

REVIEW

"KALEIDOSCOPIC" TOPOCHEMICAL PHOTOPOLYMERIZATION BEHAVIOR OF DIOLEFIN COMPOUNDS

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INTRODUCTION

Various types of organic reactions in the crystalline state, so-called "topochemical reaction", have been reported in this century.¹ Among the reactions, [2+2] photocycloaddition of diolefin crystals are one of the most intensively investigated examples.² In the topochemical reaction in a pure sense, the space group symmetry is perfectly preserved throughout the reaction as were demonstrated by the crystalline-state photopolymerization of 2,5-distyrylpyrazine (2,5-DSP)³ and photodimerization of propyl α -cyano-4-[2-(4-pyridyl)ethenyl]cinnamate.⁴

2,5-DSP was initially prepared by Franke,⁵ and in 1958 Koelsch and Gumprecht described briefly in their article of diazine-derivatives that 'it was found that the compound (2,5-DSP) was converted into a colorless insoluble polymer (?) dec. 331-331° when the solid was exposed for a few hours to ultraviolet light.⁶ Wright described in his book as if Koelsch and Gumprecht had investigated both the structure of the photoproduct and the crystal structure 2,5-DSP in detail.⁷ However, in the paper,⁶ they have not described any study on chemically correct analysis and crystallography of the resulting photoproduct at all. In 1967, one of present authors (M. H.) independently made the same observation as Franke that brilliant yellow crystal of 2,5-DSP was converted into powdery white substance under the sunlight in the course of a preparative study of pyrazine-2,5-dicarboxylic acid from 2,5-DSP. He investigated this phenomenon and concluded for the first time that a linear high-molecular-weight polymer crystal ($[\eta] > 3.0$ in CF₃COOH solution) with recurring cyclobutane units in the main chain, had been produced from 2,5-DSP crystal by the action of sunlight.⁸ After a short while, crystallographic study of 2,5-DSP and poly-2,5-DSP clearly demonstrated that the polymerization proceeded with the retention of the space group of starting 2,5-DSP crystal (*Pbca*).³ The result was the first evidence of organic reaction that proceeded in crystal lattice.

Several years later, Wegner's group reported that the space group changed from *Pbca* to *P2₁ca* during the conversion of 2,5-DSP to poly-2,5-DSP.⁹ However, this report is based on the misinterpretation of the extinction rule, and actually, it was reconfirmed that our first structural analysis was correct.¹⁰ In addition, in 1993, Eckhardt *et al.* also reported that partially oligomerized 2,5-DSP crystal belongs to a space group *Pbca*.¹¹

The fact of the retention of the space group throughout the reaction means that the crystalline-state reaction of diolefin compounds proceeds under a perfect control of the crystal lattice. This interpretation is also supported by several experimental results, *e.g.*, the reaction of propyl α -cyano-4-[2-(4-pyrimidyl)ethenyl]cinnamate crystals, in which the final yield of topochemical product is considerably dependent on irradiating temperature.¹² Namely, as far as the temperature is satisfactorily deep, the presence or absence of topochemical reactivity, and/or configuration of the photoproduct can be easily guessed from the crystal structure of starting diolefin monomer. On the other hand, in some cases, the thermal process could participate in the course of the topochemical photoreaction, making the overall reaction scheme "kaleidoscopic". These thermal processes are often caused by stress of the bond angle that is arisen by topochemical reaction and lead to the formation of unpredictable photoproducts.

Up to the present, by the topochemical reaction of diolefin compounds, a great variety of products has been obtained, reflecting the crystal structure of monomers, such as the crystalline linear polymer (Scheme 1),¹³⁻¹⁸ V-shaped-type dimer and/or cyclic dimer, depending on irradiation temperature (Scheme 2),¹² cyclic adducts (Scheme 3),^{19,20} and so on.

Particularly, concerning the highly crystalline and high-molecular-weight linear polymer, numerous kinds of polymers have been synthesized.

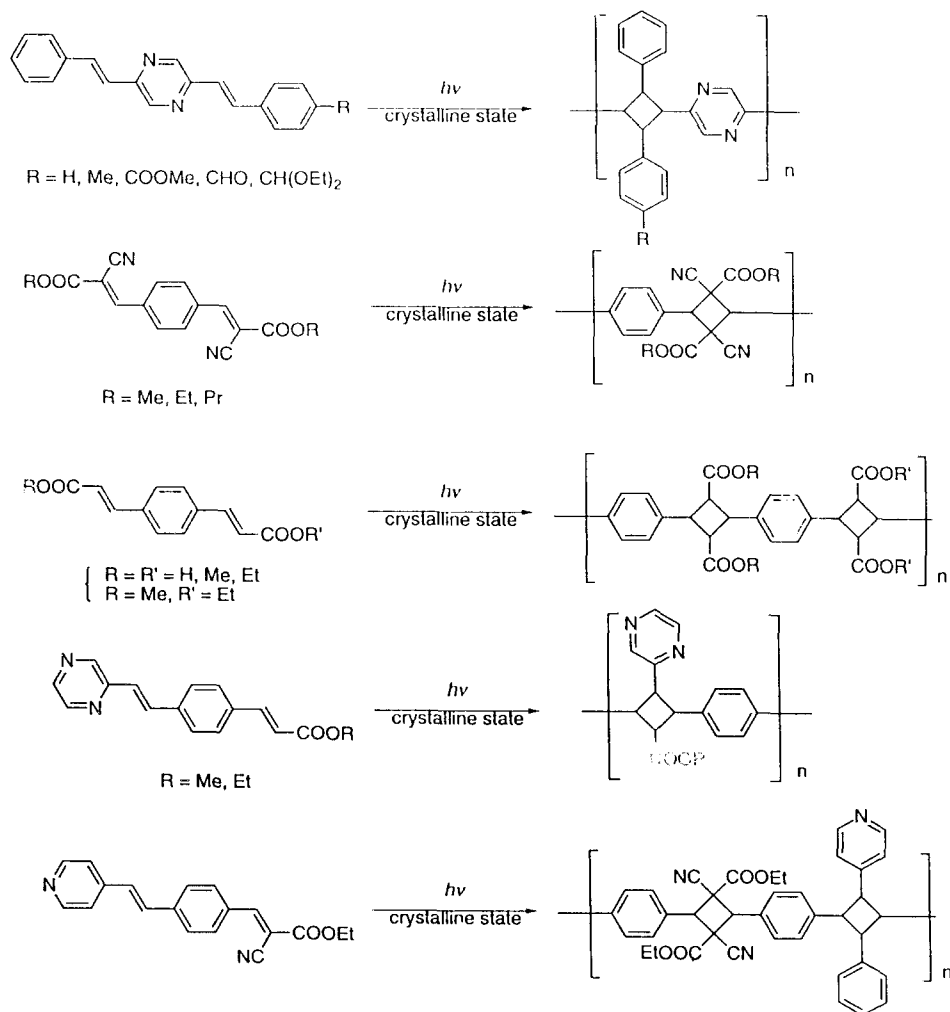
Almost of all topochemical reactions of diolefin compounds are promoted by photoirradiation. Of particular interest is that topochemical polymerization of 2,5-DSP by γ -ray irradiation was recently reported for

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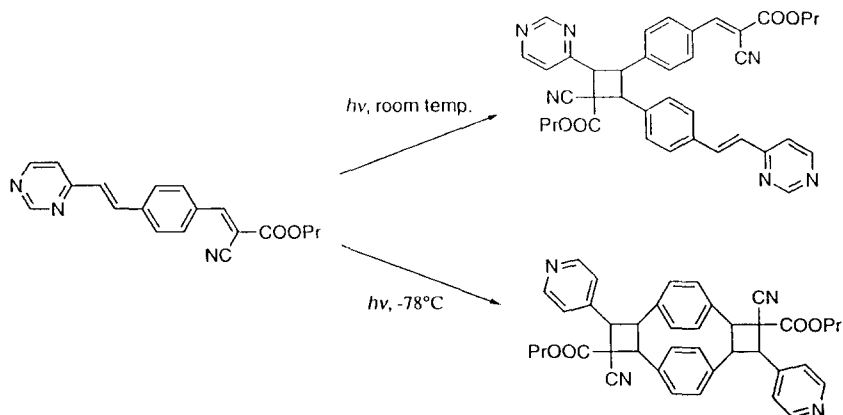
the first time by other group.²¹

In the present review, we describe the topics on the topochemical [2+2] photoreaction of diolefinic

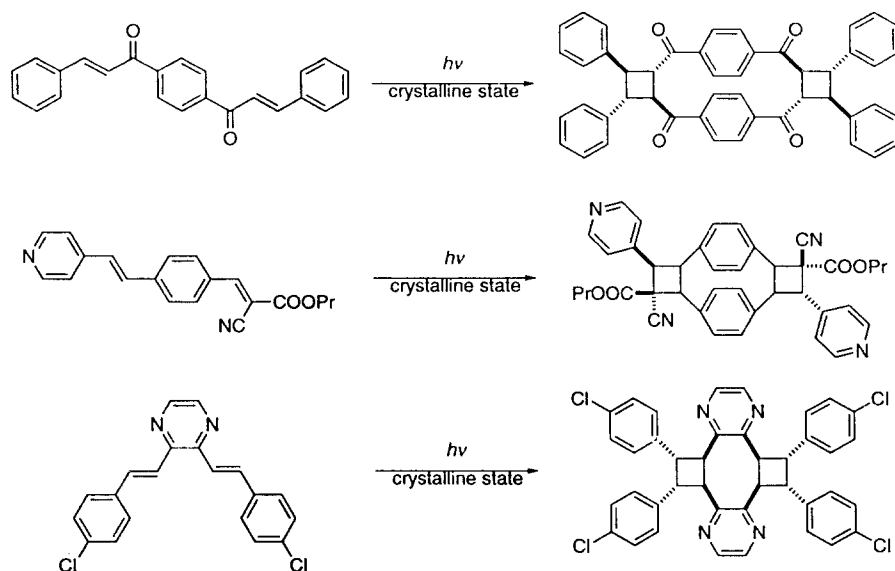
compounds, focusing on the relationship between the crystal structure and the reaction behavior or the photoproduct.



Scheme 1



Scheme 2



Scheme 3

POLYMER SYNTHESIS THROUGH TOPOCHEMICAL [2 + 2] PHOTOPOLYMERIZATION

Linear high polymers and their characteristic properties

Photoreactive diolefin crystals are roughly classified into two types, from the viewpoint of crystal packing modes: In the α -type packing, monomers are superimposed with displacement by about half a molecule in the direction of the long molecular axis, and in the β -type packing, without displacement.²² Furthermore, in the case of unsymmetric diolefin crystals, each packing of the α - and β -types is further classified into translation- and centrosymmetry-type packings. Corresponding to the molecular arrangements of these diolefin crystals, four types of photoproducts (α - and β -type, and homo- and hetero-type adducts) could be expected on the basis of the topochemical principle (Scheme 4).² Generally, high-molecular-weight polymers are obtained from α -type crystal while oligomers and cyclic adducts from β -type crystal.

Four-center-type photopolymerization of all the α -type packing diolefin crystals in Scheme 1 proceeds very rapidly to give a linear high-molecular-weight polymer with an extremely high degree of crystallinity in nearly quantitative yield.

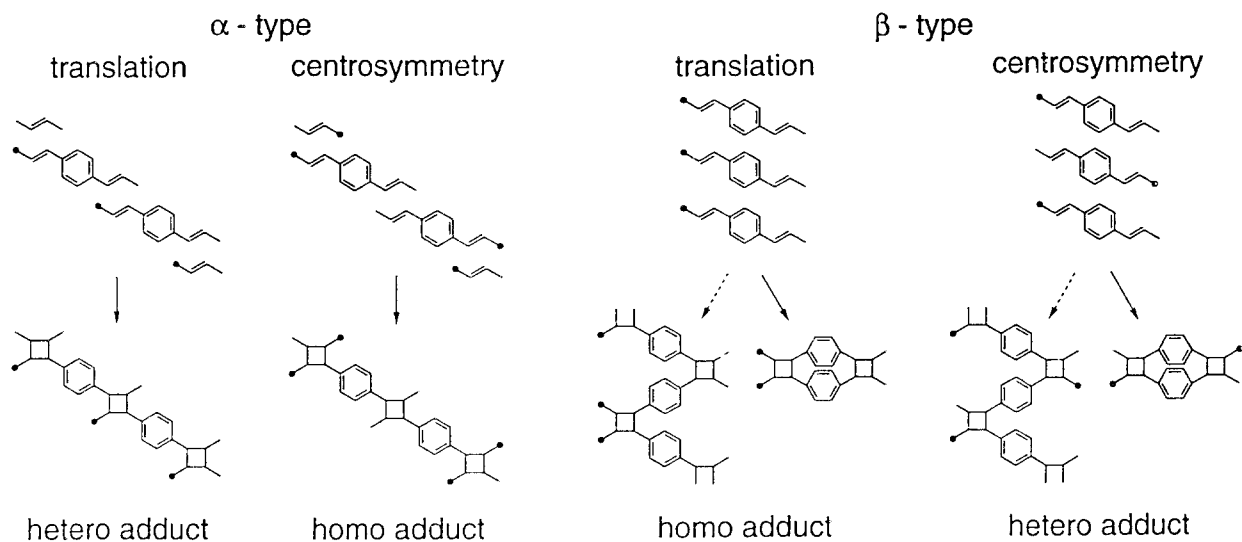
Crystal melting points of the polymers thus obtained are very high ($> 300^\circ\text{C}$) and generally higher than the temperature of thermal cleavage of the cyclobutane rings in the polymer main chain. Therefore, on heating, not the crystal melting point but topochemical thermal depolymerization is observed on these polymers by means of continuous changes of X-ray diffraction pattern and differential scanning calorimetry-thermogravimetry (DSC-TG) curves.²³

Thermal stability of the polymers is remarkably dependent on their molecular weight; that is, the higher the molecular weight, the less is the thermal stability.

Analysis of the depolymerized product shows that rigid linear polymer chains are thermally cleaved more favorably in the middle of the chain rather than at random. Such peculiar thermal behavior has been interpreted as a common characteristic of rigid rod-shaped polymer chain structures, as was theoretically simulated by Hanamura in 1988.²⁴

With the progress of topochemical photopolymerization even when the space group is retained, the appearance of resulting product becomes powdery. This behavior is based on rather slight difference in cell dimensions between starting material and the product: as the reaction proceeds, the stress, caused by the difference in unit cell parameters between the monomer and the photoproduct, accumulates, and makes the original crystal into the assembly of microcrystals. As a result, the appearance of the clear crystal changes to opaque. Except the hypothetical case, in which cell dimension is retained absolutely identical during the reaction, this phenomenon is common to all topochemical reactions, and only the difference is apparent feature of reacting crystals. Therefore, it is not essential but rather insignificant to classify the solid-state reactions into "homogeneous" and "heterogeneous" and to discuss the topochemical reaction based on the apparent difference of the crystal before and after the reaction.²⁵

Crystallographic results on 2,5-DSP and poly-2,5-DSP had pointed out a very important future possibility that an "absolute" asymmetric synthesis could be achieved in the absence of any external chiral reagents, if any prochiral molecule, *e.g.* an unsymmetrical diolefin derivative, is crystallized into a chiral crystal and if the reaction of the chiral crystal proceeds in the same manner as the 2,5-DSP crystal with retention of the crystal lattice. Such types of absolute asymmetric synthesis with a high enantiomeric yield have been



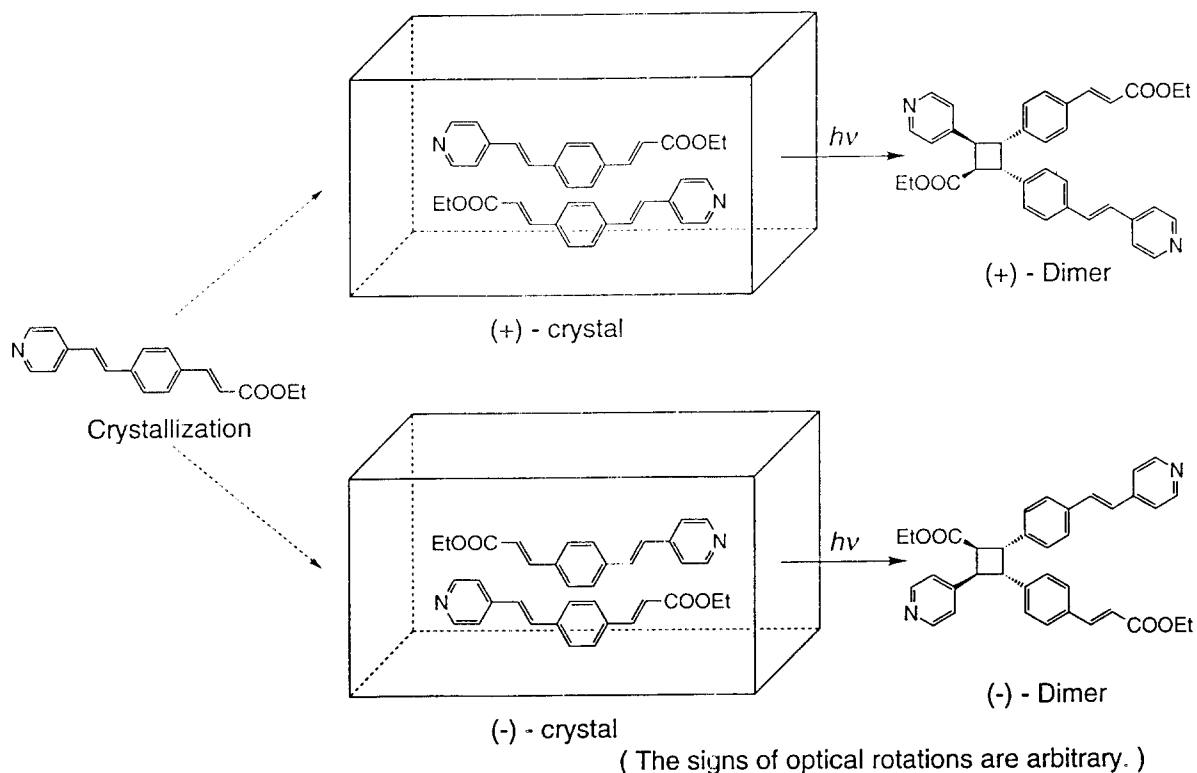
Scheme 4

performed by topochemical [2+2] photoreaction of unsymmetric diolefin crystals (Scheme 5).²⁶ However, high-molecular-weight optically active linear polymer has not yet been achieved so far.

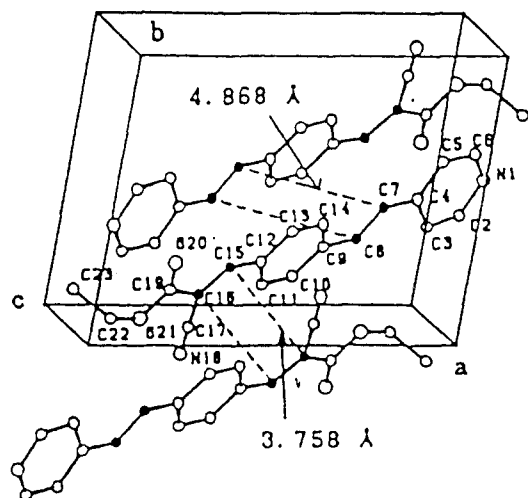
Specific topics on topochemical polymerization

Even-numbered polymerization mechanism. Ethyl α -cyano-4-[2-(4-pyridyl)ethenyl]cinnamate (**2a**) crystallizes

with photoreactive α -centrosymmetry-type packing.^{17,18} Upon UV-irradiation of **2a** crystals at room temperature, an α -homo-type linear polymer is produced with the accumulation of one type of dimer at the intermediate stage (Scheme 6). The gel permeation chromatography (GPC) profile at an early stage of the photo-products of **2a** crystals shows that the products consist of molecular species with only an "even-numbered" degree of polymerization, such



Scheme 5

Figure 1. Crystal structure of **2a**

as dimer, tetramer, hexamer, and so on. In addition, ^1H NMR and MS spectroscopy of the photoproducts shows that they have only pyridylethenyl groups at growing terminals.

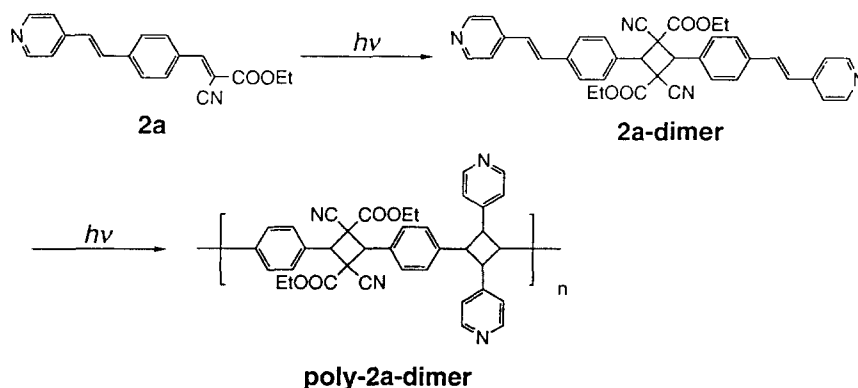
The even-numbered degree of polymerization behavior of **2a** can be interpreted from its crystal structure, in which the molecule is related to its neighboring molecules by two different inversion centers to make a plane-to-plane stack (Fig. 1). The ethylenic double bonds on the ester side, related by one inversion center, are separated by 3.758 \AA , whereas the ethylenic double bonds on the pyridyl side, related by the other inversion center, are separated by a distance of 4.868 \AA ; only the former ethylenic double bonds can react according to the topochemical principle.²² The GPC profile and the crystal structure show that the monomer reacts only with the monomer and that further chain growth occurs only between two dimer molecules. The intermolecular pyridyl ethenyl groups between the dimers must have come closer to each other within the reactive distance after the dimerization. Accordingly, the "even-numbered polymerization" mechanism can be explained on the

basis of the difference in topochemical environment of two ethylenic groups in the molecule; the polymerization proceeds through a single type of dimer, accumulated spontaneously during the photoirradiation, to give an even-numbered polymer species.

Enhancement of photopolymerizability by solvent inclusion. Propyl α -cyano-4-[2-(4-pyridyl)ethenyl] cinnamate (**2b**), which has different ester substituent from **2a**, crystallizes into an α -type packing crystal from 1-propanol solution.¹⁸ Upon photoirradiation, an α -type homo-adduct dimer (**2b**-dimer) is produced from **2b** in nearly quantitative yield (Scheme 7). However, as-prepared **2b**-dimer crystal is entirely stable on photoirradiation.

On the basis of an X-ray crystallographic study, the ethylenic double bonds in the as-prepared **2b**-dimer were confirmed to be unfavorably located for [2+2]cycloaddition. Moreover, since the length of the repeating unit in α -type linear polymers is about 7.5 \AA , according to a molecular modeling evaluation, the stacks of the double bonds in the starting crystals are preferred to have a similar length of the repeating unit (L). However, in the crystal of **2b**, $L (= 5.932 \text{ \AA})$ is apparently shorter than this range (Fig. 2a). To overcome these difficulties, enhancement of photoreactivity would be expected by detaching the center of the gravities of the dimers from each other; complexation of some kinds of spacers into these crystals may be effective for this purpose.

Recrystallization of **2b**-dimer from 1-propanol affords the crystal, **2b**-dimer \cdot PrOH, which contains solvent molecules in a 1:1 ratio. **2b**-dimer \cdot PrOH becomes photoreactive and gives the polymer having the same type of structure as the **2a** polymer (Scheme 7). As shown in Fig. 2b, the propanol molecule in **2b**-dimer \cdot PrOH is hydrogen-bonded with the pyridine nitrogen atom in the dimer. Consequently, two reactant dimer molecules are separated from each other to a suitable distance ($L = 6.736 \text{ \AA}$) and two reactive sites are contracted to a normal photoreactive range. Furthermore, the complex prepared from ethanol solution, which contains two molar equivalents of the solvent molecules also, undergoes photoreaction to give a higher molecular



Scheme 6

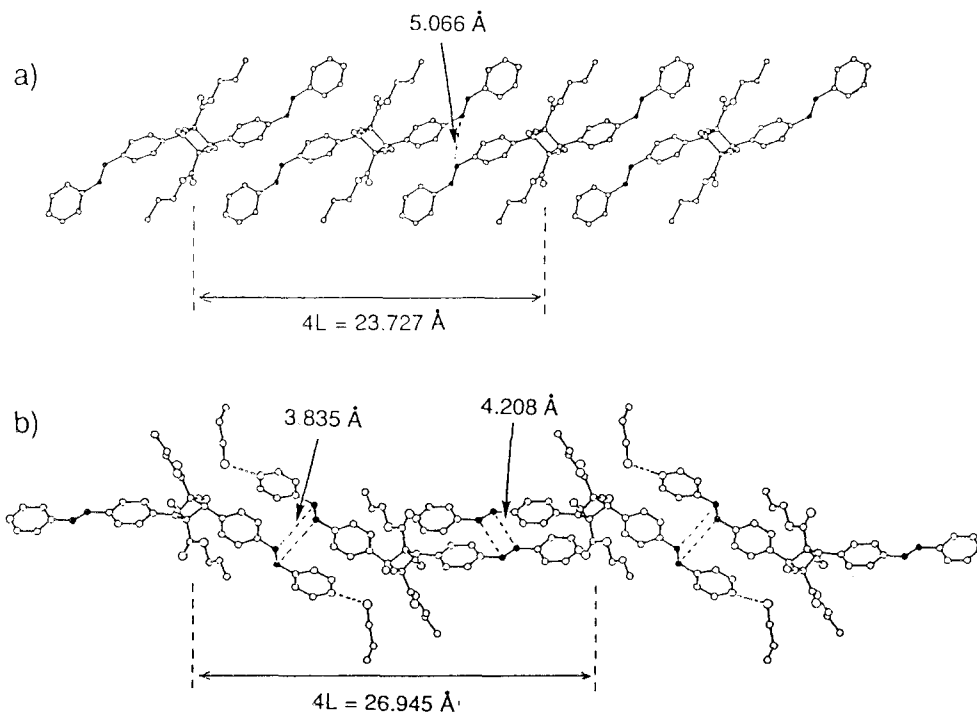


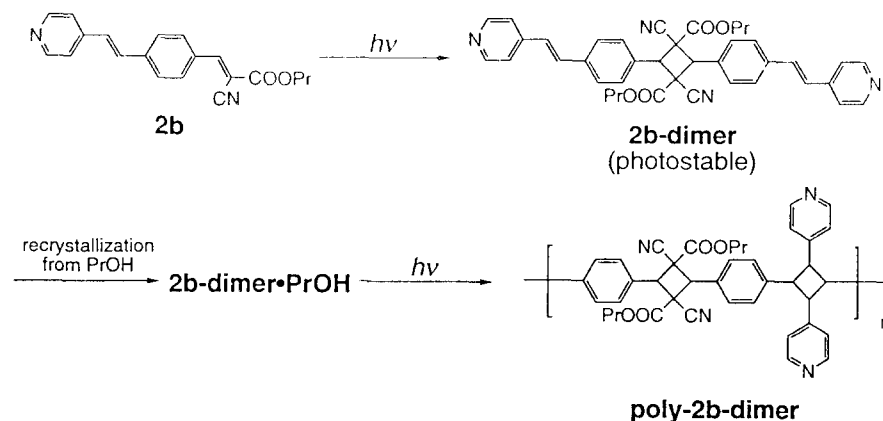
Figure 2. Crystal structures (a) as-prepared **2b**-dimer and (b) recrystallized **2b**-dimer · PrOH.

weight polymer. The formation of such inclusion complex with the solvent is rather generally observed with similar types of dimers with alcohols and some other solvents, and consequently enhances polymerizability.

Formation of stereospecifically regulated polymer. Crystals of methyl α -cyano-4-[2-(2-pyridyl)ethenyl] cinnamate (**3a**) with β -type packing are highly photoreactive and are converted into the β -hetero-type dimer (**3a**-dimer) in high yield upon photoirradiation with a cut-off filter ($> 410 \text{ nm}$) (Scheme 8).²⁷ In this case, the starting crystals are gradually transformed into an amorphous product as the photoreaction progresses. The dimer, after recrystallization from methanol/1,2-dichloroethane, gives a polymer via a tetramer with

retention of high crystallinity on further photoirradiation (Scheme 9). The ^1H NMR analysis of the tetramer (**3a**-tetramer) indicates the formation of an α -homo-type adduct by the cycloaddition of ethylenic double bonds on the ester side of **3a**-dimer. Finally, the resulting polymer has **3a**-tetramer as a repeating unit.

On the basis of the geometry of two pyridyl side olefins of **3a**-dimer, the olefinic pair is expected to yield an ϵ -type (or δ -type) cyclobutane ring (Fig. 3). Thus, the polymer structure should have a unique repeating unit in which three types of cyclobutane structures are incorporated in a sequence of $[\alpha\beta\epsilon\beta\alpha\beta^1\epsilon\beta^1]$ (or $[\alpha\beta\delta\beta\alpha\beta^1\delta\beta^1]$), where β and β^1 are of opposite absolute configuration (Fig. 4). Considering the stereochemistry of cyclobutane rings, the polymer



Scheme 7

Cyclobutane structure

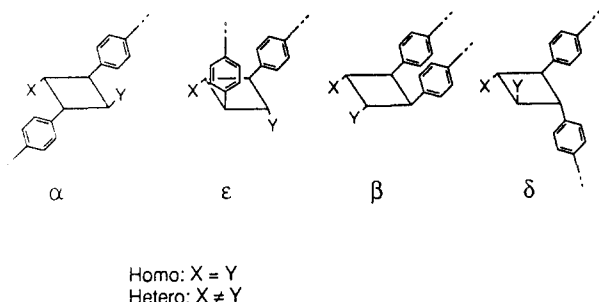


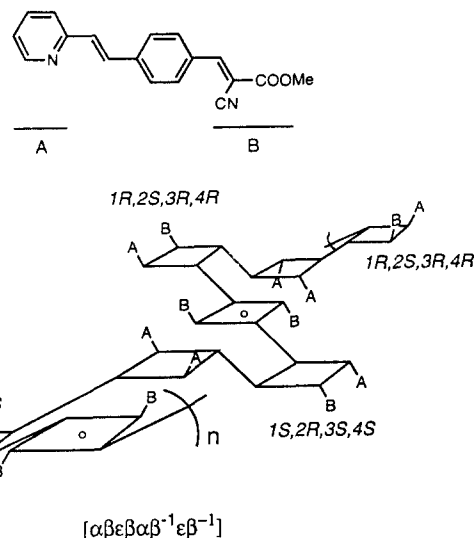
Figure 3. Structure of substituted cyclobutanes.

should be "double syndiotactic."

From the viewpoint of synthetic polymer chemistry, although the formation of stereospecific polymers (isotactic and syndiotactic) is very popular, the present polymer is the first example having a double syndiotactic structure. In addition, the polymer consists of an alternating zigzag-linear main chain structure.

Ethyl α -cyano-4-[2-(2-pyridyl)ethenyl]cinnamate (**3b**) also crystallizes with β -centrosymmetry-type packing yielding photoreactive crystals, which is converted into the β -hetero-type dimer (**3b**-dimer) nearly quantitatively upon photo-irradiation with a cut-off filter (Scheme 8).²⁷ Upon further photoirradiation, **3b**-dimer gives a tetramer with a certain amount of octamer and higher oligomers. (Scheme 9).

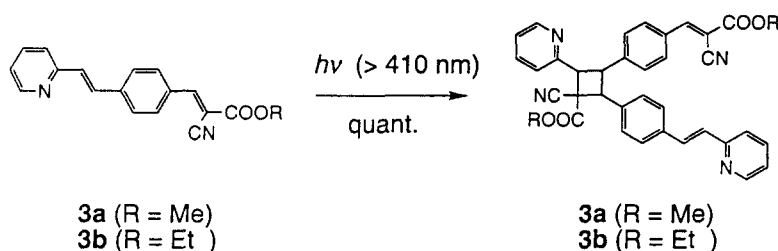
X-Ray crystallographic study shows that, in the crystal of **3b**, two molecules form a pair as is the case in the crystal of **3a**. Considering the intermolecular distances between the ethylenic double bonds, each molecule can react only with its partner in the molecular pair and not with any molecule of another pair. Since paired molecules are related by inversion center, two pairs of facing ethylenic double bonds should be equal in photoreactivity, affording two enantiomeric cyclobutanes. However, after the formation of **3b**-dimer in one molecular pair followed by the thermal process, the photoreactivity of the two pairs of ethylenic double bonds in neighboring molecular pairs should no longer be equal; the ethylenic double bonds in the pair of **3b**,

Figure 4. Schematic representation of **3a**-polymer.

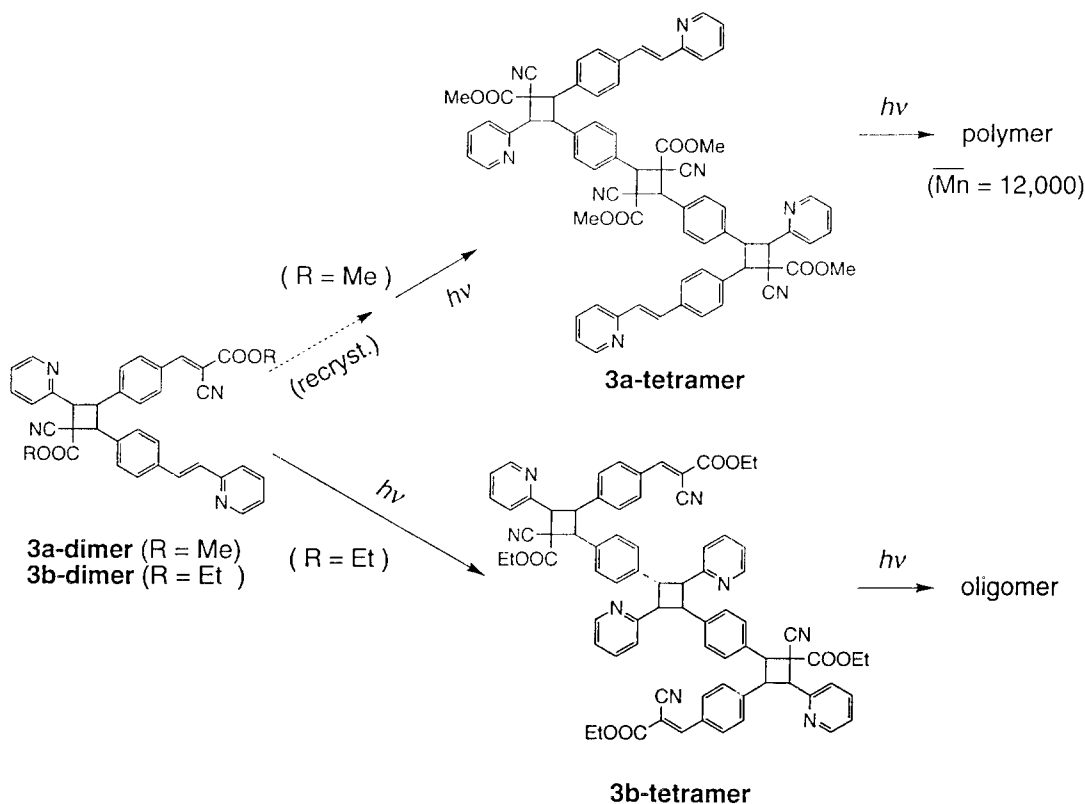
adjacent to the cyclobutane side of the **3b**-dimer, should be less reactive due to the steric repulsion of the substituents that protrude after dimerization. As a result, the alignment of dimers becomes alternative from the viewpoint of the chirality (Fig. 5).

The tetramer contains three cyclobutane rings of β -hetero, α -homo, and β -hetero-type structures. In addition, on the basis of the geometry of the two ethylenic double bonds on the ester side of the **3b**-dimer, the polymer should have a unique repeating unit in which three types of cyclobutane structures are incorporated in a sequence of $[\beta\alpha\beta^{-1}\alpha]$ where β and β^{-1} are enantiomeric ("syndiotactic"). At the same time, as is the case for **3a**, the repeating unit consists of an alternating zigzag-linear chain structure as seen in Fig. 6.

The photochemical behavior of **3b** is the first example in which the reaction of achiral molecules in an achiral crystal packing does not occur at random but stereospecifically, resulting in a syndiotactic structure. As no external chiral catalyst exists in the reaction, the above result is a unique type of "topochemical induction", which is initiated by chance in the formation of the first cyclobutane ring, but followed by syndiotactic cyclobutane formation due to steric repulsions in the crystal cavity. That is, the "syndiotactic" structure is evolved under moderate control of the reacting crystal lattice.



Scheme 8



Scheme 9

TOPOCHEMICAL REACTION OF MIXED AND MOLECULAR COMPLEX

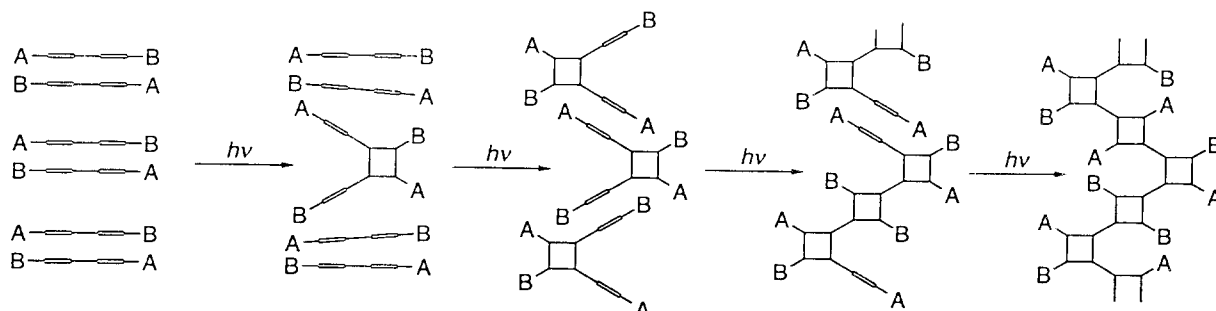
Copolymerization

The preparation of mixed crystals of olefinic compounds has been investigated from the viewpoint of topochemical copolymerization. It is well known that some pairs of isomorphous compounds form mixed crystals.²⁸ On the basis of this facts, it is expected that a pair of two diolefin compounds, of those crystal structures are isomorphous with each other in α -type packing, should form a mixed crystal with high probability and subsequently, give a crystalline linear copolymer. Though one report on the formation of a mixed crystal of 2,5-DSP and 1,4-bis[2-(2-pyridyl)vinyl]benzene has appeared,²⁹ its topochemical behavior has not been described. The first clear-cut

example of topochemical copolymerization of a diolefin mixed crystal was found for **1a** and *S*-ethyl 4-[2-(4-pyridinyl)-ethenyl]cinnamate (**1b**).³⁰

1a and **1b** were found to have isomorphous crystal structure to each other and affords crystalline polymer upon photo-irradiation. When a mixture of equimolar amounts of **1a** and **1b** is recrystallized from methanol solution, micro crystals comprising **1a** and **1b** in a molar ratio of 45:55 are deposited. The mixed crystal has a structure isomorphous to those of pure crystal, and upon photoirradiation, the mixed crystal gives a crystalline polymer having the same main chain as the homopolymers (Scheme 10).

A dimer portion can be prepared exclusively from the mixed crystal by controlling the wavelength of irradiating light. The high-performance liquid chromatogram of the isolated dimers shows three peaks; two of these are

Figure 5. Mechanism of topochemical induction of chirality in the photoreaction of **3b**.

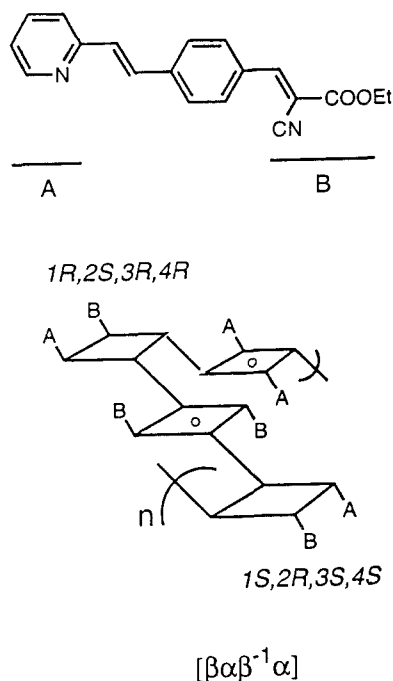


Figure 6. Schematic representation of **3b**-polymer

attributed to dimers from **1a** (OO) and from **1b** (SS), respectively, and the other one is a mixture of two mixed dimers, OS and SO. The existence of OS and SO dimers indicates the formation of a mixed crystal, resulting in the formation of a copolymer of the *O*-ethyl and the *S*-ethyl compounds. Furthermore, the existence of OO and SS dimers indicates that the molecular arrangement of **1a** and **1b** is not alternating but random in the mixed crystal because the alternating arrangement of these two diolefin molecules would give only dimers OS and SO with neither OO nor SS.

This is the first example of topochemical copolymerization in which the copolymer formation is completely substantiated on the basis of direct evidence from spectroscopic and preparative techniques. The same mixed crystal is also obtained through crystal-crystal contact by simple grinding of two monomers with an amalgamator. Irradiation of the resulting mixed crystal gives a crystalline linear copolymer having the same structure.

A perfectly ordered polymer composite by four-Center-Type photopolymerization of a molecular complex

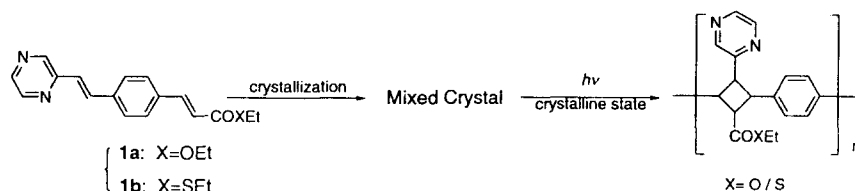
If a cocrystal of diolefin compounds which has a

regular molecular arrangement between two species could be prepared, there is a possibility of the formation of a regular copolymer by topochemical polymerization. However, although several pairs of isomorphous diolefin compounds have been reported to form photoreactive mixed crystals,³¹ formation of the cocrystal comprising two olefin compounds which are not isomorphous to each other is quite rare.³²

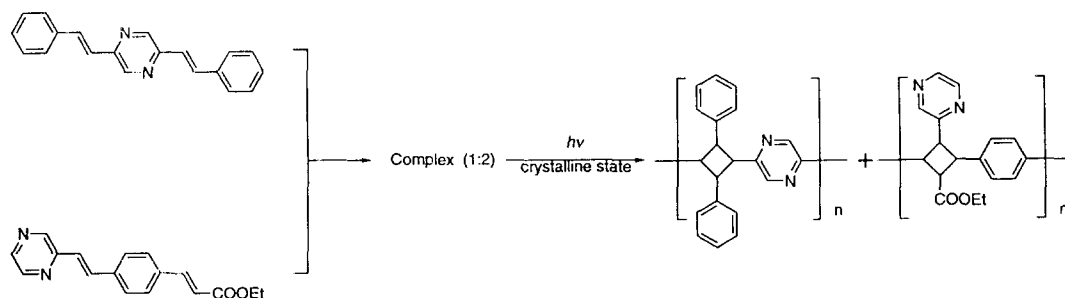
As described above, each of 2,5-DSP and **1a** gives a crystalline polymer upon UV irradiation in the crystalline state, respectively.^{3,13} On the other hand, when an equimolar mixture of 2,5-DSP and **1a** is recrystallized from benzene, yellow crystals, comprising 2,5-DSP and **1a** in a molar ratio of 1:2, deposit. The DSC curve of this crystal shows a single endothermic peak at 166 °C, which corresponds to the melting point of neither 2,5-DSP (223 °C) nor **1a** (156 °C). Furthermore, the X-ray powder diffraction pattern of the crystal is quite different from those of the homocrystals 2,5-DSP and **1a**. These results strongly suggest the formation of cocrystal of 2,5-DSP and **1a**.

Upon irradiation, the cocrystal 2,5-DSP·**1a** affords a crystalline linear high polymer. The ¹H NMR spectrum of the polymer coincides perfectly with that of a 1:2 mixture of poly-2,5-DSP and poly-**1a**. In the dimer, only 2,5-DSP-dimer and **1a**-dimer are detected by HPLC analysis, but the corresponding cross-dimer consisting of 2,5-DSP and **1a** is not detected at all. These observations by ¹H NMR and HPLC indicate that the photoproduct obtained from the cocrystal 2,5-DSP·**1a** is not a copolymer but a mixture of poly-2,5-DSP and poly-**1a** with the ratio 1:2 (Scheme 11).

X-ray crystallographic analysis of the cocrystal shows that it is not a simple mixture of 2,5-DSP and **1a**, but a molecular complex of 2,5-DSP and **1a**, in which 2,5-DSP and **1a** are comprised in a 1:2 ratio (Fig. 7). In the molecular complex, both 2,5-DSP and **1a** form columns separately along the *c*-axis with sheets perpendicular to the *a*-axis related by a glide mirror plane. The distances between the neighboring ethylenic double bonds in the same layer are 3.934 Å in the column of 2,5-DSP and 4.013 and 3.976 Å in the column of **1a**, respectively. Taking into account the distances between the neighboring ethylenic double bonds and preservation of the crystallinity during the photoreaction, the polymerization would proceed along the *a*-axis upon photoirradiation to give a perfectly ordered (alternatively layered) crystalline polymer composite; in other words, the polymer crystal should



Scheme 10



Scheme 11

comprise an alternating monolayer of poly-2,5-DSP and bilayer of poly-**1a**, as shown schematically in Fig. 8.

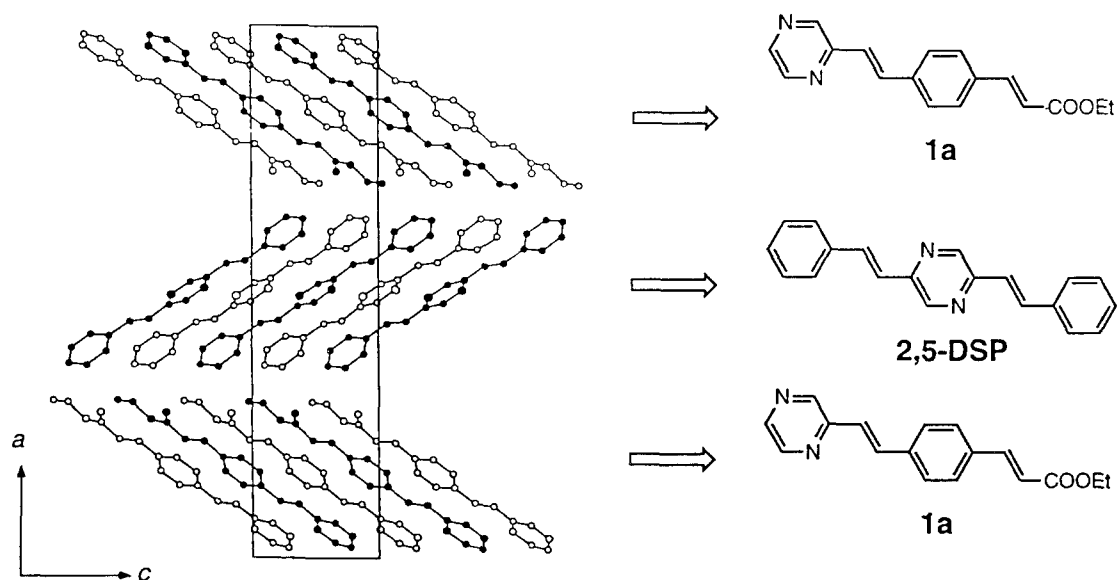
This is the first example of a topochemical reaction of a molecular complex of a perfectly ordered polymer composite.

As is the case of mixed crystal formation of **1a** and **1b**, this molecular complex can be prepared by grinding of simple mixture of 2,5-DSP and **1a** crystals. The resulting cocrystal also affords the polymer composite upon photoirradiation.

Formation mechanism of cocrystal by grinding

Mixed crystal formation by simple grinding has been widely observed on several pairs of diolefinic and diacetylenic compounds.³⁰⁻³² However, the mechanistic study such as kinetic and/or thermodynamic study on the mixed crystal formation by grinding has hardly been performed until recent years. In the case of diolefin compounds, the formation of mixed crystals has been ascertained by X-ray diffraction pattern upon grinding and by ¹H NMR and HPLC analyses of the photoproducts. Since the structure of the crystal is correctly reflected on

the structure of photoproduct, the kinetic data of crystal growth can be obtained by the analysis of the photoproduct, if the homocrystals and resulting cocrystal afford different photoproducts. We then studied the growth of the mixed crystal phase of ethyl and propyl α -cyano-4-[2-(4-pyridyl)ethenyl]cinnamate (**2a** and **2b**) by grinding in detail. In this case, each homocrystal affords α -type dimer, respectively,¹⁸ whereas the mixed crystal **2a**·**2b** affords β -type dimer upon irradiation with a cut-off filter,²⁰ and the ratio of mixed crystal included in the ground sample can be quantitatively estimated by the HPLC analysis of the photoirradiated sample. The kinetic data reveal that the mechanical treatment (grinding) is necessary for the formation of the mixed crystal nuclei, and subsequent growth of the mixed crystal phase is triggered by each of the mixed crystal nuclei. In addition, it was ascertained that the growth of the mixed crystal phase is accelerated by either thermal annealing or exposure to humidity. During the early stage of mixed crystal growth, the growth rate is nearly proportional to the surface area of the nuclei of the mixed crystal. From these experimental results, it has been suggested that the whole processes of mixed crystal

Figure 7. Crystal structure of the molecular complex of 2,5-DSP and **1a**.

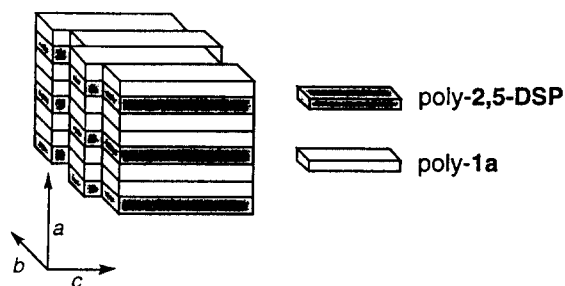


Figure 8. Schematic representation of the polymer composite poly-2,5-DSP · 1a.

formation is kinetically analogous to the photographic processes; the grinding time and the subsequent thermal annealing correspond to the exposure time and development processes, respectively.³³

NON-TOPOCHEMICAL FACTORS ON TOPOCHEMICAL [2+2] PHOTOREACTIONS

Unexpected selectivity of dimer formation

Recently several examples of diolefin crystals in which the reaction behavior deviates from the topochemical rule have been observed. For example, in the photoreaction of methyl α -cyano-4-[2-(4-pyridyl) ethenyl]cinnamate (**4**), the first reaction occurs exclusively at the pyridyl side although the distance between the ethylenic double bonds on the ester pyridyl (4.049 Å) is exactly the same as that between the ethylenic double bonds on the ester side, as shown in Fig. 9.¹⁸ A few other unsymmetrical diolefin compounds display the same regioselective behavior.³⁴

In order to elucidate this unexpected regioselective reactivity of olefins in identical topochemical environments, we calculated the reaction cavity around the ethylenic double bonds, packing potential energy of the crystal, and stabilization energy from orbital interactions between two reacting molecules.³⁵ The analyses by these three computational methods concluded that both steric factors (cavity and potential energy) and electronic factors (perturbation energy from orbital interactions) played cooperative roles in determining which C-C double bond in a molecule reacted first in [2+2] photodimerization. The steric factor is considered to be effective in the movement of olefins at an early stage of the reaction, whereas the electronic factors are effective in the addition of olefins at a later stage of the reaction.

Anomalous stability of thioester crystals

Methyl 4-[2-(ethylthiocarbonyl)ethenyl] cinnamate (**5**) crystallizes into a typical α -translation-type packing structure in which the distances between the ethylenic double bonds are 3.988 Å and 4.067 Å, respectively.³⁶ However, the crystal of **5** is entirely photostable even though it should be photoreactive based on the

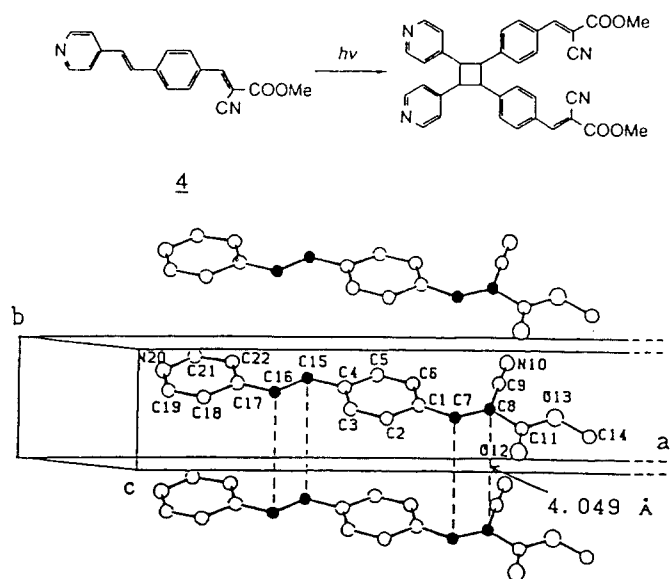


Figure 9. Crystal structure of **4**.

topochemical rule. Further studies proved that, in most diolefin derivatives, replacement of the oxygen atom of an ester moiety by a sulfur atom is possible without changing the photopolymerizable molecular arrangement.³⁷ All of these thioester derivatives and even the mixed crystals containing a small amount of thioester derivatives of 1,4-phenylene diacrylate (PDA) were found to become photostable.³⁸ Such anomalous behavior of **5** and thioester crystals cannot be explained simply in terms of the topochemical rule since this rule involves only the positional relationship between the reactive olefin pair.

In comparison of fluorescence spectra between the ester and thioester derivative crystals of PDA, the ester crystal shows a strong emission whereas the thioester crystal fluorescence much weaker. For example, the emission intensity of PDA methyl thioester crystal is about one-thousandth of that of a PDA methyl ester crystal. Furthermore, the fluorescence lifetime of mixed crystals which consist of a large amount of PDA methyl ester with a small amount of the corresponding thioester moiety is much shortened, compared to the lifetime of pure PDA methyl ester crystals. In quenching experiments in solutions of PDA ester, the fluorescence of the PDA ester is dramatically quenched by thioacetate. Similar behavior has been obtained with several types of diolefin derivatives having a thioester moiety, where crystal structures are isomorphous with the corresponding ester derivatives. From the results of the fluorescence spectroscopic study it is concluded that excitation energy at the lowest excited state of a PDA derivative having a thioester moiety is localized at the thioester group; intra- or intermolecular energy transfer from the conjugated system of the PDA to the thioester moiety must have occurred in the crystalline state to afford a photostable crystal.³⁹

CONCLUDING REMARKS

As described in this review, topochemical photoreaction of diolefin crystals affords a variety of unique products, which can not be prepared in solution reaction. Particularly, it is quite fascinating from the viewpoint of polymer synthesis since perfect control of the stereochemistry of the polymerization can be achieved as demonstrated by the topochemical reaction of **3a** and **3b**. Recently, topochemical reactions in multi-component crystal are increasingly drawing attentions, which promise to expand the variety of the reaction to a considerable extent. In the case of diolefin compounds, it is expected that a sequentially regulated copolymer or a polymer composite whose structure is perfectly controlled at molecular level, would be obtained by topochemical polymerization. In the near future, it will become one of indispensable methods for the control of polymer synthesis.

On the other hand, there are some unsolved problems in the organic solid-state chemistry, especially for the control of topochemical reactivity. For example, achieving the desired type of crystal structure for a given compound is still difficult because the factors that control the crystal packing are not yet satisfactorily understood. In this case, polymorphism makes the problems extremely complicated: slight changes in crystallization condition result in different crystal packings for an identical compound. In addition, discussion of non-topochemical factors has started only recently. Development of much more severe and sophisticated methodologies for the prediction of topochemical reactivity is required at present.

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