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Photoreactive Molecular Complex of 2,5-Distyrylpyrazine and Ethyl 4-[2-(2-Pyrazinyl)ethenyl]cinnamate. Formation of Perfectly Ordered Polymer Composite by Crystalline-State Photopolymerization

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Cocrystals have been attracting much attention in the field of organic solid-state chemistry, including CT complexes in superconductivity and inclusion complexes in molecular recognition.[1] We have recently reported on the formation of a mixed crystal from a couple of diolefinic compounds, which gave a random copolymer by repeating topochemical [2 + 2] photocycloaddition.[2] In contrast, a regulated polymer is expected to be formed by the topochemical [2 + 2] photopolymerization of a molecular complex of a couple of diolefinic compounds with an ordered molecular arrangement in the crystal. Here we report on the first example of the topochemical photoreaction of a molecular complex to afford a perfectly ordered polymer composite.

Each of 2,5-distyrylpyrazine (**1**)[3] and ethyl 4-[2-(2-pyrazinyl)-ethenyl]cinnamate (**2**)[4] has been found to give a crystalline polymer upon UV irradiation in the crystalline state, respectively (Scheme I). On the other hand, when an equimolar mixture of **1** and **2** was recrystallized from benzene, very thin, platelike yellow crystals deposited. The ^{1}H-NMR spectrum of the crystal showed that it comprised **1** and **2** in a molar ratio of 1:2. This composition ratio in the crystal was not affected upon changing the molar ratio of **1** and **2** in solution in a range from 1:1 to 1:5. In the differential scanning calorimetric curve of this crystal, a single endothermic peak was observed at 166 °C, which is different from the melting point of either **1** (223 °C) or **2** (156 °C). Furthermore, the X-ray powder diffraction pattern of the crystal was quite different from those of the homocrystals **1** and **2**. From these results, it is suggested that the crystal, obtained by recrystallization of a mixture of **1** and **2** from benzene, is not a simple blend but a cocrystal of **1** and **2** with a molar ratio of 1:2.

Upon irradiation with a 500-W super-high-pressure mercury lamp, cocrystal **1·2** afforded a crystalline polymer (η_{inh} = 1.0 dL/g: trifluoroacetic acid). The ^{1}H-NMR spectrum of the polymer revealed that all of the olefin bonds were converted into cyclobutane rings through [2 + 2] cycloaddition and perfectly coincided with that of a 1:2 mixture of poly-**1**[3] and poly-**2**.[4] Partially dimerized photoproduct crystal was obtained when cocrystal **1·2** was irradiated with wavelengths longer than 410 nm, which excite only the monomers. In the dimer crystal, only **1**-dimer and **2**-dimer were detected by high-performance liquid chromatography (HPLC), but the corresponding cross dimer consisting of **1** and **2** was not detected at all. These observations by ^{1}H-NMR and HPLC indicate that the photoproduct, obtained from cocrystal **1·2**, is not a copolymer but a mixture of poly-**1** and poly-**2**.

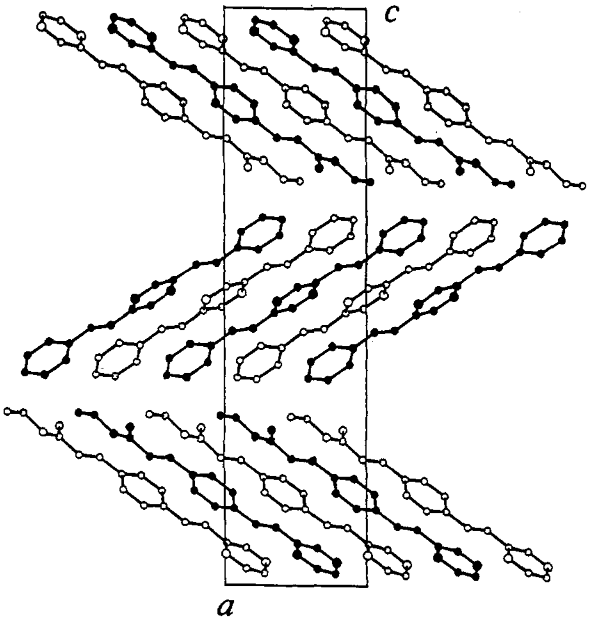
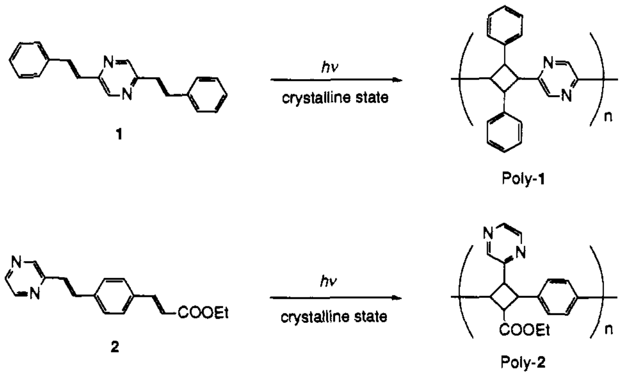


Figure 1. ORTEP drawing of complex **1·2** viewed along the *b*-axis. The black and white molecules are on the same plane, respectively, and are related with a glide mirror plane.

Scheme I



The X-ray crystallographic analysis of the cocrystal was performed (Figure 1).[5] In cocrystal **1·2**, both of **1** and **2** formed columns separately along the *c*-axis with sheets perpendicular to the *a*-axis related by a glide mirror plane. This result indicates that cocrystal **1·2** is not a mixed crystal with a *disordered* molecular arrangement but a "molecular complex" with an *ordered* molecular arrangement. The shortest distances from the carbon–carbon double bond of **2** in a certain layer to those of **1** and **2** in the neighboring layers are 7.202 and 6.655 Å, respectively, which are too far for **1** and **2** to react each other.[6] On the other hand, the distances between the neighboring carbon–carbon double bonds in the same layer are 3.934 Å in the column of **1** and 4.013 and 3.976 Å in the column of **2**, respectively, and are within the limit allowed for topochemical [2 + 2] cycloaddition.[6] Taking into account the distances between the neighboring carbon–carbon double bonds and the preservation of the

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(5) The crystal data of the complex: space group $P2_1/c$ with a = 30.380(5) Å, b = 9.629(2) Å, c = 7.494(1) Å, β = 91.28(1)°, V = 2191.6(7) Å^3, and Z = 4 (d_{calcd} = 1.25 g/cm^3). A total of 3265 reflections (maximum 2θ of 120°) were collected at room temperature on a Mac Science MXC18 diffractometer using the 2θ–ω scan method. The structure was solved by direct methods (MULTAN78) and refined with 1713 reflections ($|F_o| > 3\sigma(|F_o|)$, GOF = 0.98, R = 0.088, R_w = 0.102.

(6) Cohen, M. D.; Schmidt, G. M. *J. Chem. Soc.* **1964**, 1996.

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$$\text{complex } \mathbf{1{\cdot}2} \xrightarrow[\text{crystalline state}]{h\nu} \text{poly-}\mathbf{1}\text{ / poly-}\mathbf{2}\ (1:2)$$

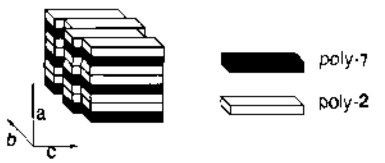

Figure 2. Schematic representation of the photoproduct of complex 1·2. Black and white rods represent single polymer chains of poly-1 and poly-2, respectively. Three arrows represent the direction of the *a*-, *b*-, and *c*-axes of the original complex before irradiation.

crystallinity during the photoreaction, the polymerization would proceed along the *a*-axis upon photoirradiation to give a perfectly ordered (alternately layered) crystalline polymer composite; in other words, the polymer crystal should comprise an alternating monolayer of poly-**1** and a bilayer of poly-**2** as shown schematically in Figure 2.

Complex **1·2** was also obtained by simple grinding of homocrystals **1** and **2**. When 1 and 2 equimolar amounts of **2** were ground with an agate mortar and a pestle for 60 min, followed by standing for 1 week at room temperature, the formation of the complex became detectable in the X-ray powder diffraction pattern, as is observed for a couple of diolefinic compounds reported in a previous paper.[7] The photoirradiation of the mixture gave the same ordered polymer composite of poly-**1** and poly-**2**.

The alignment of **1** and **2** in each column is quite similar to that in each of the homocrystals. Consequently, the formation of the complex may readily occur wtih the high tendency of the column of **1** penetrating in the crystal of **2**.[8] Similar columned stacking structures of two components have been reported for CT complexes;[10] the driving force for the complex formation is usually attributed to strong interaction(s) between the two components such as electrostatic interaction, charge-transfer interaction, and/or hydrogen bonding.[11] However, the growth of cocrystal **1·2** in the direction of the *a*-axis is very slow; the interaction between the neighboring columns is very weak. The *IR* spectrum of complex **1·2** showed the absorption due to carbonyl stretching 7 cm^{-1} lower than that of homocrystal **2** (1705 cm^{-1}). This difference may arise from the enhanced interaction between the carbonyl group in **2** and the hydrogen of the phenyl group of **1**, since the aromatic hydrogen is the closest to the carbonyl oxygen, which was ascertained on the basis of the X-ray crystallographic analysis. This interaction is, therefore, the most probable interaction between the columns of **1** and **2** to produce complex **1·2**. However, the interaction would be quite weaker than an ordinary C—H···O= hydrogen bonding[12] since the aromatic hydrogen is not directed to the lone pair of the oxygen, although the distance between the carbonyl oxygen and the aromatic proton is 2.60 Å and the C—H···O= angle is 138.0°.

This is the first example of a photoreactive complex affording an alternating layered polymer composite.

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Supplementary Material Available: Crystallographic details for the complex **1·2**, including tables of atomic coordinates, thermal parameters, bond angles, and bond lengths, and a table of distances between carbons of double bonds in the range 3.5–8.5 Å (10 pages). Ordering information is given on any current masthead page.

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[7] Kinbara, K.; Adegawa, Y.; Saigo, K.; Hasegawa, M. *Bull. Chem. Soc. Jpn.*, in press.

[8] The lattice constants of **1**:[9] *Pbca*, *a* = 20.638 Å, *b* = 9.599 Å, *c* = 7.655 Å. The lattice constants of **2**:[4] $P2_1/c$, *a* = 20.834 Å, *b* = 9.479 Å, *c* = 7.387 Å, β = 96.75°. It is noteworthy that the cell parameters of **1** and **2** are very similar to each other and that the *a*-axis of the complex is just one and one-half times as long as that of **2**.

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