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Photopolymerization of Diolefin Crystals

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Contents

I. Introduction

There are a great number of literature references to reactions in the crystalline state, e.g., cis–trans isomerization[1] or dimerization[2] of olefins, acyl migrations,[3] formation of "cage" molecules,[4] nucleophilic substitution reactions,[5] and resolution of optically active compounds.[6] It might sound curious that in crystalline state organic reactions, polymerization had been investigated more thoroughly than the reaction of small molecules since around 1950. However, no clear-cut example of a topochemical polymerization, in which all elementary steps proceed under a crystal lattice controlled process, had been found before the finding of the photopolymerization of diolefin crystals, although several efforts had been extensively made to seek such a polymerization.[7,8]

Formation of α-truxillic and β-truxinic acids from two types of cinnamic acid crystals has been known for a long time[2] and was interpreted in 1943 by Bernstein and Quimby[9] as a crystal lattice controlled reaction. In 1964 a hypothesis on the reaction behavior of cinnamic acid crystals was first visualized by Schmidt and co-workers, who correlated the crystal structure of several olefin derivatives with the photoreactivity and steric configuration of the products.[10] The result established the topochemical principle in which the reaction tends to occur with a minimum of atomic and molecular motion. That is, the environment of the olefin double bonds conforms to one of three principal types: the α-type crystal, in which the double bonds of neighboring molecules make contact at a distance of about 3.7 Å across a center of symmetry; the β-type, characterized by a lattice having one axial length of 4.0 ± 0.1 Å between translationally related molecules; and the γ-type, in which no double bonds of neighboring molecules are within 4.7 Å. On photoirradiation of cinnamic derivatives, an α-type crystal gives a centrosymmetric dimer related to α-truxillic acid ($\bar{1}$ dimer), a β-type crystal gives a dimer of mirror symmetry, related to β-truxinic acid (m-dimer), and a γ-type crystal is photostable.

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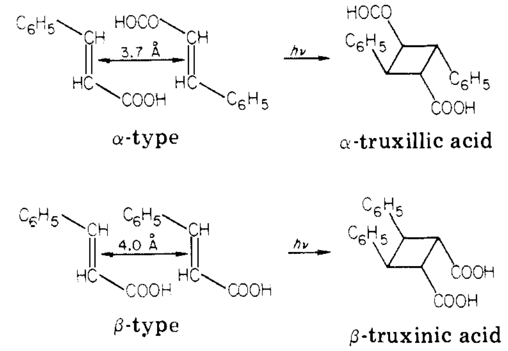
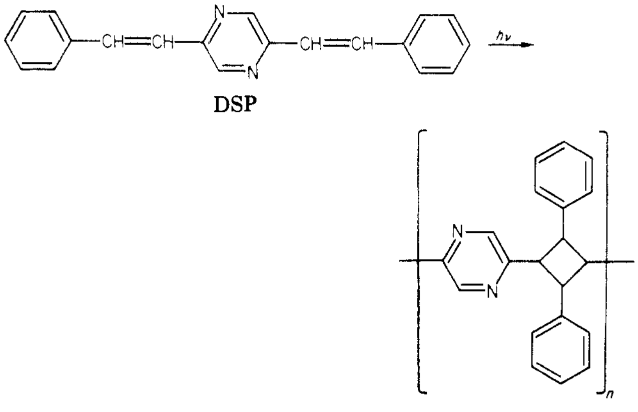
Hirshfeld and Schmidt suggested the possibility of topochemical polymerization systems if suitable contact between the reactive centers of neighboring molecules in the crystal is maintained during the polymerization.[11] Along with their postulation, Lahav and Schmidt reported the crystalline-state reaction of the dimethyl ester of *all-trans*-hexatriene-1,5-dicarboxylic acid to



yield a cyclobutane dimer as well as a polymer.[12]



In 1958 Koelsch and Gumprecht reported that brilliant yellow crystals of 2,5-distyrylpyrazine (DSP), which was prepared by Franke in 1905,[13] became white on exposure to UV irradiation, turning into an insoluble polymeric substance with a melting point of 331–333 °C.[14] The author's group independently made the same observation with DSP on exposure to sunlight and suggested a possibility of isomeric change in the crystalline state.[15] This phenomenon was further investigated, and it was concluded that the DSP crystal was converted by the action of sunlight into a linear, high molecular weight polymer crystal with cyclobutane units in the main chain. This new type of polymerization was named four-center type photopolymerization and reported in 1967.[16]

Also in 1967, Holm and Zienty announced in a patent that crystalline linear polymers were obtained by photoirradiation of a series of crystalline dibenzylidenebenzenediacetonitrile derivatives,[17] and they published the result on the photopolymerization of α,α′-bis(4-acetoxy-3-methoxybenzylidene)-*p*-benzenediacetonitrile (AMBBA) in 1972.[18]

These two findings of a new type of crystalline-state photopolymerization prompted polymer chemists to study the generality of this type of polymerization. As a consequence, a large number of diolefin crystals have been found to photopolymerize to linear high molecular weight polymers. Within the past 15 years a wide variety of studies have been carried out on the polymerization behavior, the crystallographic and kinetic features of topochemical processes of diolefin crystals, and the characteristics of polymers. It is rather surprising that the reaction of DSP was the first example of photopolymerization via a stepwise mechanism not only in the crystalline state but also in any other state.

Four-center type photopolymerization in the crystalline state is a general term for the reactions in which conjugated diolefin crystals are photochemically converted into crystals of linear polymers containing cyclobutane and aromatic groups alternating in the main chain. On the basis of mechanistic and crystallographic results it was concluded that the four-center type photopolymerization is a typical topochemical reaction in which quantitative transformation into the polymer crystal is performed under a thermally diffusionless process with retention of the space group of the starting diolefin crystal.[19] Addadi et al. achieved an elegant success on an "absolute" asymmetric synthesis through crystallization of an achiral monomer into a chiral crystal, followed by the four-center type photopolymerization.[20–22]

This review deals with the four-center type photopolymerization of diolefin crystals focusing on recent results and special topics of the topochemical polymerization.[23]

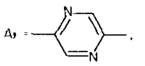
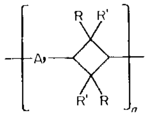
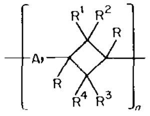
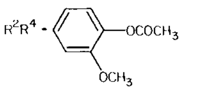
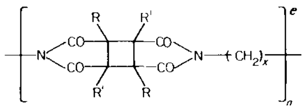
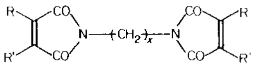
II. Chemical Structure Required for Polymerizable Diolefin Crystals

Examples of diolefin crystals reported to photopolymerize are shown in Table I. These compounds polymerize on irradiation by UV–visible light with various reactivities; DSP and *p*-CPAnPr show the highest photoreactivity among the monomers while P2VB and *p*-PDA amide polymerize slowly. As the four-center type photopolymerization is strictly crystal lattice controlled,[19] all of the diolefin crystals examined are classified by the all-or-none nature of reactivity. For example, 2,5-bis(4-methylstyryl)pyrazine and P4VB (4-pyridyl-1,2-ethenediyl-1,4-phenylene-1,2-ethenediyl-4-pyridyl) crystals are photostable though their chemical structures are very similar to either DSP or P2VB, respectively.[24] In other extreme cases, DSP and AMBBA are crystallized, depending on the environment, into two crystal forms with different photochemical behavior that are photoreactive and photostable.[18,31] As the reaction behavior of photoreactive crystals is seriously affected by reaction temperature, as exemplified of *p*-PDAEt in Table I, the polymer yield of *p*-PDAnPr may be assumed to be quantitative if the reaction temperature is properly selected.

The polymerization process forming cyclobutane rings is confirmed by IR and NMR spectral changes with the disappearance of aliphatic $>C{=}C<$ bonds and appearance of aliphatic C—H bonds. A linear polymer structure with cyclobutane units in the main chain is concluded from the observation of solution viscosity behavior and film-forming properties, in addition to spectroscopic results. Decomposition points of these polymers are not strictly definable because as-polymerized polymer crystals depolymerize thermally in the crystalline state, and the starting temperature of decomposition is decreased with increasing molecular weight.[32] As-polymerized polymer crystals are only soluble in strongly acidic solvents such as concentrated sulfuric or trifluoroacetic acids while the amorphous polymers are soluble in conventional polymer solvents such as *m*-cresol or *o*-chlorophenol.

As is obvious in Table I, preparative study of four-center type photopolymerizations has established the empirical rule that the crystalline state (2 + 2) photodimerization of olefins can be widely extended to the crystalline state photopolymerization of diolefins, such

TABLE I. Examples of Diolefin Compounds Reported To Polymerize in the Crystalline State

compound (abbreviation)	reactivity	polymer yield, % (react temp)	reduced viscosity, dL/g	decomp temp of[a] polym cryst, °C	ref[b]
					
R = Ph, R' = H, (DSP,α)[c]	very high	quantitative (−42 to 50 °C)	1.0~10	340	24
Ar = 1,4-C_6H_4, R = 2-py, R = H (P2VB)	low	quantitative (room temp)	2.0	340	24
Ar = 1,4-C_6H_4, R = $COOC_2H_5$, R' = H (*p*-PDAEt)	medium	quantitative (−25 °C)	1.4	347	25
	low	67 (room temp)	0.16		
Ar = 1,4-C_6H_4, R = COOi-C_3H_7, R' = H (*p* PDAiPr)	low	65 (room temp)	0.45	320	25
Ar = 1,4-C_6H_4, R = $CONH_2$, R' = H (*p*-PDAamide)	medium	quantitative (room temp)	1.5	405	25
Ar = 1,3-C_6H_4, R = $COOCH_3$, R' = H (*m*-PDAMe)	medium	quantitative (room temp)	oligomeric	amorphous	26
Ar = 1,4-C_6H_4, R = COO*n*-C_3H_7, R' = CN (*p*-CPAnPr)	very high	quantitative (room temp)	3.0	335	27
Ar = 1,4-C_6H_4, R = CH=C(CN)$CO_2C_2H_5$ R' = H (*p*-PDCBAEt)	high	quantitative (room temp)	1.3 [η]	245	28
					
Ar = 1,4-C_6H_4, R = CN, R^1,R^3 = H,  (AMBBA,α)[c,d]	high	quantitative (room temp)	0.44 [η]	300	18
Ar = 1,4-C_6H_4, R,R^1 = H, R^2 = COOEt, R^3 = CN, R^4 = COO*sec*-Bu	low	quantitative (5 °C)	oligomeric		20,29
					
 R,R' = CH_3, x = 3	high	quantitative (room temp)	0.21 [η]	386	30

[a] Measured by capillary method. [b] Reference for polymerization. [c] Photostable crystal is obtained under a specified purification condition. [d] α-Type packing was tentatively assigned to photoreactive crystal. [e] Structure of cyclobutane unit was tentatively represented.

as stilbazol to DSP (and P2VB), cinnamic acid to the *p*-PDA series, or α-cyanocinnamic acid to the *p*-CPA series.[27] Furthermore it should be noticed that all the polymer crystals are derived from the monomers with a rigid linear structure having the conjugated double bonds separated by the 1,4-position of an aromatic ring (2,6-position of naphthalene in one example[33]). Neither *m*-PDAMe nor bis(maleimide) in Table I[26,30] shows typical topochemical behavior, but they give the amorphous oligomer or a partially cross-linked polymer. Several other molecules having a certain flexible chain have been also reported to polymerize into the cyclobutane polymers,[34-36] but these monomer crystals behave essentially different from the conjugated diolefin crystals; for example, olefin double bonds in the pentaerythritol tetracinnamate crystal completely disappear on irradiation without any apparent change of the crystal. However, the resulting product is a nonfusible amorphous substance.

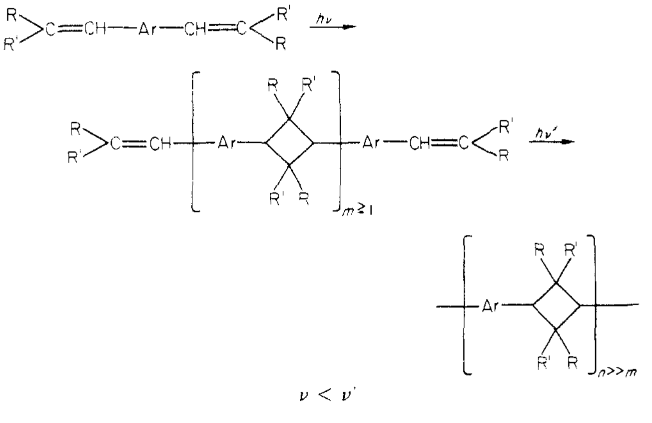
This empirical rule suggests that in the crystallization processes of photoreactive monoolefins and photopolymerizable rigid conjugated diolefins, a common intermolecular affinity plays an important role so as to allow the photoreactive molecular alignment in the crystals. This concept of the relationship between rigid linear structure and reactivity was rationalized satisfactorily by crystallographic analysis.[19] No example of extention to the photopolymerization from the photodimerization of chalcone in the crystalline state has been reported so far while a cyclic dimer formation has been found via a double photocycloaddition between two molecules.[37]

III. Polymerization Behavior of Diolefin Crystals

A. Polymerization Mechanism

The polymerization of conjugated diolefin crystals proceeds stepwise between the photoexcited olefin and the olefin in the ground state. None of these diolefin monomer crystals has been reported to be susceptible to X- or γ-rays so far.

Since the π-electron conjugation of the monomer is interrupted by the formation of a cyclobutane ring, the π-π^* electronic transition of the molecule larger than the dimer is shifted to a higher energy level than that of the monomer.



As the olefin bonds in all the monomer crystals in Table I absorb wavelengths of visible light and/or UV light and as the terminal olefin units absorb UV light ($\gtrsim$250 nm), all the conjugated diolefin monomer crystals are converted to the high polymer crystals upon irradiation by ordinary photochemical light sources such as a high-pressure Hg lamp or xenon lamp. On the other hand, on irradiation at the long-wavelength edge of the monomer ($h\nu$), only dimerization and oligomerization (the reaction between excited monomer and the terminal olefin unit of a growing chain in the ground state) proceed to result in the oligomer crystals. A high polymer is produced on successive irradiation of the oligomer with the wavelength of light that excites the terminal unit ($h\nu'$). By such a selective excitation technique, in parallel with control of the irradiation time and temperature, average molecular weight and molecular weight distribution of the final product are widely controllable. It is noteworthy, however, that successive polymerization of oligomer crystals is not completed as thoroughly as the direct polymerization from the monomer crystal by irradiation with an ordinary photochemical light source. Such a difference of polymer chain growth has been reported in the polymerization of DSP and *p*-CPAnPr.[38] In DSP, the reacting crystal expands in the course of selective oligomerization (DSP 1.244 g/cm^3 → DSP oligomer 1.18 g/cm^3), and then the crystal shrinks with subsequent polymerization (DSP oligomer 1.18 g/cm^3 → poly-DSP 1.257 g/cm^3).[31] The above difference may be interpreted by the following mechanism: during the direct polymerization by ordinary light, compared to the selective two-step polymerization, the volume change of reacting crystals is obviously gentle and, consequently, minimizes the disordering of molecular alignment in crystals.

TABLE II. Quantum Yields of Photopolymerization of DSP, P2VB, *p*-PDAMe, and AMBBA

	oligomerization		polymerization	
monomer crystal	wavelength used in irradiation, nm	Φ	wavelength used in irradiation, nm	Φ
DSP	436	1.2	365	1.6
P2VB	405	0.04		
p-PDAMe	365	1.2	313	0.7
AMBBA			(UV)	1.4

The quantum yields of the polymerization were measured by IR and UV monitoring for oligomerization of the monomer crystal and for polymerization of the oligomer crystal of DSP, P2VB, and *p*-PDAMe by using KBr pellet containing the sample.[39] In the case of AMBBA, the quantum yield was measured for overall polymerization of the monomer crystal in slurries.[18] The quantum yields (Φ) are defined as the number of olefin double bonds consumed to form cyclobutane per absorbed quantum. Thus, the theoretical maximum value is equal to 2 for the stepwise photoreaction.

Quantum yields in Table II show that the polymerizations of DSP, *p*-PDAMe, and AMBBA proceed with very high efficiency. All the conjugated diolefins, including both those photopolymerizable and those photostable in the crystalline state, behave nearly in the same manner in solution[40,41] with a few exceptions. By selective excitation of the monomer, these compounds are converted into the amorphous oligomers having cyclobutane structure with various steric configurations in fairly high yields. In contrast to the high polymerizability of the crystalline oligomer (as prepared from the monomer crystal), these oligomers are amorphous and, on further irradiation to excite the terminal olefin, do not grow into high polymers in solid state.

These striking differences in reactivity and product structure are comprehended as a matrix effect originating in the crystal lattice control ("topotactic assistance").[42] In a concentrated solution of p-PDAEt in acetonitrile, a stereoselective photodimerization via excimer formation is reported.[43,44]

Most of the polymers are easily depolymerized photochemically and thermally in solution to the corresponding monomers, as is expected from the ring cleavage reaction of a number of cyclobutane derivatives yielding two olefins. For example, poly-DSP in solution is rather quickly depolymerized to DSP nearly quantitatively upon photoirradiation[40] or by heating above 200 °C.[45] However, if poly-p-PDAR or poly-p-CPAR, in which an alkoxy carbonyl unit is attached to the cyclobutane, is irradiated with a wavelength longer than 300 nm, these polymers depolymerize only into the oligomers but not into the monomer, while the monomer is produced at an appreciable rate when they are irradiated around 225 nm.[38,46]

The prominent effect of the irradiating wavelength is explained by the following mechanism: the excitation energy in the terminal olefinic unit by light ≥300 nm is directed mostly toward cis–trans isomerization, but the excitation energy in the alkoxy carbonyl unit by light ≃225 nm cleaves the cyclobutane ring with a high efficiency.

B. Crystallographic Survey

Crystallographic analyses have been performed on several photopolymerizable diolefins and a photostable conjugated diolefin for which the data are tabulated in Table III.

The parameters in Table III do not represent the actual distances and angles involved at the moment of photoreaction but rather those in the ground state. Nevertheless the data are still meaningful for predicting the reactivity and product structure, implying that the photoabsorption leaves the molecular shape essentially unchange.[11]

The relation between crystal structure and photochemical reactivity/product structure is substantially explained by the topochemical principle that had been established by Schmidt et al.[10] Moreover, the empirical rule on a similar photoreactivity between mono- and diolefin crystals is comprehended by correlating common molecular shape and packing with common intermolecular contacts between electron-rich aromatic ring planes and electron-deficient moieties in photoreactive crystals.[19,47] In all the photopolymerizable crystals, nearly planar molecules are piled up and displaced in the direction of the molecular longitudinal axis by about half a molecule to form a parallel plane-to-plane stack, as is shown for cinnamic acid (α), DSP (α), P2VB, and p-PDAMe in Figure 1, which shows the similarity of molecular packing of these materials.[19]

All the photopolymerizable diolefin crystals are related to the center of symmetry (centrosymmetric α-type crystal to give a dimer of symmetry $\bar{1}$) and thus afford a polymer having a cyclobutane with a 1,3-trans configuration in the main chain (Figure 2).[31]

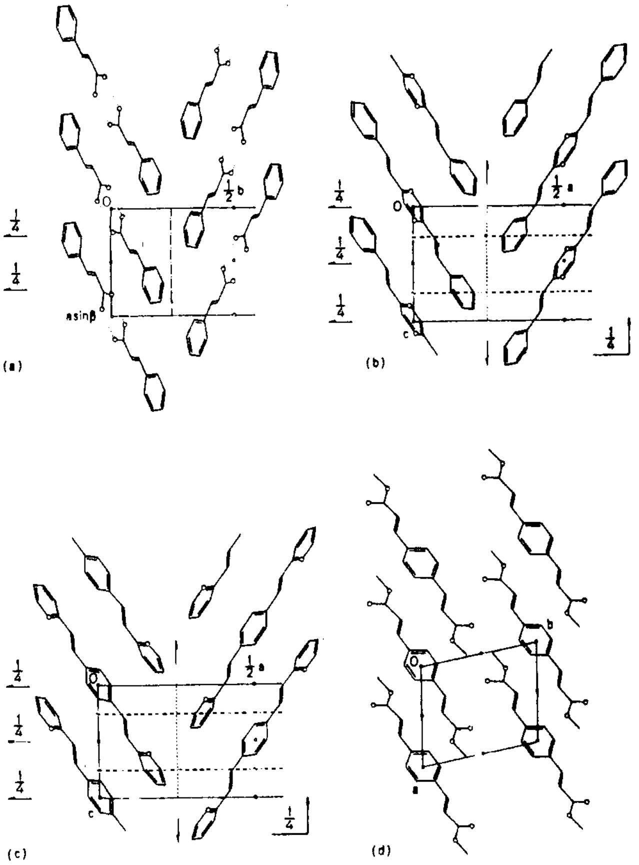


Figure 1. Crystal structures of (a) cinnamic acid (α), (b) DSP (α), (c) P2VB, and (d) p-PDAMe.

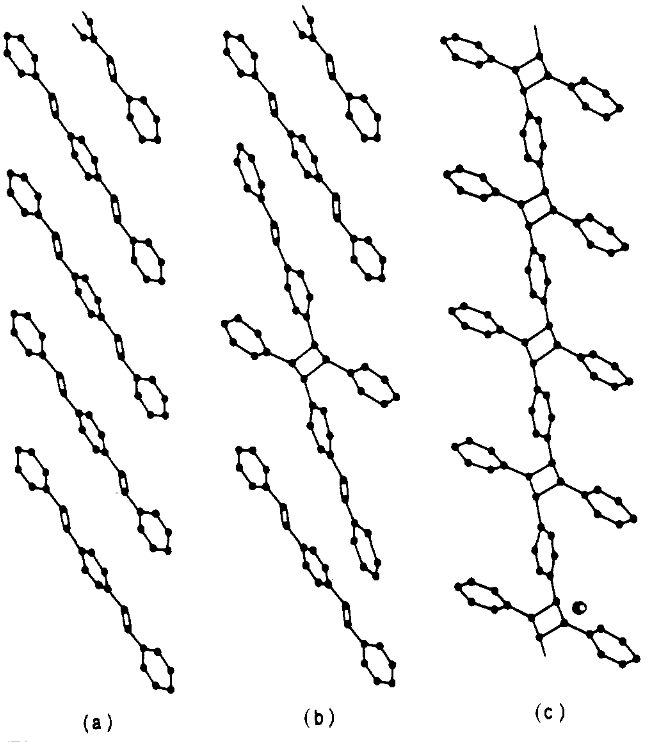


Figure 2. Schematic illustration of the conversion of (a) DSP (α) into (b) dimer and (c) polymer.

In the polymerization of DSP, the displacement of a monomeric unit in the direction of chain growth results in a contraction of 1.8% in the direction of the c-axis with crystal shrinkage (−1.0%), in contrast to the elongation of 3.0% with crystal expansion (+1.7%) of P2VB. In the polymerization of other olefin crystals,

TABLE III. Crystallographic Data of Diolefin Monomers and Their Polymers

compound	form	space group	a (α)	b (β)	c (γ)	Z	D_x	C—C distance[a]	reactivity	ref
DSP (α)	monomer	*Pbca*	20.638	9.599	7.655[b]	4	1.244	3.939	high	47
	polymer	*Pbca*	18.36	10.88	7.52[c]	4	1.257			31
DSP (γ)	monomer	$P2_1/a$	13.833	18.615 (92.63)	5.823	4	1.261	4.187 4.369	photostable	48
P2VB	monomer	*Pbca*	21.060	9.567	7.311[b]	4	1.281	3.910	low	49
	polymer	*Pbca*	18.9	10.5	7.53[c]	4	1.26			19
p-PDAMe	monomer	$P\bar{1}$	7.190[b] (95.08)	8.404 (117.06)	5.833 (78.00)	1	1.319	3.957	high	50
	polymer	$P\bar{1}$	7.82[c] (107.8)	7.42 (106.0)	6.04 (78.8)	1	1.29			19
p-PDAEt	monomer	$P2_1/a$	7.399[b]	9.894 (99.74)	10.167	2	1.242	3.970	medium	51,52
	polymer at −15 °C	$P2_1/a$	8.16[c]	9.98 (102.0)	8.62	2	1.30			19
p-PDAPh	monomer	$P2_1/c$	6.917[b]	18.584 (102.87)	7.557	2	1.293	3.917	medium	53
	polymer	$P2_1/c$	7.50[c]	17.3 (102.0)	7.50	2	1.29			19
p-CPAnPr	monomer	$P2_1/n$ ($P2_1$)	5.341	26.112 (103.81)	6.822[b]	2	1.265	3.931	high	54
	polymer	$P2_1/n$ ($P2_1$)	6.19	20.1 (96.0)	7.58[c]	2	1.25			19
m-PDAMe	monomer	$Pmn2_1$	26.419	3.960[b]	5.935	2	1.318	3.960	medium[d]	55

[a] Intermolecular distance between reactive double bonds. [b] Direction of chain growth. [c] Direction of polymer chain. [d] Formation of the dimer having a cyclobutane ring with a mirror symmetry is reported.

TABLE IV. Topotaxies and Morphological Changes in the Photopolymerization of Diolefin Crystals

monomer	group of topotaxy	coincidence of crystal symmetry between monomer and polymer	group of morphology	morphological change	molecular movement during reaction
DSP (α)	1	crystal system, space group and directions of three axes	1	large cracks	small
P2VB	1		1		
p-CPAnPr	2	crystal system, space group and direction of unit axis	2	fine cracks, fibrillization	
p-PDAEt	2		3	no cracks but deformation	large
p-PDAPh	2		3		
p-PDAMe	3	crystal system and space group	3		
m-PDAMe		amorphous	4	no change in shape	unknown
pentaerythritol tetracinnamate			4		

however, the growth direction of the polymer chain deviates from the expected direction of chain growth in the monomer crystal, and the elongations of the distance between monomeric units are not always very slight, e.g., 8.8% for *p*-PDAMe, 8.4% for *p*-PDAPh, and 11.1% for *p*-CPAnPr. On the other hand, no significant density change is observed in all the polymerizations examined ($\lesssim$4%).

Changes in the crystal structure during the polymerization were also pursued by X-ray powder diffraction and DSC-TG analysis. From the oscillations and Weisenberg photographs, all the polymers derived from conjugated rigid rod-shaped diolefin crystals are found to be oriented three dimensionally while the oligomer of *m*-PDAMe is amorphous. From the relative orientation of monomer and polymer crystals the photopolymerization of these conjugated diolefin crystals is classified into three groups according to three factors of topotactic control (crystal system, space group, and directions of the three axes) (Table IV).[19] Furthermore, morphological changes in the polymerization are classified into four groups according to apparent transformation of the reacting crystal (Table IV);[56] these are explained in correlation with the degree of topotactic control.

In Table IV the crystal system and space group of all the monomers are retained unaltered in the course of photopolymerization whereas coincidences of directions of crystal axes are variable. The correlations between unit cells of monomer and polymer crystals are illustrated for DSP (α), P2VB, *p*-PDAPh, *p*-PDAEt, and *p*-CPAnPr in Figure 3.[19]

In all the examples, monomer and polymer crystals are closely correlated in the level of unit cell dimensions, and as a result a crystal lattice controlled photopolymerization with respect to all the elementary processes including initiation, growing step, and crystallization of the polymer is concluded for the four-center type photopolymerization. This is in remarkable contrast to the polymerization of cyclic ether or vinyl type compound crystals.[7,57] The same discussion is made in a recent paper (ref 58).

However, different quantum yields of these polymerizations have not been explained satisfactorily so far, though intermolecular overlap of electronic orbitals, changes of bond angle and crystal volume, or dis-

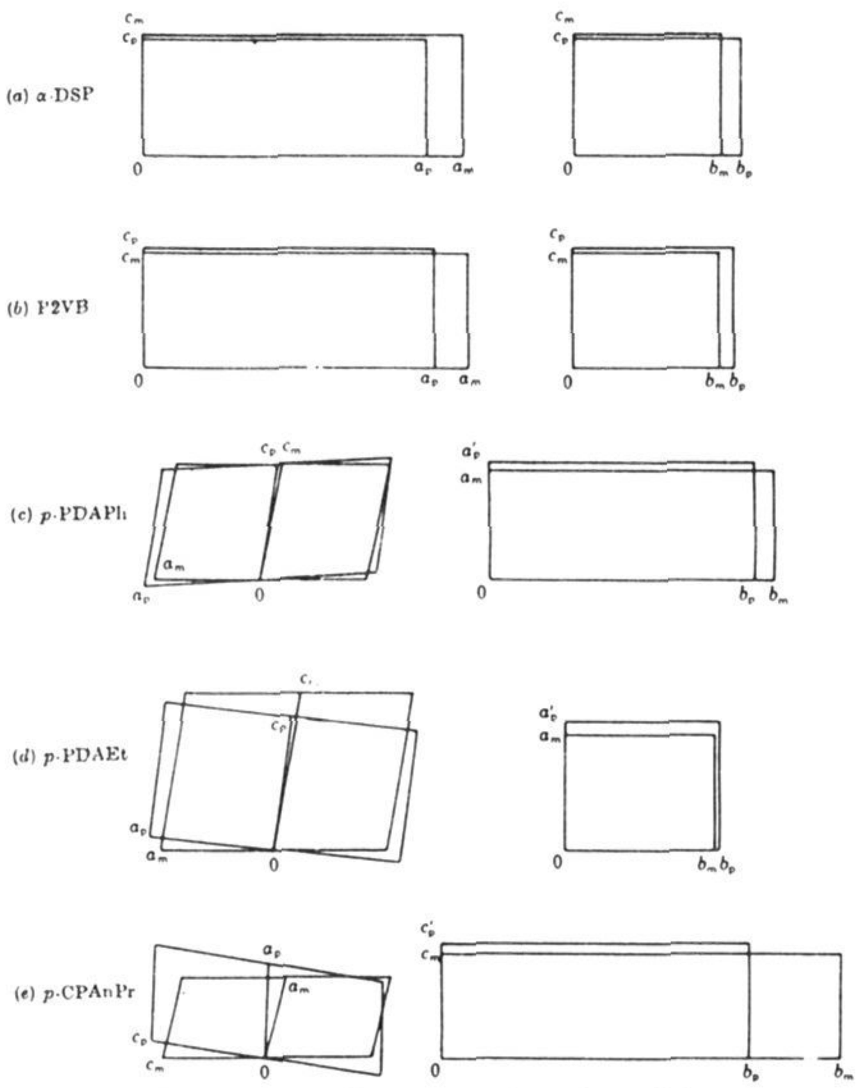


Figure 3. Relative crystallographic orientations of the monomers and the polymers: (a) DSP (α), (b) P2VB, (c) *p*-PDAPh, (d) *p*-PDAEt, and (e) *p*-CPAnPr.

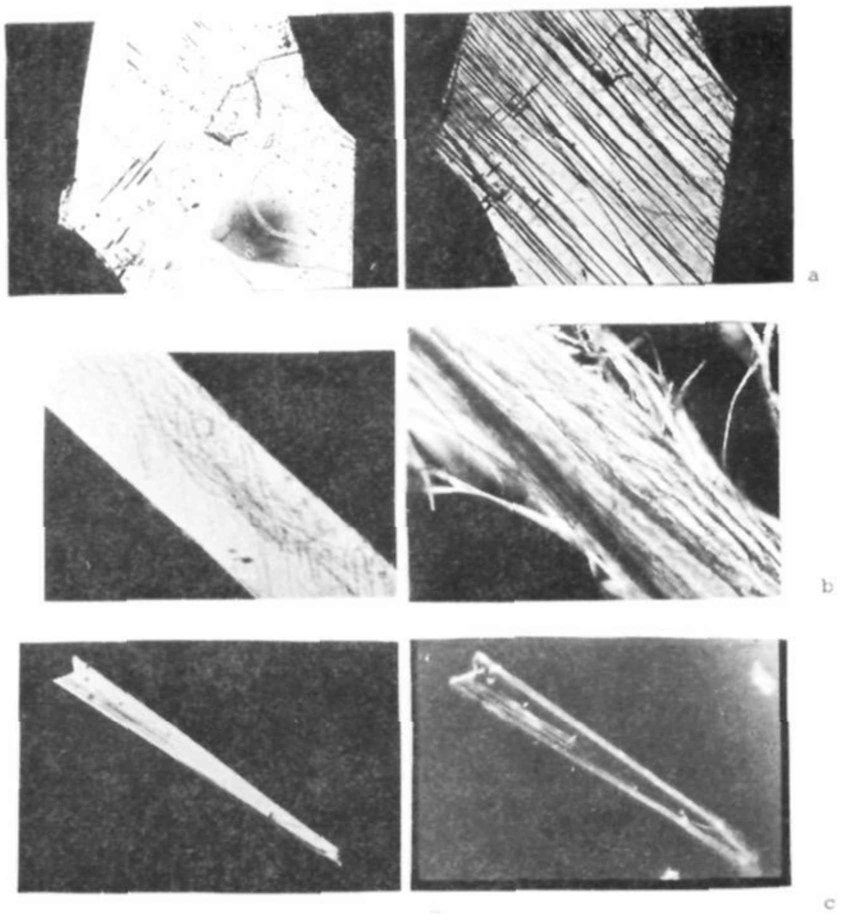


Figure 4. (a) Micrographs of monomer and partially polymerized crystals of DSP, (b) micrographs of monomer and partially polymerized crystals of *p*-CPAnPr, and (c) micrographs of *m*-PDAMe crystals and oligomer.

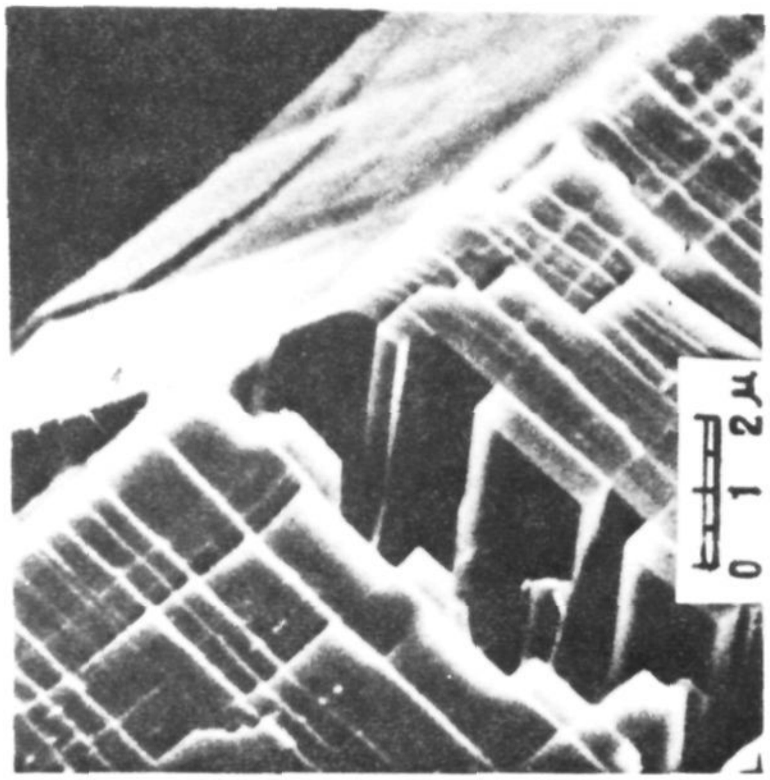


Figure 5. Scanning electron micrograph of poly-DSP (×10 000).

placement of the center of gravity of the monomeric unit during the polymerization are presumed to be related to the reactivity.

Micrographs of morphological changes in DSP (α), *p*-CPAnPr, and *m*-PDAMe (morphology groups 1,2, and 4, respectively, in Table IV) are shown in Figure 4.[56]

Upon photoirradiation of DSP (α), regular cracks are formed in the direction of chain growth which is parallel with the *c*-axis of monomer and polymer crystals. Scanning electron microscopy of poly-DSP shows aggregates of single crystals elongated in the direction of the polymer chain (Figure 5).[31]

Such crackings are explained by accumulation of molecular displacement and change of bond angle in the rigid crystal lattice.

Although crystal forms of monomers and polymers are highly related to each other, the micrographs of poly-DSP and poly-P2VB[19] crystals are quite different. The difference most likely reflects an opposite crystal volume change during the polymerization in which the DSP crystals shrink while the P2VB crystals expand. Recently, Nakanishi et al. succeeded in preparing perfect single crystal dimers from benzylidenecyclopentanone crystal derivatives, where the difference of crystal parameters between monomer and dimer are extremely slight.[59]

In the case of *p*-CPAnPr, fine cracks also run in the direction of chain growth exhibiting marked filbrillization (Figure 4). Thus, the polymer single crystal does not retain its original monomer crystal shape. In the case of diolefin crystals of morphology group 3, fine crack formation occurs in many directions, and the final crystal deforms without breaking into pieces. Pseudomorph formation is assumed to be crystal lattice controlled only for the initiation, but not for all the elementary processes. For example, *m*-PDAMe crystals gradually become amorphous without any change of the outer shape (Figure 4). Most of the polymerization of diolefin crystals that results in an amorphous product seems to give a pseudomorph.

The continuous change of the thermodiagram in polymerization was mainly studied for DSP by means of differential scanning calorimetry (DSC).[32] DSC curves obtained in the course of photopolymerization of a DSP crystal at the irradiation times of 20, 40, 50, and 70 min with a xenon lamp are shown in Figure 6 together with those of DSP and as-polymerized, recrystallized, and amorphous poly-DSP's.

At the initial stage of irradiation (20 and 40 min), the DSC curve shows a melting point depression of the

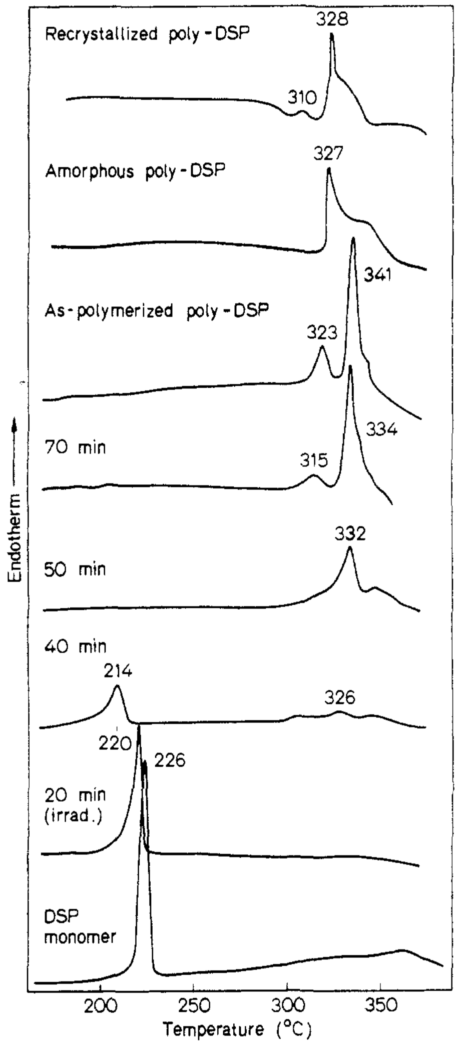


Figure 6. DSC curves of recrystallized, amorphous, and as-polymerized poly-DSP's and the curves obtained in the course of photopolymerization of DSP crystal. Light source: 500-*w* xenon lamp.

monomer from 226 to 214 °C with a broadening of the peak. This behavior is interpreted as the mixing of a small amount of oligomer with the monomer crystal. After 40 min of irradiation, the DSP curve shows broad endothermic peaks around 300–350 °C. These peaks become larger (50 min) and separate into two peaks after more than 70 min of irradiation. The smaller peak at 323 °C grows strikingly during the later stage of irradiation.

The X-ray diffraction patterns of the samples irradiated for more than 50 min are almost the same as those of high molecular weight polymer crystals except that the higher the molecular weight, the sharper are these two peaks.

Two endothermic peaks, exemplified by the poly-DSP crystal in Figure 6, are generally observed for other as-polymerized polymer crystals,[60] in which the smaller peak at the lower temperature can be attributed to thermal depolymerization in the crystalline state and the larger peak presumably corresponds to the processes involving thermal depolymerization and melting of the oligomer crystals, respectively (cf. section IVB).

The observations on continuous changes of X-ray diffraction pattern and DSC-TG curve lead to the conclusion that the polymerization is a direct rearrangement from the monomer crystal to the polymer crystal via a thermal diffusionless process.[31,60] An endothermic process was demonstrated for the photopolymerization of DSP crystals, with an enthalpy increase of about 3.7 kcal/mol. Heat of crystallization of poly-DSP crystals as polymerized was estimated to be 3.1 kcal/mol.[61]

In such a topochemical process, a strain energy caused by molecular movement is accumulated in the reacting crystal stepwise, resulting in a thermodynamically metastable polymer crystal even though a part of the strain energy is often released in several samples by cracking of the crystal at a later stage in the polymerization.

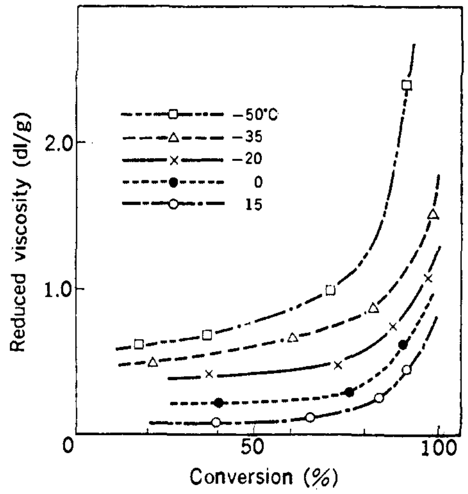


Figure 7. Plot of time vs. conversion for polymerization of *p*-PDAEt at various temperatures.

C. Kinetic Features of the Topochemical Process

It is rather a nuisance to determine the rate equation for a topochemical reaction because the method of varying the initial concentration is not usable and, in addition, the kinetic data are seriously affected by monomer crystal features such as purity, crystal size, or concentration of crystal imperfections. Even if the same apparatus and monomer crystals with the same history are employed and if photochemical condition is maintained constant as much as possible for a series of experiments in the crystal dispersed system, critical discussion based on these kinetic data should be avoided. Nevertheless, kinetic plots of the polymerization and the dimerization of several olefin crystals are apparently informative,[60,62–67] and the following characteristic features have been revealed so far in this type of crystalline-state photoreaction:

(1) The reaction proceeds by a stepwise mechanism and yields the product quantitatively over a wide range of temperatures[63,64] including extremely low temperatures as exemplified of *p*-PDAEt at 4 K.[65]

(2) Maximum reaction rate is observed at a specific temperature for individual crystals, such as at ca. −20 °C for *p*-PDAEt (mp 96 °C)[64] and at ca. 20 °C for cinnamic acid (mp, 132 °C).[66] The temperature effect on polymerization of *p*-PDAEt is shown in the range from −50 to 15 °C in Figure 7.[64]

(3) The photopolymerization readily affords a highly crystalline linear polymer in high yield as long as the polymerization temperature is sufficiently low to

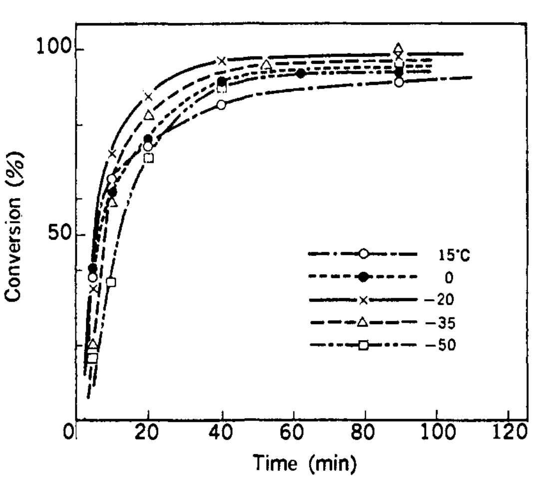


Figure 8. Plot of conversion vs. reduced viscosity for the polymerization of *p*-PDAEt at various temperatures.

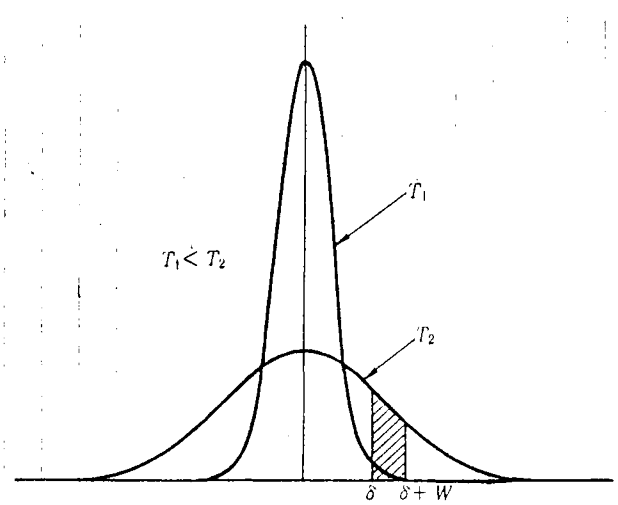


Figure 9. A model for topochemical reaction probability.

maintain the rigidity of the reacting crystal lattice. Therefore, at the same conversion, a higher reduced viscosity is observed for the product polymerized at the lower temperature, as illustrated for the polymerization of *p*-PDAEt in Figure 8.[64]

(4) The relative positions and orientations of reactive bonds in the crystals are favorably aligned for product formation, and the principal features of molecular alignment remain unaltered in that of photoproducts and, as a matter of course, in the molecular alignment at the moment of photoreaction.[10,19]

Thus, the reaction obeys first-order kinetics in most of the cases presumably independent of reaction molecularity.[66,67] In the topochemical reaction the number of molecular alignments favorable for the reaction per unit crystal volume may correspond to the concentration in solution in an ordinary sense. Since such a "concentration" is diminished with deterioration of molecular alignment in the crystal, apparent photoquantum yield in the topochemical reaction should be markedly temperature dependent. As the temperature effect is observable independently without the difficulties of heat dissipation, photochemical reaction is very convenient for studying the influence of molecular thermal motion in the crystal during the topochemical process. For example, in photodimerization of acenaphthene crystals (mp 92–93 °C), which seems to proceed via a topochemical process, the quantum yield of trans-dimer formation (φ trans) shows a maximum value at 50 °C, and in the range from 0 to 50 °C, log φ_{trans} is a linear function of T^{-1}.[62]

In order to rationalize this characteristic kinetic behavior, a reaction model has been proposed under a constant photoirradiation condition.[68] In such a condition the reaction rate is assumed to be dependent solely on the thermal motion of the molecules and to be determined by the potential deviation of two olefin bonds from the optimal positions for the reaction. The distribution of the potential deviation of two olefin bonds from the most stable positions in the crystal at 0 K is assumed to follow a normal distribution. The reaction probability, which is assumed to be proportional to the rate constant, of an unidimensional model is illustrated as the area under the curve for temperature T_2 between δ and δ + W in Figure 9.[68]

On the basis of the equation derived from the reaction model, the kinetic behavior is explained in terms of a temperature-dependent factor involving the product of reciprocal and exponential terms of temperature.

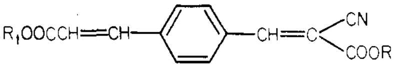
IV. Special Topics on Topochemical Photopolymerization of Diolefin Crystals

A. Absolute Asymmetric Synthesis

For the topochemical reaction the crystallization of the monomer should be considered as one of the elementary processes since the reacting partner molecules and absolute configuration of the product are determined at this stage. Sometimes, achiral molecules can be recrystallized into chiral crystals. Asymmetric resolution utilizing such chiral crystals was first demonstrated by Havinga.[69]

Since the concept of topochemically controlled reactions was established in 1964,[10] various approaches to asymmetric synthesis using a crystalline-state reaction have been attempted, most actively by a research group of the Weizmann Institute of Science, Israel.[70,71] These involve heterogeneous reactions of organic crystals with gases and liquids,[72] photoreactions in mixed crystals,[73] and polymerization of the monomer embedded in the chiral inclusion complex.[74] Among these approaches the successful "absolute" asymmetric synthesis has been performed by using the topochemically controlled system of the four-center type photopolymerization of a series of unsymmetrically substituted conjugated diolefin crystals.[20-22,29,75] (The term absolute asymmetric synthesis, in these references, is defined as the process where nonracemic chiral product is obtained from achiral material in the absence of external chiral agents.)

Addadi and Lahav have prepared ethyl 2-cyano-4-[2(*E*)-((2-butoxy)carbonyl)ethenyl)phenyl]-2(*E*)-propenoate (compound 1), of which enantiomerically



$R_1OOCCH{=}CH{-}C_6H_4{-}CH{=}C(CN)COOR_2$

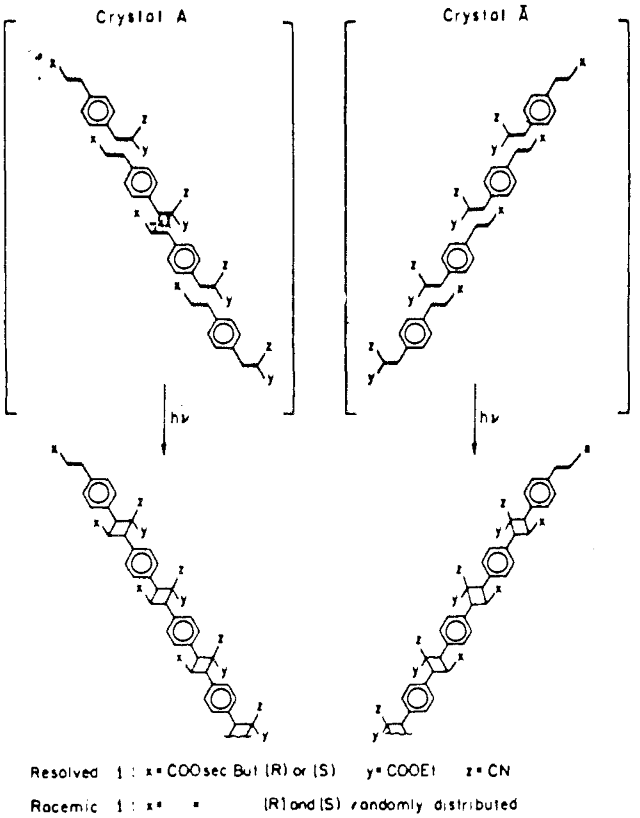
1, R = (*R*,*S*)-*sec*-butyl; ethyl
2, R_1 = 3-pentyl; R_2 = methyl

pure *S*-(+) or *R*-(−) crystals give the photodimers and oligomers in quantitative (>97%) diastereoisomeric yield.

TABLE V. Cell Constants of Compound 1 both as Pure Enantiomer and as Racemic Mixture

compound	a, Å	b, Å	c, Å	β, deg	space group	Z
(R)-(−)- or (S)-(+)-1	13.17	6.94	5.22	103.1 95.5 90.1	P1	1
racemic 1	13.35	7.03	5.41	104 93 92	P1	1

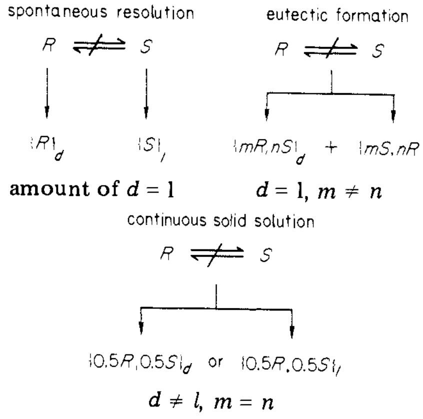
According to the "crystala engineering" on the basis of several empirical results.[19,27,76,77] Compound 1 crystallizes in one of the chiral structures A or Ā, in which molecules are translationally related (5.5–7.0 Å) and juxtaposed so as to allow a topochemical photoreaction between the nonequivalent olefin bonds. The crystal structure of the S-(+) monomer was found to be in complete agreement with the schematic model designed for this synthesis,[78] and furthermore the racemic crystal is isostructural with the crystal of the pure enantiomer, showing the extreme similarity of cell dimensions (Table V).



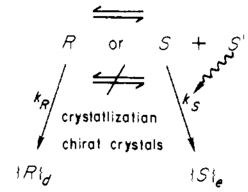
Formation of these isostructural crystals implys that every single crystal of the racemate could contain *sec*-butyl groups of both chiralities with random ratio, m/n, and an "absolute" asymmetric synthesis with quantitative enanthiomeric yield is attainable if the racemate is crystallized into one single homochiral crystal.

However, as an immiscible range exists between the enantiomeric ratio of 60:40 and 40:60 of compound 1 crystals, the precipitation of equal amounts of crystals of both chiralities is not avoidable in this region by eutectic formation. Therefore "absolute" asymmetric synthesis was carried out of the monomer crystal with low optical activity or of racemate 1 crystal prepared not under thermodynamically controlled conditions but in a metastable crystal phase such as by a rapid under cooling, with $m = n$ in each crystal. Thus the amount of "l" crystal phase is independent of the amount of "d" crystal (continuous solid solution), as represented in Scheme I.[21]

SCHEME I



SCHEME II[a]



[a] In the absence of S', $k_R = k_S$; in the presence of S', $k_R >> k_S$.

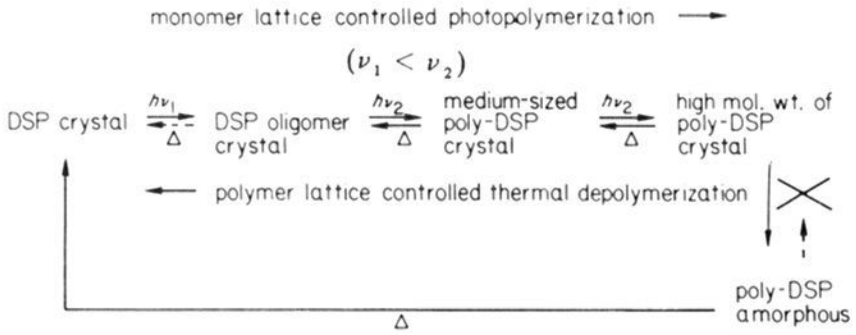
A number of crystallization procedures of racemate 1 were attempted for this purpose under various crystal growth environments, followed by the topochemical photopolymerization. Diastereoisomeric yields were established by ^1H and ^{13}C NMR spectrometric analysis of these photoproducts.

As the results, specific rotations of the products showed as high as ±35° at eight successful runs among 20 trials.[29] In any of these experiments, no net rotation was detected either of the crystal dissolved before irradiation or of the monomer recovered from the photoproducts, verifying that an asymmetric induction is due only to the chirality of the reaction site in the crystal and not to the chiral *sec*-butyl group.

In the course of further study to raise the enantiomeric yield, these chiral cyclobutane photoproducts were found to induce preferential crystallization of several diolefin monomers with similar structure in opposite chirality. That is, a d crystal of photoproducts always induces the l crystal phase of the monomer and vice versa (inversion rule).[79] As a typical example, compound 2 (R_1 = 3-pentyl and R_2 = methyl) crystallized in the presence of the chiral dimer of compound 1 always gives a photoproduct with opposite phase of the enantiomers in the range of 30–100% enantiomeric yield.

Such an efficient asymmetric induction is widely seen for crystallization in a series of these diolefin monomers; the absolute configuration of the crystal phase precipitating in excess is constantly opposite to that of the seeded crystal phase. The result is explained in terms of selective absorption of a trace amount of impurities at the growing site of a crystal, which disturbs further growth. In conclusion a general mechanism of kinetic resolution which is amplified by stereochemically sim-

SCHEME III. Reversible Topochemical Process between DSP and Poly-DSP



ilar impurity, has been proposed, as represented in Scheme II.[80]

B. Specific Character owing to Rigid-Rod-Shaped Chain Structure

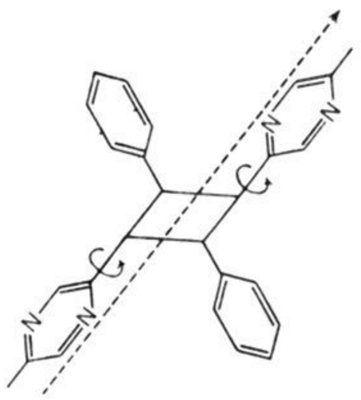
All the polymer crystals prepared via a topochemical process are powdery in appearance and are aggregates of tiny crystallites with an extremely high degree of crystallinity. As-prepared polymer crystals, however, can never be reproduced from solution, indicating a thermodynamically metastable form of these crystals.[81] Most of the polymers, either of crystalline and amorphous states as well as in solution, are converted into the monomer in high yields by heat treatment.

Thermal stability of as-polymerized polymer crystals is strikingly superior to that of amorphous polymer[82]–presumably because the as-prepared polymer crystal lattice protects the cyclobutane ring from the thermal cleavage by restricting the local movement of the polymer chain. For example, amorphous poly-DSP regenerates the monomer in 9% yield after heat treatment at 290 °C for 20 min whereas none of the monomer is detected by UV spectrometry on the sample from the as-polymerized poly-DSP crystal after heat treatment at 290 °C for 60 min.

As-prepared polymer crystals do not melt but thermally depolymerize into the oligomer crystal in the crystalline state. Then, crystal melting point is observed at the oligomer stage. The result indicates that in a high polymer the cyclobutane ring thermally cleaves at the temperature below crystal melting point, and vice versa in the oligomer. The crystalline-state thermal depolymerization, which is a common property in as-prepared polymer crystals, was confirmed to occur via a topochemical process by X-ray powder diffraction pattern.[82]

On the basis of these results, a reversible topochemical process, which is a monomer crystal lattice controlled photopolymerization and a polymer crystal lattice controlled thermal depolymerization, is established as illustrated for DSP and poly-DSP in Scheme III.[32]

Of further interest is that the X-ray diffraction pattern of the heat-treated poly-DSP crystals at 330 °C coincides exactly with that of as-prepared oligomer crystals which were prepared by selective monomer excitation (cf. section IIIA). Good coincidence of the X-ray patterns of these two oligomer crystals suggests that the thermal cleavage of the cyclobutane ring in as-polymerized polymer crystals does not proceed randomly in the molecular chain but is favored on the position in the middle of the chain.[82] Consequently, the oligomer crystal is preferentially accumulated in thermal depolymerization. Furthermore, it was demonstrated on poly-DSP[45,83] and poly-*p*-PDAMe[60] that an extremely high molecular weight polymer is thermally less stable than the same polymer with a lower molecular weight, either in the crystalline state or in solution. That is, by heat treatment these polymers depolymerize and then level off at the intrinsic viscosities specified by temperature. A plausible explanation on this unusual chain scission has been proposed in relation to the rigid-rod shaped configuration of these polymers, which contains alternating 1,3-*trans*-cyclobutane and 1,4-arylene units in the main chain; these polymers cannot be folded even when the σ bonds between the cyclobutane and aromatic rings in the chain rotate freely, as is obvious in poly-DSP (Figure 10).



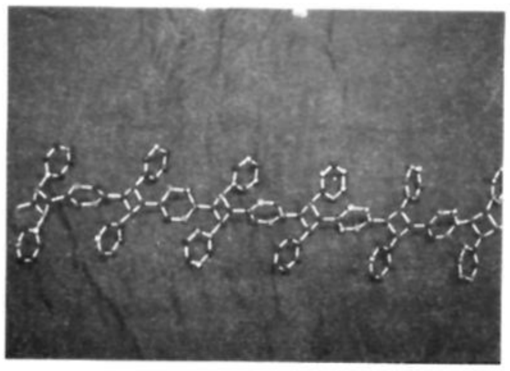


Figure 10. Molecular model of poly-DSP.

In such a rigid-rod like polymer, shearing forces should always show the greatest stress at the middle of the molecular chain to result in thermally less stable features of higher molecular weight polymer. In contrast to the rigid-rod shaped polymer, the high polymer with a cylobutane ring incorporated into the flexible main chain shows rather excellent thermal stability.[84,85] Although a few other results to support the rigid structure in solution, such as a liquid crystal behavior of poly-*p*-CPAnPr in concentrated sulfuric acid, have been reported so far,[86] hydrodynamic behavior such as the intrinsic viscosity–molecular weight relationship is not always consistent with the rigid-rod shaped structure.[81,87]

In addition to solution properties, there are vast regions remaining unexploited regarding this type of polymer and further work is much needed on the structure and property of these polymers. Preparation of a polymer single crystal with an extended chain structure will be promising if the topochemical single crystal to single crystal photodimerization technique performed by Nakanishi et al.[59,88] is developed for the photopolymerization of diolefin crystals.

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