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The Effect of the Wavelength of an Exciting Light on Four-center-type Photopolymerization in the Crystalline State

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The effect of the wavelength of an exciting light on four-center-type photopolymerization in the crystalline state has been investigated. 2,5-Distyrylpyrazine (DSP), 1,4-bis[β-pyridyl-(2)vinyl]benzene (P2VB), *p*-phenylenediacrylic acid (*p*-PDA) dimethyl ester were converted quantitatively into highly crystalline oligomers (pentamers on the average) on irradiation at the long-wavelength edge of the absorption of the monomer. On subsequent exposure to the light which is absorbed by each oligomer, the oligomer crystals *as*-polymerized were converted quantitatively into high polymer crystals. The polymer thus obtained was found to be identical with the polymer produced by the light of a xenon or a high-pressure mercury lamp. The quantum yields for the oligomerization and polymerization reactions of DSP and the *p*-PDA dimethyl ester were found to be between 1 and 2 on the basis of the number of olefinic double bonds consumed to form the cyclobutane ring. These results confirmed that the four-center-type photopolymerization in the crystalline state consists of two kinds of separable, step-by-step addition mechanisms: an oligomerization of the diolefinic compound and a growth reaction of the terminal group in the growing chain. From the crystallographic information on the DSP oligomer, the oligomerization as well as the polymerization process of DSP were concluded to proceed by a monomer lattice-controlled mechanism.

The method of investigating four-center-type photopolymerization in the crystalline state of diolefinic compounds, such as 2,5-distyrylpyrazine (DSP), its related compounds, *p*-phenylenediacrylic acid (*p*-PDA) derivatives, and *p*-benzene (α-cyano)diacrylic acid (*p*-BCA) derivatives, has recently been developed in this laboratory.[1-8)]

Many diolefinic compounds which are photopolymerizable in the crystalline state have been synthesized.[1-4)] They can be roughly classified into high and low photopolymerizable compounds according to their reaction times. For example, DSP and the *p*-PDA dimethyl ester belong to the former type, and 1,4-bis[β-pyridyl-(2)vinyl]benzene (P2VB) belongs to the latter.

A previously-reported kinetic study[5)] of the photopolymerization of DSP in the crystalline state has shown that the reduced viscosity of the polymer increases with the reaction time, that it continues to rise on irradiation even after the conversion is completed, and that the molecular weight of the polymer at a low conversion is widely distributed. From these facts, it has been concluded that the polymerization follows a step-by-step mechanism.

Recently in a X-ray crystallographic study of DSP the photopolymerization of DSP in the crystalline state was concluded to be a topochemical reaction which is lattice-controlled and which is strictly governed by the spatial arrangement of monomer molecules in a crystal.

In this paper the effects of the wavelength of an irradiating light on four-center-type photopolymerization and the quantum yields are described. The mechanism of the polymerization is discussed in terms of the oligomerization process and the growth process producing a high polymer.

Experimental

Preparation of the Monomers. DSP, P2VB, and the *p*-PDA dimethyl ester were prepared and recrystallized as has been described in earlier papers.[2,3)]

Optical Measurements. To examine the effect of the wavelength of an exciting light on the polymerization of each monomer in the crystalline state, UV and IR spectral changes were measured during polymerization upon irradiation with monochromatic light. For the UV measurements the monomer crystals were deposited on a quartz plate in

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the form of a thin layer by slow evaporation from a concentrated solution, while for the IR measurements KBr pellets containing the monomer crystals were prepared.

The exciting light was furnished by a spectroirradiator (Jasco) composed of a 2000-W xenon lamp as the light source and a grating monochromator.

To attenuate the scattered light, the UV measurements were performed by the method of an integrating sphere attached to a spectrophotometer.

The disappearing rate of the olefinic double bonds during the oligomerization and the polymerization was followed by IR analysis. In the case of the oligomerization, KBr pellets (150 mg) containing 1.5 mg of monomer crystals were prepared by pressing in an evacuated die at 9 kbars for 4 min. In the case of the polymerization of the oligomer, KBr pellets containing 6—7 mg of monomer crystals were prepared in the same way, before the measurement they were exposed to the light at the long-wavelength edge of the absorption of the monomer until the monomer was completely converted into the oligomer.

The excitation light for the measurement of the quantum yields was furnished by a grating monochromator (Shimadzu Bausch and Lomb), to which a 450 W high-pressure mercury lamp was attached as a light source. The light intensity was measured by potassium ferrioxalate actinometry.9) The actinometric estimates were checked with a thermopile (Eppley).

Preparation of the Oligomer and the Polymer. Fine crystals of the monomer (200 mg) were dispersed in 50 m*l* of water-methanol (4: 6) in a Pyrex flask; they were then irradiated for one hour at room temperature by means of a 450-W high-pressure mercury lamp with a suitable cut-off filter—for example, Corning 3-73 for DSP and P2VB, and Corning 0-52 for the *p*-PDA dimethyl ester.

In order to check the photopolymerizability of the oligomer molecules in the crystalline state, they were exposed to the light of a high-pressure mercury lamp without any color filter.

The oligomer and the polymer thus obtained were identified by means of their melting points, IR and NMR spectra, and reduced viscosities (360 mg in 100 m*l* of CF_3COOH).

Results and Discussion

Wavelength Effect on the Photopolymerization. The crystalline UV absorption of DSP, as measured in a thin layer deposited on a quartz plate, is shown in Fig. 1a (Curve 1). DSP molecules in the crystal (*orthorohmbic*, P_{bca}) are piled up plane-to-plane along the *c*-axis, to which the long axis of the molecules makes an angle of about 30°; the distance between olefinic double bonds of the nearest neighbouring molecules in 3.94 Å.6) From these facts, a dipole-dipole interaction may be supposed to exist among DSP molecules in the crystal, as in the case of *trans*-cinnamic acid.10)

It was found that, on the irradiation of crystalline DSP at a wavelength longer than 400 mμ, the UV absorption spectrum was changed into one with peaks at 350 mμ and 290 mμ, as may be seen in Fig. 1a (Curve 2), in which the band at 430 mμ was excited. Under those conditions, an IR absorption band at 970 cm^{-1} corresponding to the ν_{CH} of the *trans* HC=CH bond gradually decreased, and then reached a constant level about one-fifth of the initial value, while the monomer in KBr pellets, as measured by UV analysis at 384 mμ after dissolving each pellet in 95% ethanol, decreased and finally almost disappeared, as is shown in Fig. 2a.

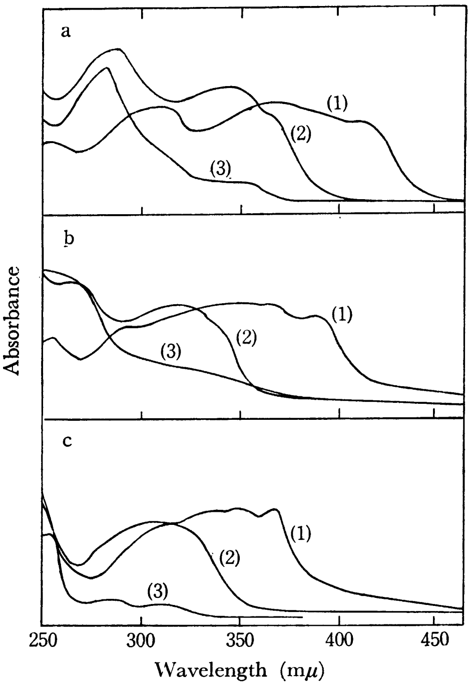

Fig. 1. The crystalline UV spectra of DSP (a): (1) non-irradiated, (2) irradiated at 430 mμ and (3) successively irradiated at 350 mμ, of P2VB (b): (1) non-irradiated, (2) irradiated at 410 mμ and (3) successively irradiated at 350 mμ, and of the *p*-PDA dimethyl ester (c): (1) non-irradiated, (2) irradiated at 360 mμ and (3) successively irradiated at 310 mμ.

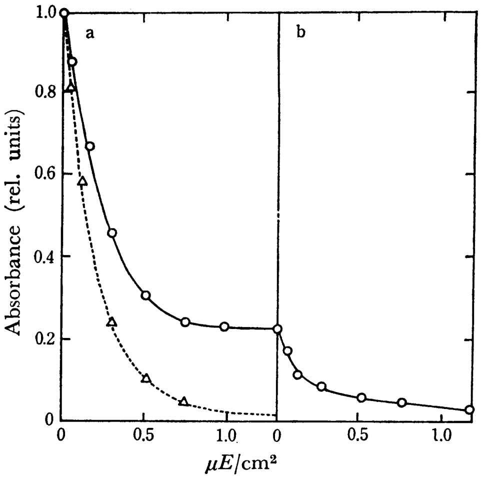

Fig. 2. Kinetics of polymerization of DSP in KBr irradiated (a) at 430 mμ and (b) at 350 mμ: the figure (—○—) corresponds to IR absorbance measurement at 970 cm^{-1}, and the one (---△---) to UV absorbance measurement at 384 mμ taken after dissolution of irradiated pellets in 95% EtOH.

These facts imply that crystalline DSP is converted into the oligomer on irradiation at a wavelength longer than 400 mμ. To confirm this, the preparative experiment described in the Experimental section was performed, and the characteristics of the product were examined.

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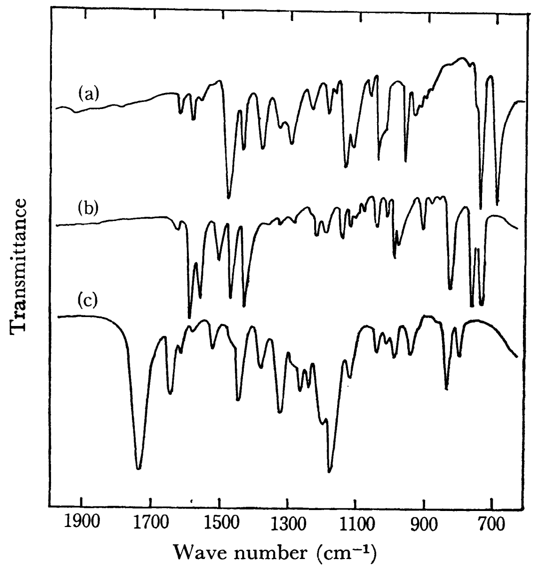


Fig. 3. IR spectra of (a) the DSP oligomer, (b) the P2VB oligomer and (c) the p-PDA dimethyl ester oligomer.

The product was quantitatively obtained from DSP, and it melted at 285—290°C. In the IR absorption spectrum, shown in Fig. 3(a), bands attributable to the olefinic double bond are recognized both at 970 cm^{-1} and 1630 cm^{-1}; they completely disappear in that of poly-DSP, as was demonstrated previously.[2] Assuming that the absorption coefficient of the product at 970 cm^{-1} is the same as that of the monomer, the product can be said to correspond to a pentamer, on the average, because the absorbance remains at one-fifth of the initial level (Fig. 2a).

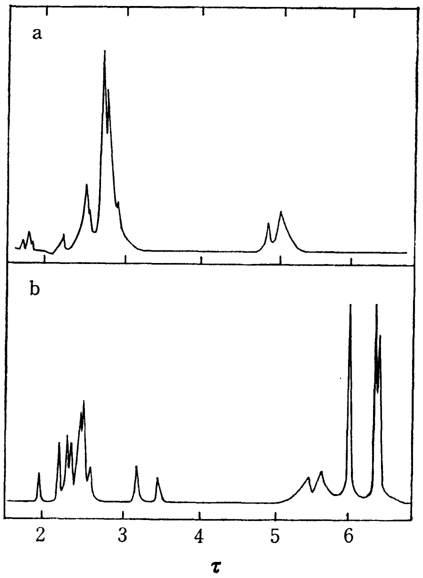


Fig. 4. NMR spectra of (a) the DSP oligomer and (b) the p-PDA dimethyl ester oligomer.

The NMR spectrum in Fig. 4a shows the peaks of protons attached to the cyclobutane ring near 5 τ, and those attached to aromatic rings at 2—3 τ. The degree of polymerization, as calculated from the ratio of the number of cyclobutane-ring protons *vs.* that of the other, was equal to about one-fifth. This value corresponds to a pentamer, in good agreement with that estimated by the IR measurements.

Upon the further irradiation of the DSP oligomer at a wavelength longer than 400 mμ, no change was any longer observed. This is reasonable because the oligomer is transparent in that wavelength region. However, the oligomer was found to be converted into a high polymer by exposure to the light at a wavelength shorter than 400 mμ. For example, the excitation at 350 mμ induced a decrease in an UV absorption band at 350 mμ, while leaving the one at 290 mμ unchanged, as may be seen in Fig. 1a (Curve 3). At the same time, the IR absorbance at 970 cm^{-1} decreased, and then completely disappeared (Fig. 2b). The product preparatively obtained was identical with the poly-DSP described previously.[2]

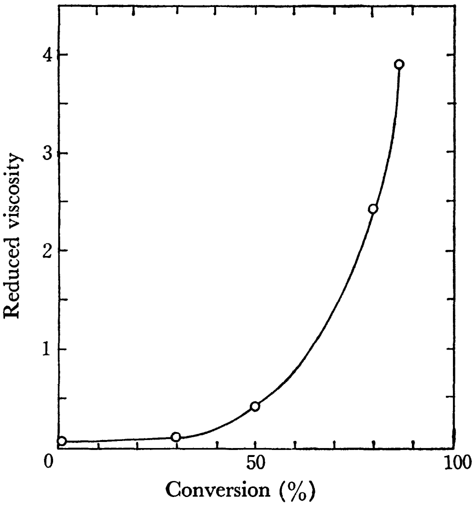


Fig. 5. The reduced viscosity as a function of conversion of olefinic double bonds (measured by IR analysis) during polymerization of the DSP oligomer.

Figure 5 shows the plot of the reduced viscosity *vs.* the conversion during the polymerization of the DSP oligomer. The reduced viscosity increased with an increase in the conversion, as in the case previously reported.[5] This demonstrates that the polymerization of the DSP oligomer proceeds by the step-by-step addition of the terminal group.

When DSP monomer crystals were irradiated at 350 mμ from the beginning, the UV and IR absorption spectra were gradually changed into those of the polymer, without apparently showing those of the oligomer on the way.

It may be concluded that, on irradiation at a wavelength longer than 400 mμ, crystalline DSP was not converted into a high polymer, but quantitatively into the oligomer (a pentamer, on the average), and that a wavelength shorter than 400 mμ was required for the further growth of the terminal group in the oligomer.

It was found that P2VB and the p-PDA dimethyl ester, which are photopolymerizable,[2,3] also oligomerized in the crystalline state on irradiation at the long-wavelength edge of the absorption (Fig. 1b, c, 3b, c, and 4b), and that each oligomer polymerized to give a high polymer on irradiation, as may be seen in Fig. 1b and

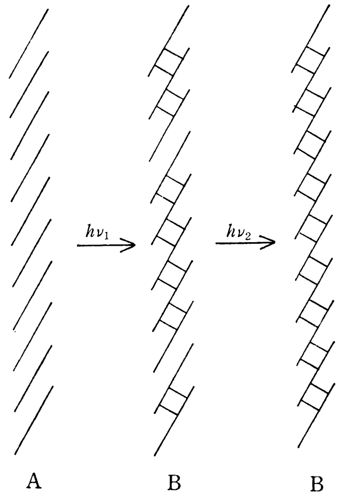
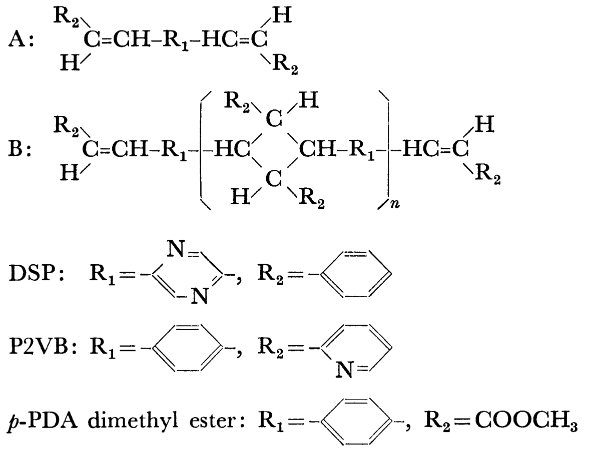


Fig. 6. The scheme of four-center-type photopolymerization in the crystalline state (see text for details).

c. The NMR spectrum of the P2VB oligomer thus obtained was almost the same as that of the poly-P2VB shown in the previous paper.[2)]

The effect of the wavelength of an exciting light on the four-center-type photopolymerization confirms the step-by-step mechanism in the polymerization suggested in a previously-reported kinetic study.[5)] The polymerization reaction in the crystalline state is schematically illustrated in Fig. 6, where A and B represent the monomer molecule and the molecule larger than the dimer with a cyclobutane ring in the main chain respectively.



The reaction scheme is as follows:

$$A + h\nu_1 \longrightarrow A^* \qquad (1)$$

$$A + A^* \xrightarrow{k_1} B \qquad (2)$$

$$A^* + B \xrightarrow{k_2} B \qquad (3)$$

$$B + h\nu_2 \longrightarrow B^* \qquad (4)$$

$$B + B^* \xrightarrow{k_3} B \qquad (5)$$

where A* and B* represent A and B in the excited state respectively. Equation (2) represents a dimerization reaction, while Eqs. (3) and (5) represent growth reactions.

Since the π-electron conjugation of A is interrupted by the formation of the cyclobutane ring to produce B, the π–π^* electronic transition energy of B can be expected to be higher than that of A (Fig. 1). Therefore, it is possible to excite A alone on irradiation at the long-wavelength edge of the absorption of A ($h\nu_1$), leaving B in the ground state.

Under those conditions, A is converted into B through Eqs. (2) and (3). This first reaction stage is designated as an oligomerization process, because the B produced in this stage is equivalent to a pentamer.

On successive irradiation with the light ($h\nu_2$) which excites B, a high polymer is produced through Eq. (5), a growth reaction of the terminal group in the growing chain. The second reaction stage is designated as a higher polymerization process.

Exposure to the light which excites both A and B from the beginning can induce the oligomerization and the polymerization reaction through Eqs. (1) to (5) successively to give a high polymer. At this time, a $A+B^* \rightarrow B$ reaction may also proceed.

The rate constants, k_1 and k_2, of these elemental reactions in the oligomerization of DSP can be estimated from the kinetic data shown in Fig. 2a. From Eqs. (2) and (3), Eq. (6) is given:

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = 2k_1[\mathrm{A}][\mathrm{A}^*] + k_2[\mathrm{A}^*][\mathrm{B}] \qquad (6)$$

Since these reactions proceed in the crystalline state, Eq. (6) does not strictly hold good in this system. However, it may be sufficient to evaluate the ratio of k_1 and k_2. It is supposed that [A*] is proportional to the absorbed light intensity, *i.e.*, $[\mathrm{A}^*] \propto 1-\exp(-\kappa[\mathrm{A}])$, in which κ is the constant related to the absorption coefficient and the light-path length. By replacing A* with $1-\exp(-\kappa[\mathrm{A}])$, Eq. (6) can be integrated to give Eq. (7):

$$[\mathrm{A}_0]-[\mathrm{A}] = (2k_1-k_2)\int_0^t[\mathrm{A}]\mathrm{d}t + k_2\int_0^t[\mathrm{C}]\mathrm{d}t \qquad (7)$$

where $[\mathrm{A}_0]$ is the initial concentration of A in a pellet, [C] is the sum of [A] and [B], and $\exp(\kappa[\mathrm{A}])>1$ is assumed. The conversion of [A] was followed by UV measurements, and that of [C], by IR measurements, as is shown in Fig. 2a.

The result that $k_2/k_1 \simeq 10$ was obtained. This result is reasonable considering that the B produced in the oligomerization process corresponds to a pentamer. The reason why k_2 is larger than k_1 could not be thoroughly explained. One possible explanation for this acceleration is that the distance between the olefinic double bonds of A and B becomes shorter than that between A and A as a result of the molecular rearrangement from A to B. However, other alternatives may be acceptable.

Quantum Yields. The quantum yields for the oligomerization and the polymerization of DSP, P2VB, and the p-PDA dimethyl ester were measured. The quantum yield, (ϕ), is defined by the equation:

$$\phi = -\,(\mathrm{d}[\text{double bonds}]/\mathrm{d}t)/I_{abs} \qquad (8)$$

where $-(\mathrm{d}[\text{double bonds}]/\mathrm{d}t)$ is the disappearing rate of the olefinic double bond per unit of volume, and where I_{abs} is the rate at which the incident light is absorbed per unit of volume of a pellet containing the sample.

There are two IR absorption bands, at 970 cm^{-1} and at 1630 cm^{-1}, attributable to the olefinic double bond. The former can be used for the measurement in DSP and P2VB, and the latter, in the *p*-PDA dimethyl ester, because they are more intense than the others.

ε_A, an IR absorption coefficient of A, was exactly determined from the calibration curve of the IR absorbance *vs.* the monomer concentration in a pellet. However, ε_B, that of B, could not be determined since B was not a homogeneous species, but an oligomer mixture with various degrees of polymerization. Hence, we assumed that $\varepsilon_B=\varepsilon_A$. This may be approximately correct because the substitutions of the olefinic double bonds in A and B are similar.

I_{abs} could not be precisely evaluated because of the ambiguity in the amount of scattered light. I_{abs} should be equal to the intermediate value between two extreme ones calculated on the assumption that the scattered light is either all lost or not lost at all.[11] The extreme values are calculated as the difference between the intensity of the radiation transmitted through a pure KBr pellet (I_{KBr}) and a pellet containing the sample (I_{sam}) in the former case, and between the incident light intensity (I_0) and I_{sam} in the latter case. I_{KBr} was about 70% of I_0 at 365 mμ under these experimental conditions.

The substitution of the upper limit of I_{abs}, I_0-I_{sam}, in the denominator of Eq. (8) gives the quantum yield at the lower limit, and *vice versa.*

The initial quantum yields for the oligomerization and the polymerization of DSP, P2VB, and the *p*-PDA dimethyl ester are summarized in Table 1. These are the values at the lower limit.

TABLE 1. QUANTUM YIELDS OF OLIGOMERIZATION AND POLYMERIZATION OF DSP, P2VB, AND THE *p*-PDA DIMETHYL ESTER

	Oligomerization		Polymerization	
	Excitation (mμ)	ϕ	Excitation (mμ)	ϕ
DSP	436	1.2	365	1.6
P2VB	405	0.04	—	—
p-PDA dimethyl ester	365	1.2	313	0.7

The quantum yields of DSP and the *p*-PDA dimethyl ester were all between 1 and 2 except for that of the polymerization of the latter. This indicates that these photoreactions all belong to one type of reaction in which, theoretically, the maximum value is equal to 2, and that they proceed very efficiently compared with the model compounds photodimerizable in the crystalline state, such as stilbazole[12] and *trans*-cinnamic acid.[13]

The true value of the quantum yield may be expected to be larger than those listed in Table 1. One of the quantum yields calculated at the upper limit was beyond 2, but the other was not. At least mechanistically, the quantum yield which is beyond 2 cannot be visualized for this kind of photopolymerization.

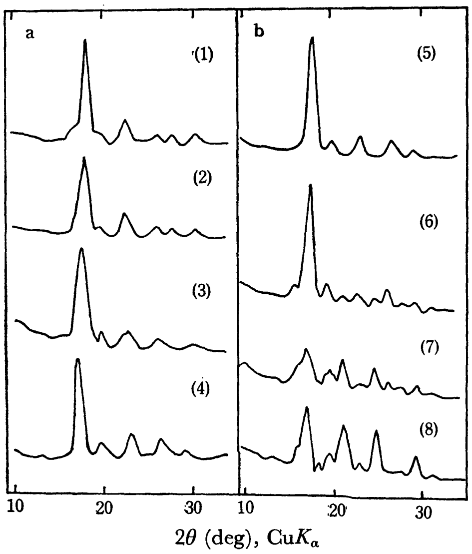


Fig. 7. The changes of X-ray diffraction diagram (a) during oligomerization of DSP: (1) monomer crystals, (2) 35% of conversion, (3) 65% and (4) 100% (*as*-oligomerized), and (b) during polymerization of the oligomer: (5) oligomer crystals, (6) 46% (7) 83% and (8) 100% (*as*-polymerized). Conversion was followed by measuring an IR absorbance at 970 cm^{-1}.

The quantum yield for the oligomerization of P2VB was 0.04. That for the polymerization could not be measured because several bands near 970 cm^{-1} overlap each other and the absorption coefficient at 1630 cm^{-1} is too low in the IR absorption spectrum of the oligomer.

The reason for the difference between the quantum yields in DSP and P2VB cannot be explained until more detailed studies of the crystal structure and the photochemical behavior of these compounds are made.

Structure of the DSP Oligomer. Figure 7 shows the changes in the X-ray diffraction diagram of DSP during the oligomerization and the polymerization. The diffraction diagram of the oligomer is clearly different from those of the monomer and the polymer.

It is noteworthy that the crystallinity of the oligomer (*as*-polymerized) is very high. Once the oligomer is dissolved in a solution, the same crystal structure cannot be reproduced by reprecipitation. In contrast to the DSP oligomer crystal (*as*-polymerized), the recrystallized oligomer could not be photopolymerized. This observation suggests that the thermodynamically quasi-stable oligomer crystals are produced, as in the case of the high polymer crystals *as*-polymerized.[7]

From these facts it is evident that both the oligomerization and the polymerization proceed through a direct rearrangement from the monomer crystals to the polymer crystals by means of a three-dimensional, monomer-lattice-controlled mechanism.

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