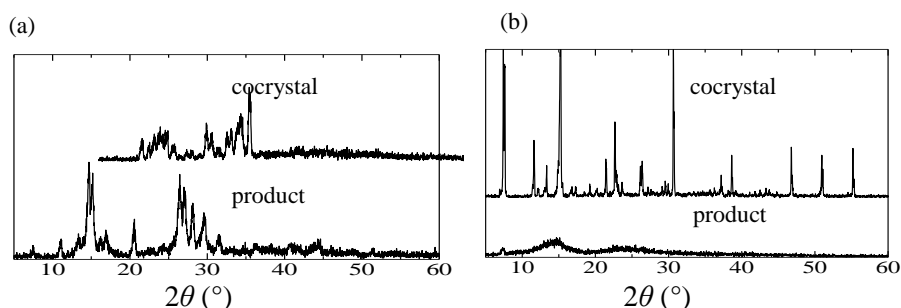
## 2. Photopolymerization of Cocrystals

Photopolymerization in solid state of cocrystals were carried out under UV irradiation at 30 °C, and the results are summarized in Table 2. The RCQ/**2** cocrystals changed to insoluble pale pink prism under UV irradiation for 24 h. In the IR spectra of photopolymerization products, the characteristic absorption assigned to the quinoid skeleton of RCQ and **2** in cocrystals disappeared completely, and the absorption bands of aromatic ring appeared. These changes were identical to that of alternating copolymers obtained in the solution copolymerization of RCQ and **2**. The powder XRD patterns of **1c/2** cocrystal and photopolymerization product are shown in Figure 1(a). The sharp diffraction pattern of the photopolymerization product indicates that none of the crystallinity of the **1c/2** cocrystal had been lost after polymerization. These results indicate that the photopolymerization in solid state of RCQ/**2** cocrystals proceed topochemically, and give the crystalline alternating copolymers composed of RCQ and **2**.

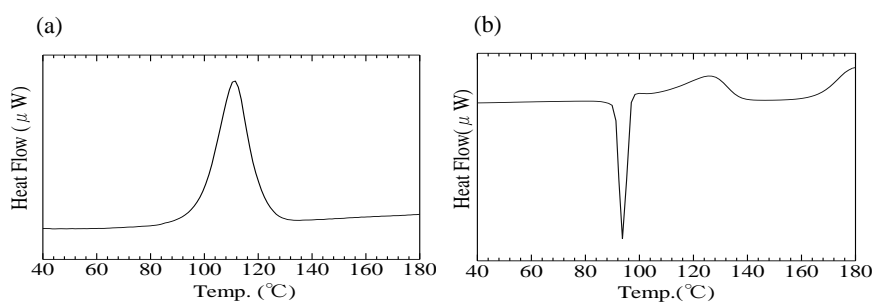
The RCQ/**3** cocrystals also changed to soluble pale yellow prism under UV irradiation, and gave the alternating copolymers with molecular weight in the range of 9700 to 22000. However, the powder XRD pattern of alternating copolymer obtained by photopolymerization of **1a/3** cocrystal showed only amorphous halo (Figure 1(b)). This indicates that photopolymerization in solid state of RCQ/**3** cocrystals did not proceed topochemically.

**Table 2:** Photopolymerization of Cocrystals composed of RCQs and Quinoid Acceptors.

Cocrystal	Time / day	Product form	$M_n$
1a / 2	1	Pale pink prism	ND
1b / 2	1	Pale pink prism	ND
1c / 2	1	Pale pink prism	ND
1a / 3	14	Pale yellow prism	9700
1b / 3	7	Pale yellow prism	16100
1c / 3	45	Pale yellow prism	22000



**Fig.1:** Power XRD patterns of cocrystal and photo-polymerization product of **1c/2** (a) and **1a/3** (b).



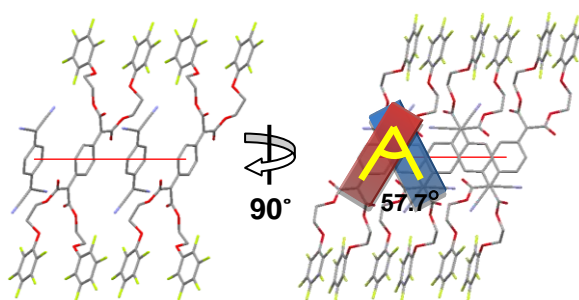
**Fig. 2:** DSC thermograms of **1c/2** (a) and **1c/3** (b) cocrystals.

### 3. Thermal Polymerization of Cocrystals

The thermal polymerization reactivity of cocrystals was investigated by DSC measurement. RCQ/2, **1a/3**, and **1b/3** cocrystals showed exothermic peaks below the melting point of cocrystals (Figure 2(a)). This suggests that the thermal polymerization in solid state proceed in those cocrystals. On the other hand, **1c/3** cocrystal showed only endothermic peaks assignable to the melting point of cocrystals, indicating that no thermal polymerization in solid state occurred (Figure 2(b)).

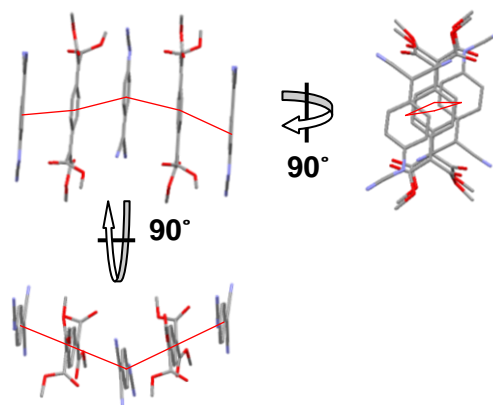
### 4. Crystal Structure Analysis:

The result of X-ray crystal-structure analysis of single crystal of **1c/2** cocrystal is shown in Figure 3. The **1c** and **2** molecules formed a one-dimensional column with an alternating stacked arrangement and a torsion angle of  $57.7^\circ$ . The stacking axis, which is the line connecting the center of gravity of **1c** and **2**, was straight, and the distance between the reactive exomethylene carbon atoms in **1c** and **2** was  $3.8 \text{ \AA}$ , which is suitable value for topochemical polymerization (about  $4 \text{ \AA}$ ). It is considered that the polymerization reaction in **1c/2** cocrystal proceeds through successive bond formation between exomethylene carbon atoms with no movement of the center of gravity of **1c** and **2** molecules.



**Fig. 3:** Molecular packing structure of **1c/2** cocrystal (The red line is stacking axis).

In a single-crystal of **1a/3** cocrystal, the **1a** and **3** molecules also formed an alternating stacked arrangement. However, the stacking axis of **1a** and **3** was not straight but zigzag as shown in Figure 4. It is suggested that the solid-state polymerization of **1a/3** cocrystal did not proceed topochemically because the stacking axis was not straight.



**Fig. 4:** Molecular packing structure of **1a/3** cocrystal (The red line is stacking axis).

### Conclusion:

Cocrystals composed of RCQ (**1a-1c**) and quinoid acceptors (**2**, **3**) were prepared, and the polymerization reactivity in solid state and crystal structure of those cocrystals were investigated. The solid-state polymerization of RCQ/2 cocrystals proceeded topochemically under UV irradiation or heating, and gave the insoluble alternating copolymer crystals. On the other hand, the RCQ/3 cocrystals changed into the soluble amorphous copolymers in solid state. From the X-ray crystal structure analyses of single crystals, both of RCQ/2 and RCQ/3 cocrystals formed an alternating stacked arrangement. However, the stacking axis of RCQ/2 cocrystal was straight, while that of RCQ/3 cocrystal was zigzag. These results suggested that it is very important that the stacking axis is straight to proceed of the topochemical copolymerization of RCQ/acceptor cocrystals.

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