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Solid-State Photopolymerization

Cis-Specific Topochemical Polymerization: Alternating Copolymerization of 7,7,8,8-Tetrakis(methoxycarbonyl)quinodimethane with 7,7,8,8-Tetracyanoquinodimethane in the Solid State**

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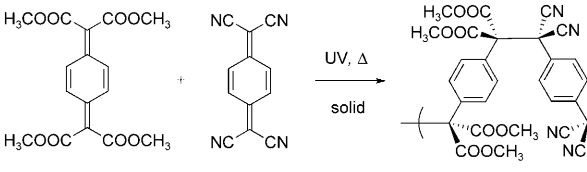
Solid-state polymerization has received considerable attention as an environmentally friendly polymerization method in recent years. In particular, topochemical polymerization as a specific case of solid-state polymerization has been a focus of great interest because it may offer the possibility of providing polymers with highly controlled structures in terms of regioselectivity, stereoregularity, molecular weight, and so on. Since topochemical polymerization proceeds with no movement of the center of gravity of the monomer molecules and only slight rotation of the monomer molecules around the center of gravity, the crystallographic position and symmetry of the monomer crystals are retained in the resulting polymer crystals. Such monomers may not always be accessible or easily obtained owing to strict requirements, and only a limited number of monomers, such as derivatives of diacetylene,[1] 2,5-distyrylpyrazine,[2] triene and triacetylene,[3] muconic acid and sorbic acid,[4] and 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethanes,[5] have been known to undergo topochemical polymerization. Almost all topochemical polymerizations observed for diacetylenes, 2,5-distyrylpyrazines, trienes and triacetylenes, muconic acids and sorbic acids, and 7,7,8,8-tetrakis(alkoxycarbonyl)quinodiemthanes take place in a *trans*-specific polymerization mode to yield zigzag-type polymers with a *trans* conformation. Interestingly, there are no reported examples of the formation of a polymer with a *cis* conformation by a topochemical polymerization. From the viewpoint of "crystal engineering", concepts from supramolecular chemistry, such as host–guest interactions, charge-transfer perfluorophenyl–phenyl π–π interactions, and hydrogen-bond interactions, have been introduced to align monomer molecules into a column with the requirements for topochemical polymerization. Many successful examples of this approach have been reported for the solid-state polymerization of diacetylenes, triacetylenes, dienes, and trienes.[6]

7,7,8,8-Tetrakis(methoxycarbonyl)quinodimethane (**1**) is a topochemically polymerizable monomer in the solid state and an interesting compound which shows amphoteric behavior in both copolymerization and charge-transfer-complex formation in solution. That is, **1** formed charge-transfer complexes with electron-donating monomers, such as styrene derivatives and vinyl ethers, and also underwent copolymerization with them as an acceptor monomer to form the corresponding alternating copolymers.[7] Moreover, **1** could form a charge-transfer complex with the strongly electron-accepting-substituted quinodimethane 7,7,8,8-tetracyanoquinodimethane (**2**), and also underwent spontaneous alternating copolymerization with **2** as a donor monomer in acetonitrile.[7] This unusual behavior prompted us to construct a crystalline charge-transfer complex of **1** and **2**, and to investigate the polymerization reactivity of the complex crystal. We succeeded in obtaining a crystalline charge-transfer complex and also found that topochemical alternating copolymerization can be induced by exposure of this complex to UV light and heat to yield an alternating copolymer with a *cis* conformation (Scheme 1). Herein we describe the first example of *cis*-specific topochemical copolymerization in substituted quinodimethanes on the basis of crystal-structure analysis of the crystalline charge-transfer complex and its polymer crystal obtained by UV irradiation and heating.

The monomer **1** was prepared according to the method reported previously[5] and obtained in 16% yield as yellow cubic crystals by recrystallization from a mixture of chloroform and *n*-hexane (1:3 v/v). When a solution of **1** in acetonitrile was mixed with a solution of **2** in acetonitrile at room temperature, an orange color developed immediately as a result of the formation of a charge-transfer complex. Cooling of the resulting solution in a refrigerator at −20°C for 12 hours yielded an orange-colored platelet crystal, which did



1 **2** poly(**1**·**2**)

Scheme 1. *Cis*-specific copolymerization between **1** and **2**.

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not show a melting point because of its spontaneous polymerization upon heating. To determine the composition of the crystalline charge-transfer complex, we dissolved the orange crystal completely in deuterated chloroform and measured its ^{1}H NMR spectrum. Integration of the peak at $\delta = 7.44$ ppm assigned to **1** and the peak at $\delta = 7.56$ ppm assigned to **2** revealed a 1:0.97 ratio of **1** to **2** and indicated definitively that the orange crystal consisted of a 1:1 charge-transfer complex.

To investigate the polymerization behavior of the crystalline charge-transfer complex (**1·2** cocrystal), we subjected a crystalline sample of **1·2** to UV irradiation with a high-pressure Hg lamp or heating in the dark. We also carried out the spontaneous solution copolymerization of **1** with **2** in acetonitrile at 60 °C for comparison. When the **1·2** cocrystal was exposed to UV light at 25 °C in vacuo for 18 hours, or was heated at 60 °C in vacuo for 3 hours, it became transparent and colorless (upon UV irradiation) or pink (upon heating) and then afforded polymeric products in quantitative yield (Table 1). In the solution polymerization, the polymeric white product precipitated gradually with time. These polymeric products are insoluble in common organic solvents, such as benzene, chloroform, acetone, tetrahydrofuran, dimethyl sulfoxide, trifluoroacetic acid, and hexafluoroisopropyl alcohol, and even in concentrated sulfuric acid.

The polymeric products derived from the **1·2** cocrystal and from the spontaneous solution copolymerization of **1** with **2** were only characterized by IR spectroscopy, elemental analysis, and powder X-ray diffraction (XRD) owing to their insolubility in common organic solvents.

Characteristic absorption bands at 1577 and 1546 cm^{-1} assigned to the exocyclic conjugated carbon–carbon double bonds of **1** and **2** in the **1·2** cocrystal disappeared completely in the IR spectra of the polymeric products, which were identical to that of the alternating copolymer obtained in the spontaneous solution copolymerization of **1** and **2** in acetonitrile (Table 1, entry 3). The results of elemental analysis of the polymeric product obtained in the solid-state polymerizations were in good agreement with the calculated values for the alternating copolymer of **1** with **2**.

Thermal polymerization of the **1·2** cocrystal in the solid state in vacuo was investigated by electron spin resonance (ESR) spectroscopy. When the **1·2** cocrystal was heated at 132 °C, the ESR spectrum showed a broad triplet peak at a *g* value of 2.0033 with a coupling constant of 5.0 G. This peak was assigned to the two equivalent *ortho* hydrogen atoms of the phenylene group and strongly supports the hypothesis that the bis(methoxycarbonyl)benzyl moiety of **1** and/or the dicyanobenzyl moiety of **2** functions as a propagating radical.

Table 1: Solid-state photopolymerization and thermal polymerization of the **1·2** cocrystal in vacuo and spontaneous solution copolymerization of **1** with **2** in acetonitrile.

Entry	Compound	Amount [mg]	Light source	*T* [°C]	*t* [h]	Conv. [%]
1	**1·2** cocrystal	52.7	Hg lamp	25	18	100
2	**1·2** cocrystal	54.3	dark	60	3	100
3[a]	**1**/**2** monomer	84.1/51.0	dark	60	22	52.7

[a] Spontaneous solution copolymerization in acetonitrile, 25 mL.

The powder XRD patterns of the **1·2** cocrystal and polymeric products (poly(**1·2**)) obtained by solid-state photopolymerization and spontaneous solution copolymerization are shown in Figure 1. The very sharp diffraction pattern of the poly(**1·2**) product obtained by solid-state photopolymerization indicates that none of the crystallinity of the **1·2** cocrystal had been lost after completion of the polymerization. Moreover, the powder XRD pattern of the poly(**1·2**) product obtained by solid-state polymerization is significantly different from that of the product obtained by spontaneous solution copolymerization. These findings indicate that the polymerization of the **1·2** cocrystal in the solid state proceeds under the influence of the crystal lattice to form an alternating copolymer with a highly controlled structure.

To understand the polymerization reaction of the **1·2** crystal, we investigated the crystal structures of both the **1·2** cocrystal and the polymeric product by X-ray crystallography.[8] A single-crystalline sample of the **1·2** cocrystal suitable for X-ray crystal-structure determination was obtained by recrystallization from acetonitrile. During measurement at 123 K, polymerization of the **1·2** crystal did not take place. The molecular packing structures of the **1·2** crystal and the polymer crystal are shown in Figure 2 along with a schematic diagram of the change in the crystal structure on polymerization.

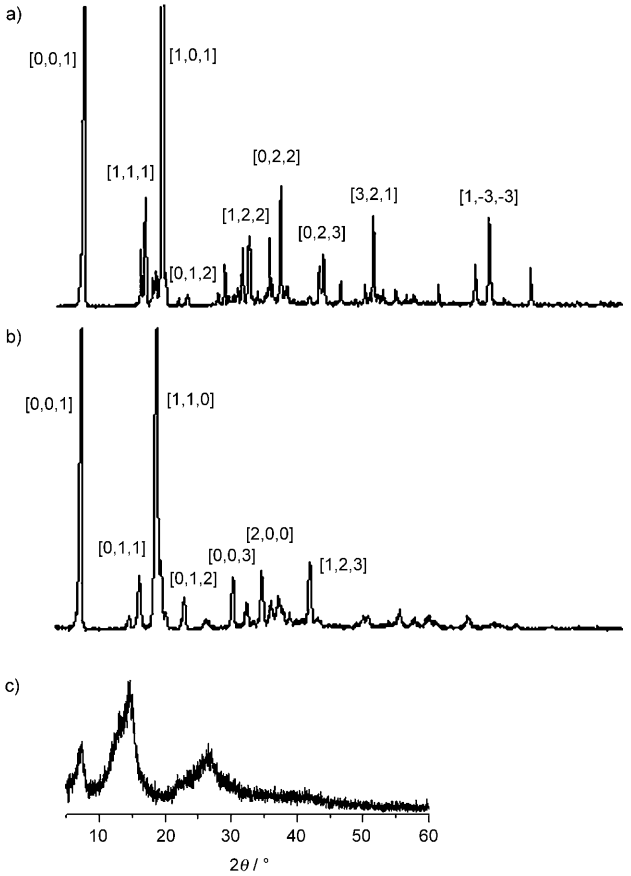

Figure 1. Powder XRD patterns of a) the **1·2** cocrystal, b) poly(**1·2**) obtained by solid-state photopolymerization, and c) poly(**1·2**) obtained by spontaneous solution polymerization.

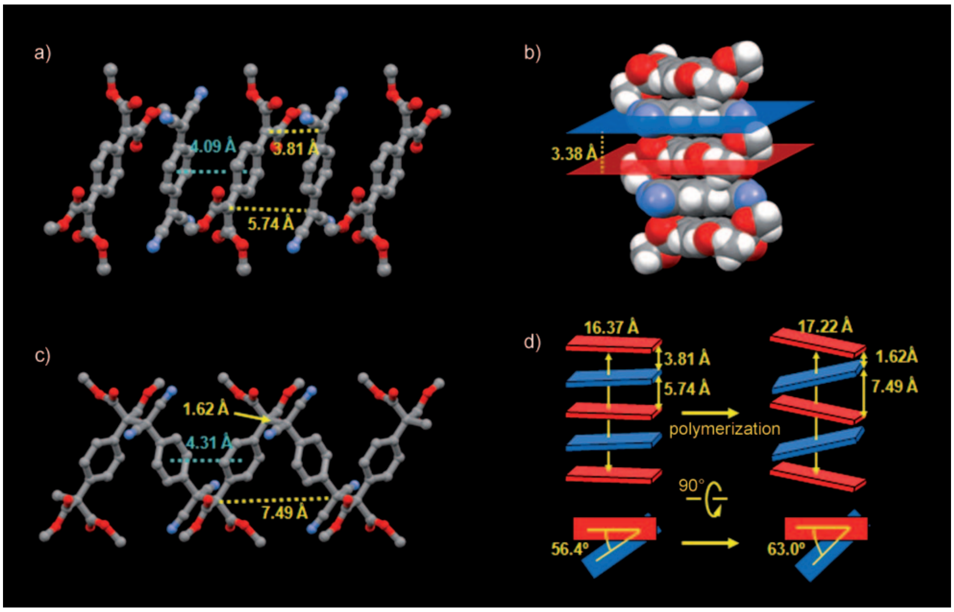

Figure 2. Molecular packing diagrams of a) the **1**·**2** cocrystal, b) the **1**·**2** cocrystal as a space-filling model, and c) the polymer crystal (poly(**1**·**2**)); d) schematic diagram of the crystal-structure change on polymerization. Hydrogen atoms are omitted for clarity.

The **1**·**2** cocrystal belongs to the space group $P\bar{1}$ (No. 2) and has a triclinic unit cell with $a = 7.7988(3)$, $b = 8.1224(3)$, $c = 11.8862(4)$ Å and $\alpha = 76.603(3)$, $\beta = 79.720(3)$, $\gamma = 61.862(3)°$ in which two molecules are included. Molecules **1** and **2** form a one-dimensional column along the *a*–*b* diagonal in the *ab* plane with an alternating stacked arrangement and a torsion angle of 56.4° (Figure 2), in contrast to the crystalline charge-transfer complex of **2** and tetrathiafulvalene in which the two molecules are stacked separately.[9] In the **1**·**2** cocrystal, the interplanar distance between **1** and **2** is 3.38 Å, the distance between the centers of gravity of the quinodimethane molecules is 4.09 Å, and two distances (a short distance of 3.81 Å and a long distance of 5.74 Å) are observed between the reactive exomethylene carbon atoms in **1** and **2**. The short distance is close to that observed (about 4 Å) between reacting carbon atoms in topochemically polymerizable monomers.[1–5]

The polymer crystal (poly(**1**·**2**)) belongs to the space group $P\bar{1}$ (No. 2), which is the same as that of the **1**·**2** cocrystal, and has a triclinic unit cell with $a = 7.0153(9)$, $b = 7.8433(9)$, $c = 12.1307(14)$ Å and $\alpha = 80.101(5)$, $\beta = 86.502(6)$, $\gamma = 70.580(6)°$ in which two molecules are included. The polymer crystal structure reveals that the polymerization reaction occurs consistently along the *a*–*b* diagonal in the *ab* plane, that is, along the stacks of alternating **1** and **2**. Moreover, the polymerization reaction certainly takes place between **1** and **2** at the exomethylene carbon atoms, whereby the exomethylene carbon atoms separated by a short distance of 3.81 Å are connected to form a carbon–carbon single bond with a length of 1.62 Å, and those separated by a long distance of 5.74 Å move away from each other to a distance of 7.49 Å. The polymerization exactly produces an alternating copolymer with a *cis* conformation, in which the distance between the centers of two aromatic rings has been increased to 4.31 Å, and the torsion angle has increased to 63.0°. The lattice lengths decrease during polymerization, as shown in the volume shrinkage of the unit cell from 644 to 620 Å^3; however, there is some stretching of the stacks of alternating **1** and **2** because of the expansion of the γ angle from 61.8 to 70.5°. The change in the distance between the centers of gravity of molecules **1** and **2** during the polymerization corresponds to an increase of about 5%. This amount is different from the change observed for addition polymerizations of unsaturated monomers, in which case volume shrinkage usually takes place because of a covalent-bond-forming reaction. In the case of the topochemical polymerization reaction, the movement of both **1** and **2** should be kept to a minimum to leave the crystal structure intact. It is considered, therefore, that the polymerization reaction in the **1**·**2** cocrystal proceeds through successive bond formation between reactive exomethylene carbon atoms separated by the shorter distance (3.81 Å) and with no movement of the center of gravity of the molecules. In this way, an alternating copolymer with a *cis* conformation is formed.

In conclusion, it was found that **1** and **2** exist together as a 1:1 charge-transfer complex in an orange-colored crystal, and that topochemical polymerization of the cocrystal takes place through a radical mechanism to afford an alternating copolymer with a *cis* conformation, as determined by ESR measurement and single-crystal structure analysis of the **1**·**2** cocrystal and the corresponding polymer crystal. No *cis*-specific topochemical copolymerization of quinodimethane-type monomers has been reported previously. Detailed studies on the cocrystal structures of 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethanes with **2** and their reactivity toward solid-state copolymerization are now in progress.

Experimental Section

Cocrystallization of **1** and **2**: A cocrystal of **1** and **2** was obtained as an orange platelet by crystallization from a 1:1 mixture of **1** and **2** in acetonitrile at −20 °C. The cocrystal had no melting point (the color changed from orange to pale pink upon heating).

Polymerization: Some of the **1**·**2** cocrystal was put in a Pyrex ampoule, which was degassed under reduced pressure and then sealed. Photopolymerization was carried out in vacuo under UV irradiation with a high-pressure mercury lamp (Fuji Glass Work Type HB-400, 400 W) at a distance of 12 cm. The temperature of the ampoule at the irradiated position was 25 °C. The polymer yield was determined gravimetrically after removal of the residual monomer with chloroform. Thermal polymerization was carried out by placing the ampoule in an oil bath at 60 °C for the required polymerization time. Poly(**1·2**): IR (KBr): $\nu = 2962$ (CH), 2225 (CN), 1766 (C=O), 1747 (C=O), 1499 (C=C), 1433 (C=C), 1416 (C=C), 1266 (C-O), 1201 (C-O), 1015 (CH), 934 (CH), 820 cm^{-1} (CH); XRD ($\text{Cu}_{K\alpha 1}$/40 kV/40 mA, 2θ (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); elemental analysis calcd (%) for $C_{28}H_{20}N_4O_8$: H 3.73, C 62.22, N 10.37, O 23.68; found: H 3.71, C 62.29, N 10.59, O 23.41.

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[8] X-ray diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector by using graphite-monochromatized $\text{Cu}_{K\alpha}$ radiation ($\lambda = 1.54187$ Å). Direct methods (SIR-2004) were used for the solution of the structure.[10] All calculations were performed with the observed reflections [$I > 2\sigma(I)$] with the program CrysalStructure crystallographic software package[11] except for refinement, which was performed with SHELXL-97.[12] All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. Crystal-structure data for the **1·2** cocrystal: platelet, $C_{14}H_{10}N_2O_4$, $M_r = 270.24$, $0.10 \times 0.10 \times 0.10\ \text{mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.7988(3)$, $b = 8.1224(3)$, $c = 11.8862(4)$ Å, $\alpha = 76.603(3)$, $\beta = 79.720(3)$, $\gamma = 61.862(3)°$, $V = 643.78(4)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.394\ \text{g cm}^{-3}$, $T = 123.1$ K, $\mu(\text{Cu}_{K\alpha}) = 0.880\ \text{mm}^{-1}$, $2\theta_{\text{max}} = 136°$, 6875 reflections collected, 1849 unique ($R_{\text{int}} = 0.067$) reflections. The final $R1$ and $wR2$ values were 0.0485 [$I > 2.0\sigma(I)$] and 0.1420 (all data), respectively. Crystal structure data for poly(**1·2**): platelet, $C_{14}H_{10}N_2O_4$, $M_r = 270.24$, $0.10 \times 0.10 \times 0.10\ \text{mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.0153(9)$, $b = 7.8433(9)$, $c = 12.1307(14)$ Å, $\alpha = 80.101(5)$, $\beta = 86.502(6)$, $\gamma = 70.580(6)°$, $V = 620.11(13)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.447\ \text{g cm}^{-3}$, $T = 123.1$ K, $\mu(\text{Cu}_{K\alpha}) = 0.914\ \text{mm}^{-1}$, $2\theta_{\text{max}} = 136°$, 11245 reflections collected, 3054 unique ($R_{\text{int}} = 0.279$) reflections. The final $R1$ and $wR2$ values were 0.1377 [$I > 2.0\sigma(I)$] and 0.4058 (all data), respectively.

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