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Topochemical Photoreactions of Unsymmetrically Substituted Diolefins. 2.[†] Photopolymerization of 4′-(Alkoxycarbonyl)-2,5-distyrylpyrazines

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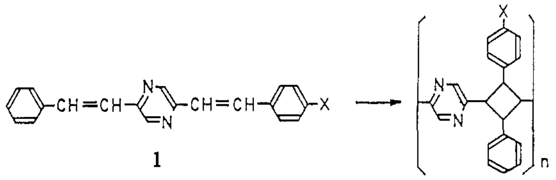
ABSTRACT: Four kinds of crystals, 4′-(alkoxycarbonyl)-2,5-distyrylpyrazines (**1a–d**), showed an extremely high photoreactivity and gave highly crystalline linear polymers (**2a–d**) of high molecular weight (η_{inh}: 0.8–2.4) having cyclobutane rings in the main chain. The photochemical and thermal behaviors of resulting polymers were similar to those of poly(2,5-distyrylpyrazine) (poly-DSP); these polymers photodepolymerize exclusively into the starting diolefins in solution, whereas in the film state in the air these polymers degrade photooxidatively, accompanied with an unusual deterioration of the pyrazine moiety. Heat treatment of poly(4′-(methoxycarbonyl)-2,5-distyrylpyrazine) (**2a**) under reduced pressure gave 4′-(methoxycarbonyl)-2,5-distyrylpyrazine (**1a**), DSP, and bis(methoxycarbonyl)-2,5-distyrylpyrazine as sublimation products, indicating the competing occurrence of the symmetric and asymmetric thermal cleavages of the cyclobutane ring. X-ray crystal structure analysis showed that the molecules in these crystals of **1a** and **1b** were packed in the hetero α-type (head-to-tail) arrangement. The reactivity of the monomers and the structure of the photoproducts are reasonably explained on the basis of the molecular arrangement in these monomers.

Introduction

[2 + 2] topochemical photopolymerization was first reported on the reaction of 2,5-distyrylpyrazine (DSP) crystal.[1,2] On photoirradiation, an extremely highly crystalline poly-DSP is formed quantitatively from the α-type (head-to-tail) DSP crystal, in which the intermolecular reactive double bonds are arranged in parallel at a distance of 3.939 Å across a center of symmetry.[3] Since then, a great number of highly crystalline linear polymers have been prepared from diolefinic compound crystals by repeating step-by-step [2 + 2] topochemical photocyclodimerization.[4]

Recently we found a number of unsymmetrically substituted photoreactive diolefinic crystals that afford various types of photoproducts, such as a homo- or a heteroadduct types of the polymers and dimers[5–8] or a cyclophane.[9] In the topochemical photoreaction of the α-type unsymmetric diolefinic crystals that results in the heteroadduct type cycloaddition, the photoproduct is expected to be a highly stereoregulated linear polymer having alternating substituents of 1,4-arylene and a cyclobutane ring of the same chirality. Furthermore, in a special case, the monomer arrangement resulted in the formation of a chiral crystal, giving optically pure oligomeric substances on photoirradiation.[10]

In this paper, we report the photoreaction of several kinds of unsymmetrically substituted diolefin crystals having DSP skeleton. These are 4′-(methoxycarbonyl)-, 4′-(ethoxycarbonyl)-, 4′-(propoxycarbonyl)-, 4′-(butoxycarbonyl)-, 4′-cyano-, and 4′-(trifluoromethyl)-2,5-distyrylpyrazines (**1a–f**).



1

2

(1)

X: H, 2,5-distyrylpyrazine (DSP)
X: COOR (R: Me (**a**), Et (**b**), Pr (**c**), Bu (**d**))
X: CN (**e**)

Structures and properties of the resulting polymers were investigated by ordinary spectroscopic measurements. Moreover, the crystallographic studies were carried out of two photoreactive crystals, **1a** and **1b**, to correlate the photoreactivity of the monomer and the structure of the photoproduct with the molecular arrangement in the monomer crystal.

Experimental Section

Measurements. Melting points of the monomers were measured by a Laboratory Devices MEL-TEMP and are uncorrected. ^{1}H NMR spectra were measured in trifluoroacetic acid (TFA-d_1) by a JEOL PMX-60SI or a JEOL GX-400 spectrometer with tetramethylsilane (TMS) as an internal standard. Infrared spectra were measured by a JASCO IR-810 infrared spectrophotometer. Thermogravimetric differential scanning calorimetry (TG-DSC) curves were recorded on a Rigaku Thermoflex TG-DSC instru-

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ment under a nitrogen stream with the heating rate of 5 °C/min for about 5 mg of the sample. The inherent viscosities were measured at 30 °C with an Ostwald viscometer at a concentration of 0.30 g/dL in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Ultraviolet absorption spectra were measured on a Shimadzu UV-260 spectrophotometer at a concentration of 0.01 g/L in HFIP. X-ray powder diffraction analyses were carried out with a Rigaku Rotaflex RU-200 X-ray diffractometer.

2-Methyl-5-styrylpyrazine. 2-Methyl-5-styrylpyrazine was prepared by the aldol condensation of 2,5-dimethylpyrazine (10.60 g, 0.100 mol) with benzaldehyde (13.50 g, 0.125 mol) in an excess amount of benzoic anhydride (56.56 g, 0.250 mol) at 180 °C for 20 h. The product was separated by silica gel (WAKO GEL C-200) column chromatography: yield 30.0%; mp 90–91 °C (lit. mp 90 °C);[11] IR (KBr) 1500 (s), 1460 (s), 1360 (m), 1160 (m), 1040 (s), 970 (s), 740 (s), 695 (s) cm^{-1}; ^{1}H NMR (60 MHz in $CDCl_3$) δ 8.45 (s, 1 H), 7.80–6.90 (m, 7 H), 2.50 (s, 3 H), 8.40 (s, 1 H).

Benzoic 2,5-Distyrylpyrazine-4′-carboxylic Anhydride. The aldol condensation of 2-methyl-5-styrylpyrazine (1.96 g, 0.010 mol) with 4-formylbenzoic acid (6.00 g, 0.040 mol) in benzoic anhydride (36.20 g, 0.160 mol) at 160 °C for 6 h gave benzoic 2,5-distyrylpyrazine-4′-carboxylic anhydride: yield 76.1%; mp 173–175 °C; IR (KBr) 1780 (s), 1720 (m), 1635 (w), 1605 (m), 1225 (s), 1060 (m), 755 (m), 700 (s) cm^{-1}; ^{1}H NMR (60 MHz in TFA) δ 9.45 (s, 1 H), 9.00 (s, 1 H), 8.40–7.50 (m, 18 H); UV (ϵ in HFIP) 378.2 (37 000), 316.0 (21 600), 235.8 nm (35 900).

The recrystallization of benzoic 2,5-distyrylpyrazine-4′-carboxylic anhydride from dimethylformamide/chloroform resulted in the formation of 2,5-distyrylpyrazine-4′-carboxylic acid: yield 72.0%; mp 330–332 °C dec (DMF/$CHCl_3$); IR (KBr) 3000 (m), 2680 (m), 2550 (m), 1680 (s), 1640 (m), 1610 (m), 1300 (s), 980 (s), 770 (s) cm^{-1}; ^{1}H NMR (60 MHz in TFA) δ 9.40 (s, 1 H), 9.00 (s, 1 H), 8.30–7.23 (m, 14 H).

4′-(Alkoxycarbonyl)-2,5-distyrylpyrazine (1a–d). Esterification was performed by refluxing in each of four kinds of alcohols with hydrogen chloride in the cases of methanol and ethanol or with concentrated H_2SO_4 in the cases of 1-propanol and 1-butanol. All of the crystals were pale yellow plates.

1a: yield 96.7%; mp 241–243 °C (benzene); IR (KBr) 1720 (s), 1640 (m), 1610 (m), 1440 (m), 1285 (s), 980 (s), 770 (s) cm^{-1}; ^{1}H NMR (400 MHz in TFA) δ 9.43 (s, 1 H), 9.00 (s, 1 H), 8.35–7.45 (d, 2 H; d, 2 H; m, 9 H), 4.10 (s, 3 H); UV (ϵ in HFIP) 377.4 (25 700), 314.4 nm (15 000). Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.38; H, 5.52; N, 8.07.

1b: yield 88.8%; mp 246–247 °C (benzene/hexane); IR (KBr) 1700 (s), 1635 (m), 1600 (m), 1480 (m), 1280 (s), 980 (s), 765 (s) cm^{-1}; ^{1}H NMR (60 MHz in TFA) δ 9.43 (s, 1 H), 9.03 (s, 1 H), 8.40–7.30 (d, 2 H; d, 2 H; m, 9 H), 4.65 (q, 2 H), 1.63 (t, 3 H); UV (ϵ in HFIP) 378.4 (39 000), 312.4 nm (22 200). Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.35; H, 5.44; N, 7.74.

1c: yield 92.5%; mp 205–207 °C (AcOEt/hexane); IR (KBr) 1710 (s), 1630 (m), 1600 (m), 1480 (m), 1275 (s), 975 (s), 760 (s) cm^{-1}; ^{1}H NMR (60 MHz in TFA) δ 9.33 (s, 1 H), 8.95 (s, 1 H), 8.20–7.25 (d, 2 H; d, 2 H; m, 9 H), 4.43 (t, 2 H), 1.95 (m, 3 H), 1.15 (t, 3 H); UV (ϵ in HFIP) 381.2 (63 200), 316.2 nm (34 400). Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.57; H, 5.87; N, 7.39.

1d: yield 81.5%; mp 160–161 °C (benzene/hexane); IR (KBr) 1715 (s), 1635 (m), 1605 (m), 1485 (m), 1280 (s), 980 (s), 765 (s) cm^{-1}; ^{1}H NMR (400 MHz in TFA) δ 9.45 (s, 1 H), 9.05 (s, 1 H), 8.30–7.40 (d, 2 H; d, 2 H; m, 9 H), 4.52 (t, 2 H), 1.86 (m, 2 H), 1.60 (m, 2 H), 1.07 (t, 3 H); UV (ϵ in HFIP) 378.2 (68 700), 313.8 nm (39 300). Anal. Calcd for $C_{25}H_{24}N_2O_2$: C, 78.10; H, 6.29; N, 7.29. Found: C, 77.98; H, 5.99; N, 7.12.

4′-Cyano- and 4′-(Trifluoromethyl)-2,5-distyrylpyrazines (1e, 1f). Similarly, **1e** and **1f** were prepared by the aldol condensation of 2-methyl-5-styrylpyrazine (1.50 g, 7.65 mmol) with 4-cyanobenzaldehyde (3.75 g, 29.5 mmol) and 4-(trifluoromethyl)benzaldehyde (3.99 g, 22.9 mmol), respectively, in an excess amount of benzoic anhydride (25.22 g, 110 mmol). Both of the crystals were pale yellow plates.

1e: yield 63.2%; mp 211–212 °C (benzene/hexane); IR (KBr) 2240 (s), 1635 (m), 1605 (m), 1510 (m), 1365 (m), 1160 (s), 980 (s) cm^{-1}; ^{1}H NMR (400 MHz in TFA) δ 9.56 (s, 1 H), 8.98 (s, 1 H), 8.20–8.04 (d, 1 H; d, 1 H), 7.88 (s, 5 H), 7.80–7.44 (d, 1 H; d, 1 H; m, 4 H); UV (ϵ in HFIP) 378.2 (42 800), 311.0 nm (23 500). Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.25; H, 4.78; N, 13.52.

1f: yield 29.0%; mp 218–219 °C (benzene/hexane); IR (KBr) 1635 (m), 1620 (m), 1485 (m), 1330 (s), 1170–1110 (s), 1075 (s) cm^{-1}; ^{1}H NMR (60 MHz in TFA) δ 9.48 (s, 1 H), 9.10 (s, 1 H), 8.40–7.20 (m, 13 H); UV (ϵ in HFIP) 375.4 (25 000), 310.0 nm (14 700). Anal. Calcd for $C_{21}H_{15}N_2F_3$: C, 71.58; H, 4.29; N, 7.95. Found: C, 71.45; H, 4.22; N, 7.95.

Photopolymerization. Photoirradiation was undertaken with an Ushio USH-500D super-high-pressure mercury lamp (500 W). Finely powdered crystals of **1a–f** (100–300 mg) were dispersed in 100 mL of H_2O/MeOH (9/1 v/v) containing a few drops of a surfactant (Nikkol TL-10FF) and irradiated with a rigorous agitation for 3–20 h under nitrogen atmosphere at room temperature by the mercury lamp through a water filter from the outside. After photoirradiation, the products were collected by filtration and washed with a large amount of water. The reactivity of the monomers was monitored by IR and ^{1}H NMR spectral changes. The results of photoirradiation for 3 h are shown in Table I. The photoreactive yellow crystals gradually turned into white powder.

2a: IR (KBr) 1725 (s), 1615 (m), 1485 (m), 1285 (s), 1115 (s), 980 (m), 700 (s) cm^{-1}; ^{1}H NMR (400 MHz in TFA) δ 8.82 (s, 1 H), 8.70 (s, 1 H), 7.95 (d, 2 H), 7.30–7.00 (m, 7 H), 5.40–4.70 (m, 4 H), 4.12 (s, 3 H); UV (ϵ in HFIP) 284.6 (6100), 240.0 nm (10 900).

2b: IR (KBr) 1715 (s), 1610 (m), 1480 (m), 1280 (s), 1105 (s), 1020 (m), 700 (s) cm^{-1}; ^{1}H NMR (400 MHz in TFA) δ 8.85 (s, 1 H), 8.69 (s, 1 H), 7.99 (d, 2 H), 7.40–7.00 (m, 7 H), 5.40–4.40 (br m, 6 H), 1.54 (t, 3 H); UV (ϵ in HFIP) 284.0 (9900), 238.2 nm (17 900).

2c: IR (KBr) 1720 (s), 1615 (m), 1500 (m), 1280 (s), 1110 (s), 940 (m), 700 (m) cm^{-1}; ^{1}H NMR (400 MHz in TFA) δ 8.85 (s, 1 H), 8.00 (d, 2 H), 7.40–7.00 (m, 7 H), 5.50–4.40 (br m, 6 H), 1.98 (m, 2 H), 1.16 (t, 3 H); UV (ϵ in HFIP) 284.8 (10 600), 240.2 nm (19 300).

2d: IR (KBr) 1720 (s), 1620 (m), 1480 (m), 1290 (s), 1120 (s), 1020 (m), 700 (m) cm^{-1}; ^{1}H NMR (400 MHz in TFA) δ 8.85 (s, 1 H), 8.72 (s, 1 H), 8.00 (d, 2 H), 7.30–7.05 (m, 7 H), 5.45–4.40 (br m, 6 H), 1.94 (q, 2 H), 1.05 (t, 3 H); UV (ϵ in HFIP) 284.2 (8000), 240.1 nm (14 200).

Photodegradation, Photodepolymerization, and Thermal Depolymerization. **2a** film was prepared by casting a HFIP solution on a glass plate and evaporating the solvent slowly under atmospheric pressure. The polymer film was irradiated by a 500-W super-high-pressure mercury lamp (Ushio U.S.H.-500D) under argon atmosphere or in the air, and the behaviors were monitored by UV and IR spectral changes.

A HFIP solution of **2a** was irradiated with the same light source under argon atmosphere. After irradiation, inherent viscosity was measured (0.30 g/dL, 30 °C). Moreover, a TFA solution of the polymer in an NMR tube was irradiated, and NMR spectra were used to study the structural changes of the polymer at regular time intervals during irradiation.

To check the thermostability of polymers, **2a** crystals were placed into a 30-mL round-bottom flask and they were heated for 10–20 h under argon atmosphere at 150, 200, and 240 °C. After the heat treatment, IR and NMR spectra and inherent viscosity were measured. The polymer was also heated for 8 h at 260–290 °C under vacuum to investigate the degraded products. The sublimed products were analyzed by NMR and thin-layer chromatography (TLC) in comparison to the authentic samples.

Crystallographic Analysis. Plate-shaped crystals of monomer **1a** and **1b** were grown from ethylbenzene and *m*-xylene, respectively. The specimens used were a fragment of a plate 0.7 × 0.4 × 0.1 mm for **1a** and 0.25 × 0.2 × 0.05 mm for **1b**. Diffraction intensities of **1a** were measured for the specimen sealed in a thin-walled glass capillary to avoid the presumable deterioration of the crystal specimen by exposure to X-rays in the presence of oxygen. A high value of R for **1a** may be due to the absorption of X-rays by the glass capillary. The crystal data and intensity data were obtained from measurements on a Philips PW1100 diffractometer by using graphite-monochromated Cu Kα radiation. All reflections within the range of $2\theta < 120°$ for **1a** and $2\theta < 130°$ for **1b** were collected by use of a 2θ–ω scan mode. Out of 1943 and 1849 reflections, 1069 and 1001 were greater than

Table I
Photochemical Behavior of 1a–f (DSP–X) and Their Polymer Properties[a]

compd	X	reactivity	$\eta_{\mathrm{inh}}{}^{b}$	product morphology	mp (dec), °C
1a	COOMe	very high	1.55	cryst	310
1b	COOEt	very high	0.87	cryst	310
1c	COOPR^n	very high	2.36	cryst	336
1d	COOBu^n	very high	1.81	cryst	301 (195[c])
1e	CN	low		amorph	396
1f	CF_3	no			

[a] Photoirradiation by a 500-W high-pressure mercury lamp for 3 h. [b] 0.30 g/dL (30 °C, HFIP). [c] Phase transition point.

2σ (I) and were used for the structure determination of **1a** and **1b**, respectively. No correction was made for absorption. Crystal data of **1a** and **1b** are shown in Table III. The structure of **1a** was solved by the direct method using MULTAN76, and that of **1b** was assumed to be isostructural with **1a**. The parameters were refined by the block-diagonal least-squares method using $w = 1/|F_{\mathrm{obsd}}|^2$ for $F_{\mathrm{obsd}} > 60$, 1.0 for $1 < F_{\mathrm{obsd}} \leq 60$, and 0.2 for $F_{\mathrm{obsd}} \leq 1$. The final R values of **1a** and **1b** were 0.107 and 0.067, respectively. Atomic scattering factors were taken from ref 12.

Results and Discussion

Photopolymerization Behavior. Photochemical behavior of the monomers **1a–f** and properties of the photoproducts are shown in Table I.

The crystals of ester monomers (**1a–d**) showed an extremely high photoreactivity in the crystalline state and gave high-molecular-weight polymers (η_{inh} 0.87–2.36) on photoirradiation for 3 h. These polymers (**2a–d**) had endothermic peaks at the temperature above 300 °C: **2a** at 310 °C; **2b** at 310 °C **2c** at 336 °C; **2d** at 301 °C, by DSC (see Table I). However, the endothermic peaks of these four polymers are not as sharp as that of poly-DSP. Moreover, on the TG curve an abrupt weight loss is seen at the temperatures of the endothermic peaks. The TG-DSC result suggests that the endothermic peaks of these polymers correspond not to their crystal melting temperatures but to the decomposition temperatures. The crystal of **1e** was of a low photoreactivity, and more than 60% was recovered after irradiation for 15 h. The endothermic temperature (396 °C by TG–DSC) of the amorphous photoproduct of **1e** was higher than those of the photoproducts of **1a–d**. The crystal of **1f** was photostable on irradiation for more than 20 h.

Structure and Properties of the Polymers. The structure of the photoproducts **2a–e** was studied by IR and NMR spectra. For example, the IR absorption peaks at 1630 and 970 cm^{-1} of **1a**, which correspond to the olefinic double bonds, disappeared in the spectrum of **2a**, and also the absorption of carbonyl group shifted to the higher wavenumber (1710 → 1720 cm^{-1}) in **2a**. In the NMR spectrum of **2a**, the signals of olefinic protons between δ 7.1 and 8.2 were not seen, whereas new signals appeared between δ 4.7 and 5.3. These new signals correspond to cyclobutane ring protons. The other three polymers, **2b–d**, exhibited IR and NMR spectra similar to those of **2a**. These results indicate that the polymerization of **1a–d** proceeded through [2 + 2] photocycloaddition between double bonds, resulting in a linear polymer having cyclobutane rings in the main chain. Although the cyclobutane structure was confirmed in the polymer chain of **2e**, the structure was not stereoregulated.

The mass spectrum of the oligomer of **1a** was measured to elucidate the structure of cyclobutane ring. The oligomer was isolated at the intermediate stage of the photopolymerization of **1a** for 2 h by using a 500-W super-high-pressure mercury lamp. In the mass spectrum of the oligomer prominent peaks were seen at m/e 282 and 400, other than the peak of the monomer **1a** (m/e 341). These two peaks of m/e 282 and 400 obviously correspond to 2,5-distyrylpyrazine (DSP) and 4′,4″-bis(methoxycarbonyl)-2,5-distyrylpyrazine (Table II).

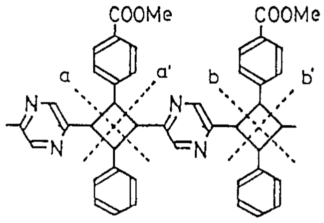

Figure 1. Modes of cleavage of the cyclobutane ring in the polymer **2a**.

Table II
Electron Impact (MS), Photochemical, and Thermal Cleavage of the Cyclobutane Ring in the Polymer 2a

mode of cleavage[a]	cleaved product	m/e	photochemical cleavage	thermal cleavage
a and b a′ and b′	monomer **1a**	341	obsd	obsd
a′ and b	DSP	282	not obsd	obsd
a and b′	bis(methoxycarbonyl)-distyrylpyrazine	400	not obsd	obsd

[a] See Figure 1.

The MS result indicates linear polymer structure of **2a**, which should be derived from the hetero α-type (head-to tail) crystal structure of **1a** as shown in eq 1.

X-ray powder diffraction analysis showed that the polymers **2a–d** were highly crystalline and, in particular, except for **2d**, were very similar to each other, suggesting the same type of molecular arrangement in these crystals.

Photooxidation and Photodepolymerization of the Polymer. **2a–d** gave a thin film from a HFIP solution. As poly-DSP is known to be very susceptible to the photooxidative circumstance as well as to the thermal and photochemical depolymerization conditions,[4,13] it is of interest to investigate these properties of the polymers in the present study.

The IR spectral change of **2a** film on the irradiation in air is shown in Figure 2. On photoirradiation for 1.5 h, the absorption peak assigned to a new carbonyl group was observed at 1760–1720 cm^{-1}, indicating the occurrence of photooxidation of the polymer. Moreover, an absorption of the pyrazine ring at 930 and 1480 cm^{-1} decreased, while a new absorption at 2250 cm^{-1}, which is assigned to a cyano group, appeared. On irradiation the film became brittle, and no film could be obtained from a HFIP solution of the photoirradiated product. From the UV and IR spectra and TLC analysis, neither of the monomer **1a** nor DSP was detected after the photooxidation of **2a**. From the results, the photooxidative deterioration of the pyrazine ring in the polymer is obvious as is observed for the poly-DSP.[13] For the initial step of the deterioration of the pyrazine ring, it is presumed that the biradical from the cleavage of the cyclobutane ring attacks the nitrogen in the pyrazine ring to result in a radical cation. However, the photooxidative degradation mechanism has not been made clear yet. On the other hand, the thermal treatment of crystalline **2a** at 240 °C in air for 20 h did not cause the oxidative deterioration of the pyrazine ring at all, although a certain part of the residue was insoluble in HFIP nor in TFA.

To study the photochemical behavior of these polymers in solution, we monitored the changes of the inherent viscosity during the irradiation of a HFIP solution of **2a**.

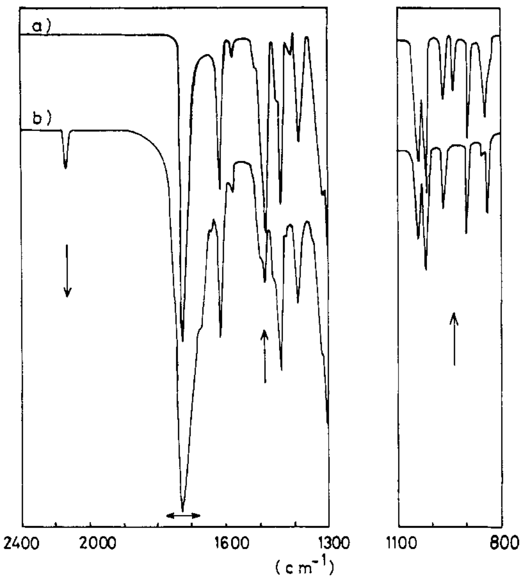

Figure 2. IR spectral change of **2a** film on photoirradiation in the air. (a) **2a** film; (b) photoirradiated **2a** by a 500-W super-high-pressure Hg lamp for 1.5 h.

The inherent viscosity reduced to one-third of the starting value after the irradiation for 30 min, suggesting a rapid photochemical scission of the main chain. In the UV spectrum, the new absorption peak appeared at 377.5 nm after irradiation for 10 min. This peak is attributed to the absorption of the monomer **1a**. In the NMR spectrum of the photoirradiated **2a** in a TFA solution, the peaks of olefinic and pyrazine ring protons of the monomer (δ 9.10 and 9.50) appeared, whereas the peaks of cyclobutane ring decreased. After irradiation for 5 h, only the signals of **1a** were seen in the NMR spectrum. These results indicate that the polymer depolymerized finally into the monomer **1a** with a high conversion by photoirradiation in solution (a and b or a′ and b′ cleavages in Table II). Such a highly selective photocleavage of the cyclobutane ring is satisfactorily explained by steric repulsion of the four substituents on the cyclobutane ring.[14]

Thermal Depolymerization of the Polymer. Polymer **2a** (η_{inh} 2.15) in the crystalline state was placed for 10 h under argon atmosphere at 150, 200, and 240 °C, respectively. The inherent viscosity reduced from 2.15 to 1.84 and 1.39 on heating at 200 and 240 °C, respectively, while it did not change on heating at 150 °C for 10 h. The viscosity changes indicate that the scission of the main chain of the polymer occurred at 200 °C or above, although the endothermic peak due to the scission was not seen clearly by the DSC curve.

By thermal treatment of **2a** at 260–290 °C under vacuum for 8 h, a yellow solid of more than 50% by weight was sublimed. From the IR spectrum and TLC study, the sublimed yellow solid was identified as the monomer **1a** as a major product, with minor amounts of DSP and 4′,4″-bis(methoxycarbonyl)-2,5-distyrylpyrazine, indicating that all the possible modes of cleavages (a and b, a′ and b′, a′ and b, or a and b′) proceed competitively in the thermal treatment. Then, it is concluded that the thermal cleavage of cyclobutane in the polymer **2a** does not occur as selectively as in the case of photochemical cleavage but proceeds via both symmetric and asymmetric cleavage of the cyclobutane ring (Table II).

Table III
Crystallographic Data of 1a, 1b, and DSP

	1a	1b	DSP
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	$Pna2_1$	$Pna2_1$	$Pbca$
a, Å	7.371 (6)	7.555 (7)	20.638
b, Å	9.639 (8)	9.553 (9)	9.599
c, Å	24.567 (20)	25.463 (23)	7.655
Z	4	4	4
D_X, g cm^{-3}	1.303	1.288	1.244
V, Å^3	1746	1838	1517
final R	0.107	0.067	0.086
C–C dist, Å	3.885 (24) 3.904 (23)	3.974 (13) 4.000 (13)	3.939
ref	present study	present study	(3)

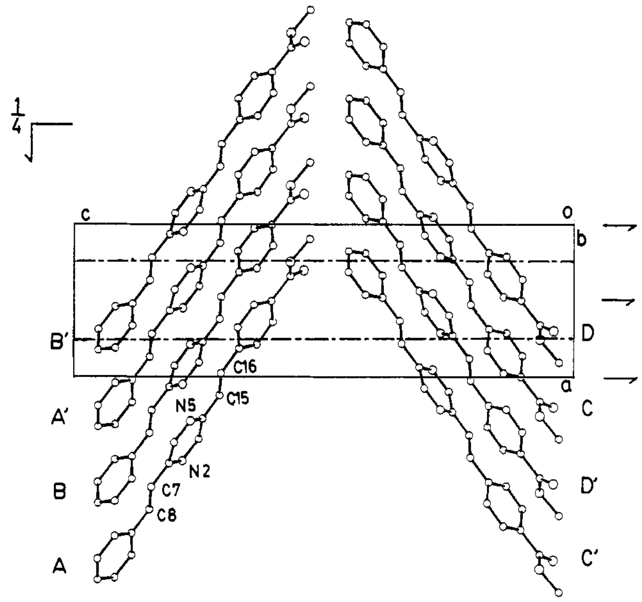

Figure 3. Crystal structure of **1a** viewed along the b axis. Molecules A and A′ (B and B′, C and C′, D and D′ are also) are the a translation equivalents. A and B are related by an a-glide plane on (010), A and C are related by a n-glide on (100), and A and D′ by a diad screw along c: A ($-1 + x, y, z$), A′ (x, y, z), B ($^1/_2 + x, ^1/_2 + y, z$), B′ ($^1/_2 + x, ^1/_2 - y, z$), C ($^3/_2 - x, -^1/_2 + y, ^1/_2 + z$), C′ ($^1/_2 - x, -^1/_2 + y, ^1/_2 + z$), D ($2 - x, 1 - y, ^1/_2 + z$), D′ ($1 - x, 1 - y, ^1/_2 + z$).

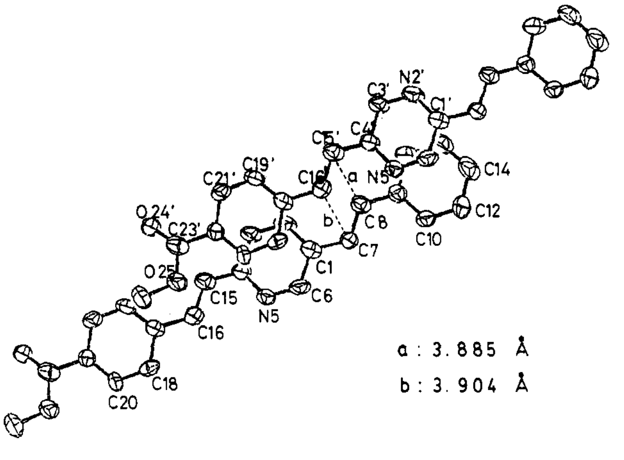

Figure 4. Overlapping of reacting molecules in **1a** crystal viewed along the normal of the mean plane of the molecule. The two molecules are the a translation equivalents.

Crystal Structures. Crystal data of the monomers **1a** and **1b** are shown in Table III with those of DSP for comparison. Both crystal structures **1a** and **1b** are essentially isostructural. The crystal structure of **1a** viewed along the b axis is shown in Figure 3. The overlapping of the reacting molecules along the normal of the mean plane of the molecule is shown in Figure 4. In these two crystals of the reactive double bonds are 3.885 (24) Å for C(7)···C(16′) and 3.904 (23) Å for C(8)···C(15′) in **1a** and 3.974 (13) Å and 4.000 (13) Å for the same carbons in **1b**.

Only these two sets of distances in **1a** and **1b** are within the range of normal reactive ones. Such a discordant distance of reactive double bonds has been reported in several photopolymerizable diolefinic compounds.[5-7,15]

Correlation between the Structure of the Polymer and the Molecular Arrangement of the Monomer. As seen in Figure 3, the molecules translated by *a* are arranged in a herringbone manner with those related by a diad screw along *b* and an *a*-glide plane on (010). The crystal is polar in *c* as is clear from its crystal class (2/*mmm*), and the methyl ester group of **1a** and the ethyl ester group of **1b** are arranged on the same side of the molecule. Consequently, the double bonds in the stack, which belong to the molecules translated by *a*, react to form a cyclobutane ring upon photoirradiation, resulting in a linear heteroadduct polymer elongated along *a*. Thus, the polymer chains should grow in the direction of *a* to give the cyclobutanes in the same chirality. But the polymers are racemic since there exist molecular stacks of immediate neighbors related to the original one by an *a*-glide plane parallel to (010).

The benzene ring in one molecule overlaps with the pyrazine ring in the neighboring molecule (Figure 4). This type of parallel stacking of aromatic rings has been observed in DSP[3] and 1,4-phenylenediacrylate crystals.[16] The phenyl groups in reactable molecules exist in parallel, as well as the substituted phenyl groups, and the perpendicular distances between the pyrazine rings of reactable molecules are not in parallel and range from 3.40 to 3.69 Å. Then, the planes of unsubstituted and substituted phenyl groups exist almost in parallel, but the planes of the two benzene rings and the central pyrazine ring are not parallel. The dihedral angles between the planes of the two benzene rings and pyrazine ring are 10° in **1a** and 14° in **1b**.

The mass spectrum of the oligomer and X-ray crystal structure analysis of the monomer showed that the crystal of monomer **1a** is packed in the α-type (head-to-tail) arrangement and gives the heteroadduct polymer. Moreover, as the X-ray powder diffraction and NMR spectrum of the cyclobutane unit in resulting polymer are very similar in all of four ester monomers (**1a–d**), the crystal structures of these monomers are expected to be isostructural. Similar to the DSP crystal, in the crystals of monomer **1a** and **1b** (see Table III),[3] the polymer chains also grow in one direction (**1a** and **1b** → *a* axis, DSP → *c* axis). The X-ray powder diffraction of three ester polymers (**2a–c**) are very similar, except for **2d**. Moreover, the structures and properties of the four polymers (**2a–d**) are close to those of poly-DSP. These results indicate that the photopolymerization of **1a–d** are of the crystal-to-crystal transformation, as in the case of DSP. In contrast to the DSP crystal, however, in both **1a** and **1b** crystals, the distances of reactive double bonds are discordant although these distances are within reactive ones. The reacting C···C distance (C(8)···C(15′)) is shorter than the other reacting C···C distance (C(7)···C(16′)) in **1a**. These distances in **1b** are 3.974 Å for C(8)···C(15′) and 4.000 Å for C(7)···C(16′). This is presumed to be due to the ester O atom with lone-pair electrons, which causes it to approach the benzene ring slightly.

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Registry No. **1a**, 112963-65-2; **1b**, 115339-38-3; **1c**, 115339-39-4; **1d**, 115339-40-7; **1e**, 115339-41-8; **1f**, 115339-42-9; **2a** (SRU), 115339-47-4; **2a** (homopolymer), 112963-66-3; **2b** (SRU), 115339-48-5; **2b** (homopolymer), 115339-44-1; **2c** (SRU), 115339-49-6; **2c** (homopolymer), 115339-45-2; **2d** (SRU), 115339-50-9; **2d** (homopolymer), 115339-46-3; 2-methyl-5-styrylpyrazine, 115339-36-1; 2,5-dimethylpyrazine, 123-32-8; benzaldehyde, 100-52-7; 4-formylbenzoic acid, 619-66-9; 4-cyanobenzaldehyde, 105-07-7; 4-(trifluoromethyl)benzaldehyde, 455-19-6; benzoic 2,5-distyrylpyrazine-4′-carboxylic anhydride, 115339-37-2; 2,5-distyrylpyrazine-4′-carboxylic acid, 115363-10-5.

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