Preparation of a Crystalline Linear High Copolymer by Topochemical Photopolymerization of Diolefin Mixed Crystals

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ABSTRACT: A mixed crystal (**1c**) of ethyl 4-[2-(2-pyrazyl)ethenyl]cinnamate (**1a**) and *S*-ethyl 4-[2-(2-pyrazyl)ethenyl]thiocinnamate (**1b**) was obtained by cocrystallization from a methanol solution. Mixed crystal **1c** had an isomorphous structure to those of pure crystals **1a** and **1b** and, upon irradiation, gave a crystalline linear copolymer (η_{inh} = 1.9 dL/g) having the same main chain as those of the homopolymers. The copolymer formation was ascertained by the isolation of a mixed dimer comprising **1a** and **1b**. A mixed crystal of **1a** and **1b** was also obtained through crystal–crystal contact by simple grinding of two monomers with an amalgamator. Irradiation of the resulting mixed crystal gave a crystalline linear copolymer (η_{inh} = 0.6 dL/g) having the same structure.

Introduction

There have been several reports concerning the topochemical [2 + 2] photodimerization of mixed crystals of olefin compounds to give mixed dimers.[1] By contrast, there is no obvious example of topochemical photocopolymerization of a mixed crystal of diolefin compounds, although the topochemical photodimerization of olefin compounds can be extended to the topochemical photopolymerization of diolefin compounds.[2]

Though an isolated report on the formation of a mixed crystal of 2,5-distyrylpyrazine and 1,4-bis[2-(2-pyridyl)-ethenyl]benzene has appeared, the topochemical behavior of this mixed crystal was not mentioned in detail.[3] In our laboratory, the preparation of mixed crystals of diolefin compounds has been investigated from the viewpoint of topochemical photocopolymerization. However, most couples of the diolefin compounds did not form a mixed crystal but, rather, separated into pure crystals.

We have also attempted to prepare mixed crystals from several couples of unsymmetric diolefin compounds. Ethyl and propyl α-cyano-4-[2-(4-pyrimidyl)ethenyl]cinnamates arranged in the β-translation-type and β-centrosymmetry-type packings, respectively;[4] upon irradiation they gave amorphous oligomers. A mixed crystal of these compounds arranged in a β-centrosymmetry-type packing, which was isomorphous to that of propyl ester; upon irradiation it gave only amorphous oligomers.[5] Moreover, ethyl and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates, which arranged in an α-type packing, also formed a mixed crystal. However, the molecular arrangement of the mixed crystal drastically changed into a β-type packing to give, upon irradiation, [2.2]paracyclophane derivatives in quantitative yield instead of the expected linear copolymer.[6]

It is well-known that some couples of two isomorphous compounds form a mixed crystal, of which the crystal structure is isomorphous to each pure crystal.[7] On the other hand, it has been reported that most α-type unsymmetric diolefin crystals topochemically photopolymerize into crystalline linear polymers.[8] On the basis of these facts, we considered that a couple of two diolefin compounds, which are isomorphous to each other in α-type packing, should possibly form a mixed crystal and, subsequently, give a crystalline linear copolymer.

We recently found that ethyl 4-[2-(2-pyrazyl)ethenyl]-cinnamate (**1a**)[8b] and *S*-ethyl 4-[2-(2-pyrazyl)ethenyl]-thiocinnamate (**1b**)[9] crystallized in an α-type packing and that these crystals, upon irradiation, gave crystalline linear polymers (Scheme I). Moreover, the crystal structures of the two diolefin compounds were isomorphous to each other, suggesting the possibility of mixed-crystal formation.

In the present paper, we report on the formation and topochemical behavior of a mixed crystal of **1a** and **1b**, resulting in the first example of clear-cut topochemical photocopolymerization.

Results and Discussion

A mixed crystal of **1a** and **1b** was formed not only by recrystallization from a methanol solution but also, surprisingly, by simple grinding of two monomers with an agate mortar and pestle, or an amalgamator.

Topochemical Behavior of a Mixed Crystal of 1a and 1b Prepared by Recrystallization from a Methanol Solution. When a mixture of equimolar amounts of **1a** and **1b** was recrystallized from a methanol solution, microcrystals (**1c**) comprising **1a** and **1b** in a molar ratio of 45:55 were deposited.

1c showed a lower photoreactivity than those of **1a** and **1b** in the crystalline state; irradiation of **1c** for 24 h at room temperature with a 500-W super-high-pressure mercury lamp gave a crystalline polymer (**3c**) (η_{inh} = 1.9 dL/g). The ^{1}H NMR spectrum of **3c** showed the same signals as those of **3a** and **3b**, except for signals arising from the alkyl protons in the ester groups. On the basis of the ^{1}H NMR spectral evidence, it is concluded that polymer **3c** also has an alternating structure of an α-homotype cyclobutane ring and a 1,4-phenylene skeleton in the main chain (Scheme I).

As shown in Figure 1, the X-ray powder diffraction pattern of **1c** (e) is identical with those of pure crystals **1a** (a) and **1b** (c). The identical pattern implies that the crystal structure of **1c** is isomorphous to those of pure crystals **1a** and **1b**. On the other hand, the X-ray powder diffraction pattern of polymer **3c** (f) is quite different from those of homopolymers (**3a** (b) and **3b** (d)), which were obtained by topochemical photopolymerization of **1a** and **1b**, respectively. If the mixed system comprises a mixture of two pure crystals, the X-ray powder diffraction pattern of polymer **3c** would be the overlap of those of two pure crystals. Thus, the difference in the X-ray diffraction pattern between these polymers strongly suggests the formation of a copolymer.

A dimer portion (**2c**) was prepared and isolated as follows. Irradiation of **1c** was carried out at wavelengths

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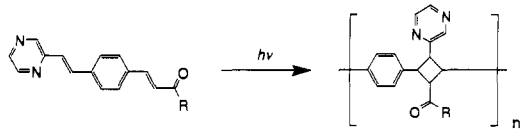
Scheme I



1a : R = OEt
1b : R = SEt
1c : R = OEt / SEt (recrystallized from MeOH)
1d : R = OEt / SEt (prepared by grinding)

3a : R = OEt ; ηinh = 8.2
3b : R = SEt ; ηinh = 1.5
3c : R = OEt / SEt ; ηinh = 1.9 (obtained from 1c)
3d : R = OEt / SEt ; ηinh = 0.6 (obtained from 1d)

longer than 410 nm by using a cut-off filter in order to excite only the monomers; then, dimer **2c** was separated from trimer and oligomers by preparative TLC (Scheme II).

Parts a and b of Figure 2 show the high-performance liquid chromatograms of dimers of **1a** (OO) and of **1b** (SS), which were obtained in a similar manner. The chromatogram of **2c** shows three peaks (Figure 2c); two of them are attributed to dimers OO and SS. The peak between the peaks of dimers OO and SS, in the order of retention time, is assigned to be a mixture of two mixed dimers of **1a** and **1b** (OS; R^1 = -OEt, R^2 = -SEt or R^1 = -SEt, R^2 = -OEt in Scheme II) on the basis of its mass spectrum analysis (m/e = 580, M^+).

The chromatographic evidence offers the following conclusion: The existence of dimer OS indicates the formation of a mixed crystal, resulting in the formation of a copolymer of **1a** and **1b**; the existence of dimers OO and SS means that the molecular arrangement of **1a** and **1b** in mixed crystal **1c** is not alternating, because the alternating arrangement of **1a** and **1b** would give only dimer OS without either OO or OS.

If a mixed crystal has a random arrangement and photodimerizes in quantitative yield, the ratio of the resulting two homodimers and mixed dimer would coincide with the statistical value (1:1:2).[6b] In this reaction, however, since the resulting dimer reacts to give a trimer and oligomers, even by the photoexcitation of the monomer, the degree of mixing of **1a** and **1b** in mixed crystal **1c** could not be precisely determined only by the molar ratio of the resulting dimers. However, the nonstoichiometric ratio of **1a** and **1b** (45:55) in mixed crystal **1c** and the proportions of OO, OS, and SS (1:4.9:2.9) strongly suggest that a mixed crystal of **1a** and **1b** should have a random arrangement (a solid solution); thus, the photoproduct should be a random copolymer comprising **1a** and **1b** monomer units. This is the first example of topochemical photocopolymerization, in which the copolymer formation was completely substantiated by the spectroscopic results.

Topochemical Behavior of a Mixed Crystal 1a and 1b Prepared by Grinding of a Mixture of the Crystals. When an equimolar amount of pure crystals **1a** and **1b** was mixed by grinding for 10 min with an agate mortar and pestle or by agitation for 30 min with an amalgamator, the resulting crystal mixture (**1d**) showed a similar photoreactivity to that of **1c**, suggesting the formation of a mixed crystal of **1a** and **1b** through crystal–crystal contact. In the latter method, a slight increase in the temperature of the sample was observed (ca. 50 °C). However, since this temperature was much lower than the melting points of either crystal **1a** or **1b** and since a fine powder shape of the crystal mixture was maintained, melting of the crystal mixture could be ruled out during agitation with the amalgamator.

Irradiation of **1d** for 7 h at room temperature with a 100-W high-pressure mercury lamp gave a crystalline polymer (**3d**) (η_{inh} = 0.6 dL/g). Since the ^{1}H NMR spectrum of **3d** is identical with that of **3c**, it is concluded that polymer **3d** has the alternating structure of an α-homotype cyclobutane ring and a 1,4-phenylene in the main chain (Scheme I).

As shown in Figure 1, the X-ray powder diffraction pattern of **1d** (g) is very similar to that of **1c** (e) as well as those of **1a** (a) and **1b** (c), indicating that the crystal structure of **1d** is also isomorphous to that of **1c**, as well as those of **1a** and **1b**. Furthermore, the different diffraction pattern of polymer **3d** (h) from the overlap of those of **3a** (b) and **3b** (d) also indicates that **3d** is a copolymer comprising **1a** and **1b** monomer units.

As shown in Figure 2d, a high-performance liquid chromatogram of a dimer portion (**2d**), which was isolated from the photoproduct of **1d** in a manner similar to **2c**, shows three peaks of OO, OS, and SS in a ratio of 1.0:5.0:2.5.[10] From these results it is concluded that only through crystal–crystal contact by grinding could the **1a** and **1b** crystals be transformed into a mixed crystal, resulting in a formation of a copolymer of **1a** and **1b**.

Although the X-ray diffraction pattern of **1d** is similar to that of **1c** and HPLC of **2d** to that of **2c**, the X-ray diffraction pattern and inherent viscosity of **3d** were different from those of **3c**. These differences strongly suggest that **1c** and **1d** have any differences in the degree of mixing of **1a** and **1b** and/or the degree of crystallinity, which cannot be detected by X-ray diffraction measurement, whereas, the difference may be amplified during the polymerization, resulting in a different morphology between **3c** and **3d**.

There have been some reports concerning the formation of mixed crystals by grinding of two compounds in the solid state. However, in these reports the combinations are limited to the compounds having strong intermolecular interactions such as host–guest[11] and CT complex systems.[12] In contrast, it is very unusual that **1a** and **1b**, in which no particular intermolecular interaction exists, except for the van der Waals force, readily form a mixed crystal through a crystal–crystal contact only by grinding the two crystals.

Further study is still in progress to elucidate the formation mechanism of the mixed crystal and to estimate the applicability of this simple formation of a mixed crystal to several other couples of photoreactive olefin crystals.

Experimental Section

Measurements. The infrared spectra were measured on a Jasco IR-810 spectrophotometer, and the ^{1}H NMR spectra were measured by a JEOL PMX-60SI or a JEOL GX-400 instrument. The mass spectra were measured on a Shimadzu GCMS-QP2000 instrument. The melting points were measured by a Laboratory Devices MEL-TEMP and are uncorrected. High-performance liquid chromatography (HPLC) was performed on a steel column (4 mm × 250 mm) packed with LiChrosorb Si 60 (5 μm; Merck and Co.) at a flow rate of 0.5 mL/min using a mixture of $CHCl_3$ and CH_3OH (100:0.5) as an eluent, and the absorbance at 254 nm was monitored on a Shimadzu SPD-2A spectrophotometric detector. Differential scanning calorimetry (DSC) was measured on a Shimadzu DSC-50 instrument under a nitrogen stream with a heating rate of 5 °C/min for about 5 mg of the sample. X-ray powder diffraction analyses were carried out with a Rigaku Rotaflex RU-200 spectrometer (λ = 1.541 84 Å).

Preparation of the Mixed Crystal of 1a and 1b (1c) by Recrystallization from Methanol. Monomer **1a** was prepared as previously described.[4] Monomer **1b** was prepared from the corresponding acid chloride and ethanethiol by an usual procedure. A mixture of **1a** and **1b** in an equimolar amount (1.42 mmol) was recrystallized from methanol (200 mL), giving a mixed crystal of **1a** and **1b** (**1c**) in a molar ratio of 45:55. The stoichiometry was confirmed by its ^{1}H NMR. Mp: 155–161 °C (DSC analysis). IR (KBr): 1700, 1630, 1610, 1180, 1030, 980, 840, 760 cm^{-1}.

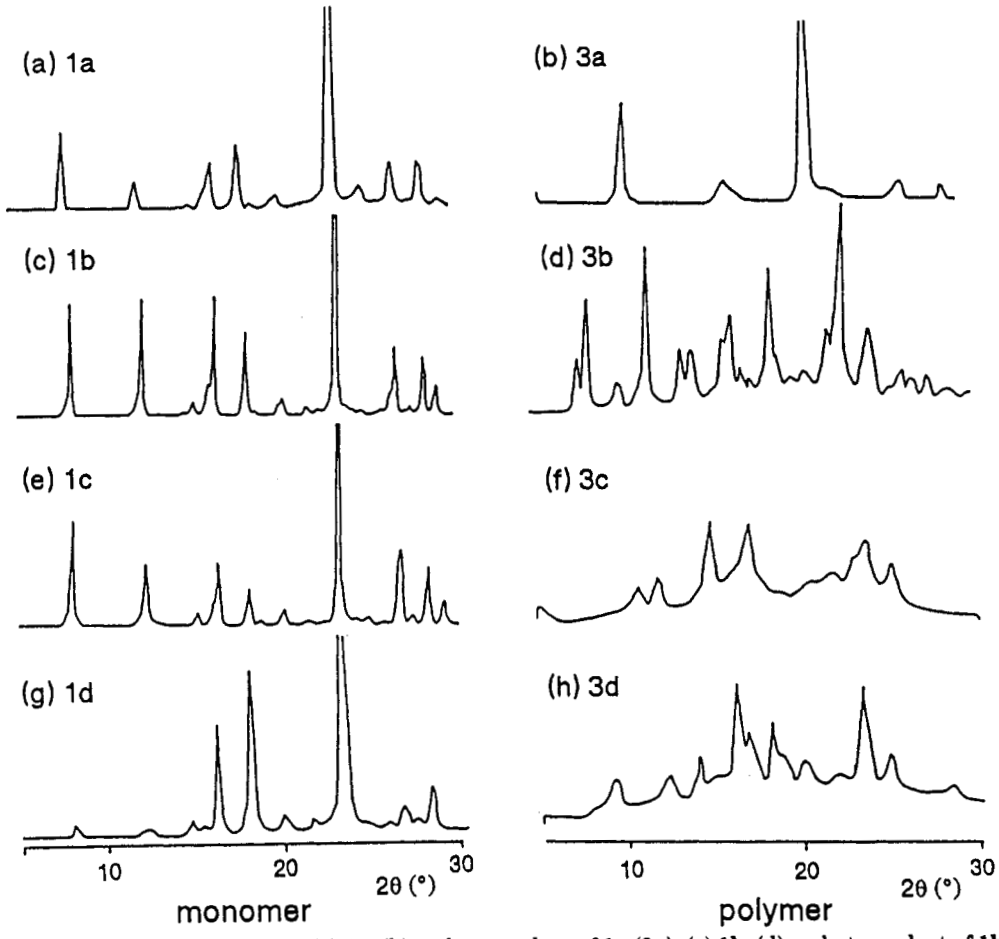
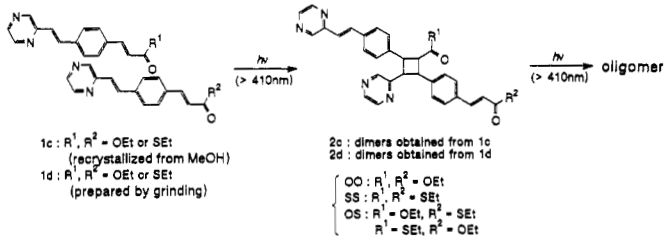


Figure 1. X-ray powder diffraction patterns: (a) **1a**, (b) a photoproduct of **1a** (**3a**), (c) **1b**, (d) a photoproduct of **1b** (**3b**), (e) a mixed crystal of **1a** and **1b** prepared by recrystallization from a methanol solution (**1c**), (f) a photoproduct of **1c** (**3c**), (g) a mixed crystal of **1a** and **1b** prepared by grinding (**1d**), and (h) a photoproduct of **1d** (**3d**).

Scheme II



Preparation of the Mixed Crystal of 1a and 1b (1d) by Grinding of a Mixture of 1a and 1b Crystals. A mixture of the pure crystals **1a** and **1b** in an equimolar amount (0.20 mmol) was agitated for 30 min by using an amalgamator (GC-HMIX; G-C Dental Industrial Corp.) to give a mixed crystal of **1a** and **1b** (**1c**). Mp: 152–160 °C (DSC analysis). IR (KBr): 1700, 1630, 1610, 1180, 1030, 980, 840, 760 cm^{-1}.

Preparation of the Dimers. A finely powdered crystal of **1a**, **1b**, **1c**, or **1d** (100 mg) was dispersed in water (90 mL) and was irradiated with a 500-W high-pressure mercury lamp (Ushio USH-500D), set outside of the flask, through a Kenko L42 filter (cutoff <410 nm) at room temperature with vigorous stirring until the monomer was completely consumed. Dimers were separated from oligomers by preparative TLC (silica gel, CH_2Cl_2/CH_3OH = 100/0.5).

OO. 4%. ^1H NMR ($CDCl_3$): δ 0.90 (t, 3 H, J = 7 Hz), 1.34 (t, 3 H, J = 7 Hz), 3.8–3.9 (m, 2 H), 4.1–4.2 (m, 1 H), 4.27 (q, 2 H, J = 7 Hz), 4.63 (d, 2 H, J = 6 Hz), 4.8–4.9 (m, 1 H), 6.43 (d, 1 H, J = 16 Hz), 7.04 (d, 1 H, J = 16 Hz), 7.09 (d, 2 H, J = 8 Hz), 7.36 (d, 2 H, J = 8 Hz), 7.41 (d, 2 H, J = 8 Hz), 7.51 (d, 2 H, J = 8 Hz), 7.60 (d, 1 H, J = 16 Hz), 7.67 (d, 1 H, J = 16 Hz), 8.21 (s, 1 H), 8.26 (s, 1 H), 8.35 (s, 1 H), 8.39 (s, 1 H), 8.52 (s, 1 H), 8.59 (s, 1 H). MS: m/e 560 (M^+).

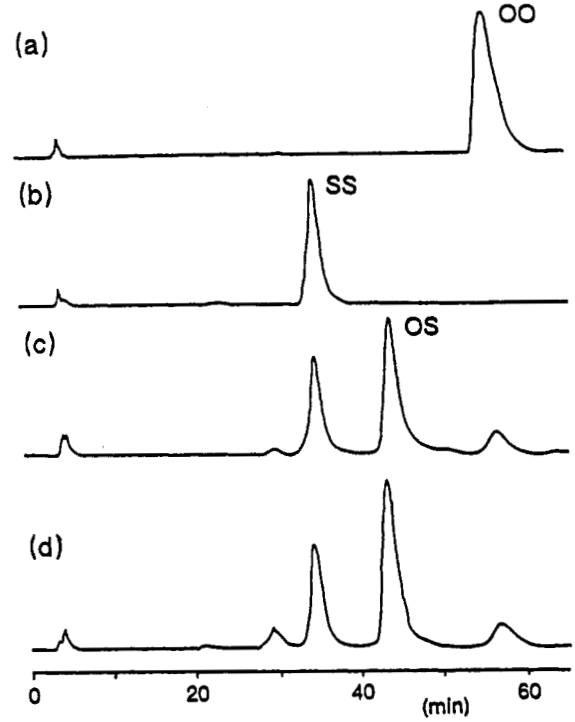


Figure 2. High-performance liquid chromatogram of the dimers: (a) the dimer of **1a** (OO), (b) the dimer of **1b** (SS), (c) the dimer of **1c** (**2c**), and (d) the dimer of **1d** (**2d**).

SS. 5%. IR (KBr): 2230, 1720, 1600, 980, 840 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.94 (t, 3 H, J = 7 Hz), 1.32 (t, 3 H, J = 7 H), 2.5–2.6 (m, 1 H), 2.7–2.8 (m, 1 H), 4.36 (dd, 1 H, J = 10 Hz, J' = 6 Hz),

4.63 (dd, 1 H, J = 10 Hz, J' = 7 Hz), 4.69 (dd, 1 H, J = 10 Hz, J' = 6 Hz), 4.85 (dd, 1 H, J = 10 Hz, J' = 7 Hz), 6.69 (d, 1 H, J = 16 Hz), 7.09 (d, 2 H, J = 8 Hz), 7.10 (d, 1 H, J = 16 Hz), 7.38 (d, 2 H, J = 8 Hz), 7.40 (d, 2 H, J = 8 Hz), 7.51 (d, 2 H, J = 8 Hz), 7.58 (d, 1 H, J = 16 Hz), 7.70 (d, 1 H, J = 16 Hz), 8.23 (s, 1 H), 8.27 (s, 1 H), 8.40 (s, 1 H), 8.47 (s, 1 H), 8.57 (s, 1 H), 8.70 (s, 1 H). MS: m/e 592 (M^+).

2c (5%) and **2d** (7%) were a mixture of the dimers OO, SS, and OS. Their ^{1}H NMR spectra were the same as those of OO and SS, except for a signal of the alkyl group in esters. The mass spectra of **2c** and **2d** showed m/e 560 (OO, M^+), 576 (OS, M^+), and 592 (SS, M^+).

Photoirradiation. Photopolymerization was carried out as follows. Method 1: Finely powdered crystals (100 mg) were dispersed in 300 mL of water containing a few drops of a surfactant (Nikkol TL-10FF) and irradiated with a 100-W high-pressure mercury lamp (Eikousha EHB WF-100), set inside of the flask, through a Pyrex glass filter with vigorous stirring under a nitrogen atmosphere. Method 2: Finely powdered crystals (100 mg) were dispersed in 90 mL of water containing a few drops of a surfactant (Nikkol TL-10FF) and irradiated with a 500-W super-high-pressure mercury lamp (Eikousha EHB WF-500), set outside of the flask, through a Kenko UV30 filter (cutoff <280 nm) with vigorous stirring under a nitrogen atmosphere.

3c. IR (KBr): 1720, 1660, 1400, 1180, 1020 cm^{-1}. ^{1}H NMR (TFA-*d*): δ 0.9–1.1 (m, 3 H), 2.7–2.9 (m, 1 H), 3.9–4.1 (m, 1 H), 4.3–4.5 (m, 0.5 H), 4.5–4.7 (m, 0.5 H), 4.85 (bs, 1 H), 5.00 (bs, 2 H), 7.1–7.3 (bs, 2 H), 7.3–7.5 (bs, 2 H), 8.61 (s, 1 H), 8.66 (bs, 1 H), 9.38 (bs, 1 H).

3d. IR (KBr): 1710, 1630, 1310, 1180, 1020 cm^{-1}. ^{1}H NMR (TFA-*d*): δ 0.9–1.1 (m, 3 H), 2.7–2.9 (m, 1 H), 3.9–4.1 (m, 1 H), 4.3–4.5 (m, 0.5 H), 4.5–4.7 (m, 0.5 H), 4.85 (bs, 1 H), 5.00 (bs, 2 H), 7.1–7.3 (bs, 2 H), 7.3–7.5 (bs, 2 H), 8.61 (s, 1 H), 8.66 (bs, 1 H), 9.38 (bs, 1 H).

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(4) The molecular arrangements of unsymmetric diolefin crystals are classified into four types: α- or β-type and translation- or centrosymmetry-type. Corresponding to the molecular arrangements, the photoproducts are also classified into four types: α- or β-type and homo- or hetero-type. These classifications are described in detail in the following literature: Maekawa, Y.; Kato, S.; Saigo, K.; Hasegawa, M.; Ohashi, Y. *Macromolecules* **1991**, *24*, 2314.

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(9) A crystal structure and topochemical behavior of **1b** will be published elsewhere.

(10) We carried out the irradiation of the simple mixture of each pure powder crystal, **1a** and **1b**, without any appreciable mixing by grinding and then separated the dimer portion by preparative TLC. HPLC of the dimer portion showed two peaks due to OO and SS dimers without any attributable peak to OS dimer.

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Registry No. **1a**, 135645-85-1; **1b**, 135645-86-2; (**1a**)(**1b**) (copolymer), 135658-83-2; **1a** (dimer), 135645-87-3; **1b** (dimer), 135645-88-4; **2c**, 135645-89-5; **2d**, 135645-90-8.