Structure Analysis of Monomer and Polymer Crystals in the Photoinduced Solid-State Polymerization Reaction of Diethyl *cis,cis*-Muconate

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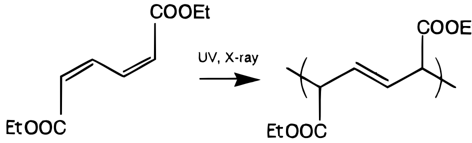
In a series of papers,[1−4] we reported the characteristic features of the light-induced solid-state polymerization reaction of diethyl *cis*,*cis*-muconate (EMU) monomer crystal.



This solid-state polymerization reaction was speculated to be a "topochemical" and a "topotactic" reaction. In the topochemical polymerization, the reactions progress under structural restraint by the crystal lattice, and so the resultant polymers have highly controlled chemical structures.[5−17] In the topotactic reaction, the daughter crystal is oriented in a three-dimensional, specfic manner with respect to the monomer crystal, that is, the single-crystal-to-single-crystal reaction. The topotactic polymerization of diacetylenes was already known as a typical example.[15−17] In the present case of EMU, the symmetry of the crystal lattice of monomers was speculated to be preserved even after the polymerization reaction and the single-crystalline morphology of the original monomer was actually retained in the polymer product.[1−4] From these characteristic features, the solid-state polymerization of EMU was speculated to be a "topochemical" and a "topotactic" reaction, as mentioned above. The EMU monomer is also important in the sense that the EMU molecule may be assumed to be one of the "normal" organic compounds consisting of "popular" butadiene and ester groups. In other words, a clarification of the polymerization mechanism of the EMU monomer crystal will give us a possibility to widen the research field of the polymerization reaction, which makes it easier to control the bulk structure and the related physical properties of the general polymer substances.

Despite such an expectation, however, we had encountered a hard wall which disturbed our effort to clarify the mechanism of the topotactic polymerization reaction of the EMU monomer. This is because the structural change in the polymerization reaction occurs rapidly in a time scale of several tens of minutes under the irradiation of a powerful X-ray beam, which has made it actually impossible to collect the X-ray reflection data necessary for the analysis of the detailed 3-dimensional crystal structure by a conventional AFC (automatic four-circle diffractometer) or an imaging plate system.

Recently we introduced an X-ray CCD camera system which can collect the X-ray reflection data quickly and sufficiently quantitatively. In fact, in the shortest case in our experience, about 5000 reflections could be collected in only 66 s from the standard cytidine single crystal, and a reasonable structure could be obtained from these reflection data (see Appendix).[18] Then we were challenged to measure the X-ray diffraction pattern of the EMU monomer crystal by using this 2-dimensional X-ray CCD camera system. At the same time we expected to trace the structural change during the solid-state polymerization reaction in the 3-dimensional full mode.

In this communication, we will report the result of the crystal structure analysis of the initial monomer crystal and the final polymer crystal in order to confirm our speculation about the topochemical polymerization reaction of the EMU sample. In addition, though preliminarily, some information could be obtained about the structural change in the course of the polymerization reaction. We consider that the first barrier could be overcome for the interpretation of the light-induced polymerization reaction mechanism of the EMU crystal.

Experimental Section. Samples. The synthesis method of EMU was already reported.[1−3] The needle-shaped single crystals of EMU were prepared from a methanol−water solution at room temperature. To avoid an occurrence of light-induced reaction during the preparation of the samples, all the processes were made under a weak red lamp in the dark room.

X-ray Measurements. The X-ray diffraction measurement was carried out by using a Nonius Kappa CCD system with the graphite-monochromatized Mo Kα line ($\lambda = 0.710\,73$ Å) as an incident source from the vacuum-tube-type X-ray generator (maximum 60 kV × 60 mA), where the X-ray power was reduced to 40 kV × 45 mA in order to avoid the acceleration of the polymerization reaction. The exposure time was 10 s for one shot. The sample was oscillated in a range of 3° over a rotation angle of 0−180° around the needle axis. It took 13 min to collect the 60 shots in total for one set of reflections. The measurements were carried out repeatedly for 10 h starting from the virgin monomer crystal.

The structure analysis was carried out by using the softwares DENZO and SCALEPACK[19] for the determination of the cell constants, the indexing of reflections, and the evaluation of the integrated intensities of the reflections and the softwares SIR92[20] (semi-invariants representation) for the direct analysis of the structure. R_{merge}, a measure of the exactness of the intensity evaluation, was ca. 4.9%. The reliability factors were in the range of $R = 4.3\%$ and $R_{\mathrm{w}} = 4.3\%$ for the initial stage of the monomer single crystal, for example.

Results and Discussion. Crystal Structure of the Monomer. By measuring the time dependence of the diffraction intensity of the monomer crystal, we found that the reflections of the monomer crystal were observed to have almost unchanged intensities for about

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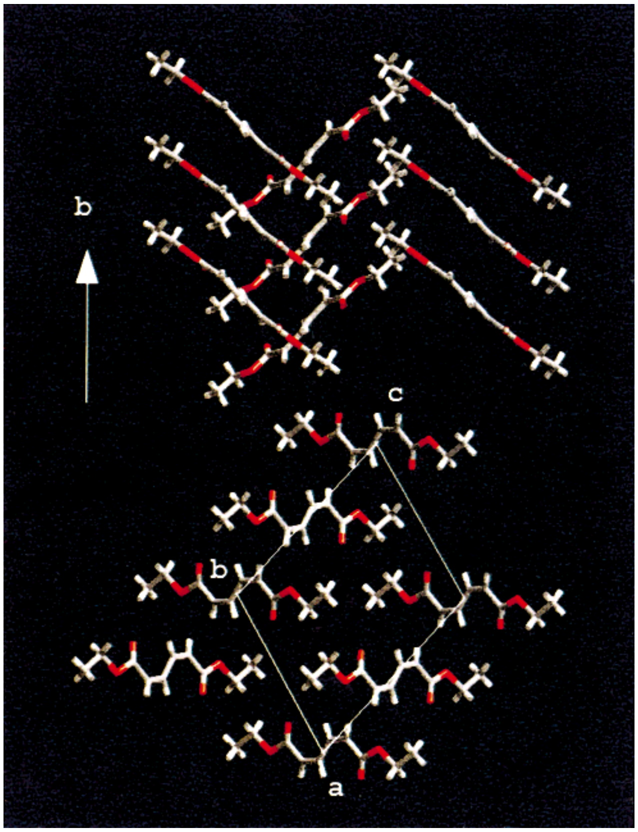

Figure 1. Crystal structure of the EMU monomer at the earliest stage of the polymerization reaction. The monomer molecules are packed in a cylindrical column along the *b* axis, in which light-induced polymerization occurs and the polymer chains are formed keeping the *b* axis orientation (see Figure 2).

60 min after starting the X-ray beam irradiation, and then the intensities gradually changed as the polymerization started. In other words, the X-ray diffraction patterns collected until 60 min, at least, after the start of experiment may be assumed to originate mainly from the monomer crystal. Recently we carried out the simultaneous measurement of Raman scattering and X-ray scattering of the EMU monomer single crystal, and clarified that no polymer component could not be detected, at least in the earliest stage of the irradiation with the beams.[21]

The crystal structure analysis of the initial monomer crystal was made by using a set of the X-ray data collected for the earliest 13 min of measurements. The observed 5260 reflections were indexed by a monoclinic unit cell with $a = 10.2320(24)$ Å, $b = 4.9310(6)$ Å, $c = 11.4970(28)$ Å, and $\beta = 107.146(10)°$. The space group is $P2_1/c{-}C_{2h}{}^5$ and the two molecules are included in this unit cell. Figure 1 shows the packing structure of monomer molecules in the unit cell. Table 1 shows the fractional coordinates of the atoms. Table 2 shows the geometry of a monomer molecule and the intermolecular nonbonded interatomic distances. The intensity data are available as Supporting Information. As seen in Figure 1, the molecules are almost planar, and the ester and ethyl groups are approximately in the trans conformation. The unit cell consists of the two columns in which the molecules are packed along the column axis or the *b* axis. The shortest distance between the butadiene carbon atoms of the adjacent monomers is about 3.8 Å, which is in the range of distances acceptable for the solid-state polymerization reactions.[5−13]

Table 1. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Ethyl *cis,cis*-Muconate

	x	y	z	U_{eq} (Å^2)[a]
O(1)[b]	0.7117(1)	−0.0178(2)	0.2402(1)	0.0880(8)
O(2)	0.7570(1)	0.2180(3)	0.0920(1)	0.1149(9)
C(3)	0.4746(2)	0.4352(4)	0.0445(2)	0.077(1)
C(4)	0.5400(2)	0.2569(4)	0.1283(2)	0.082(1)
C(5)	0.6788(2)	0.1556(3)	0.1469(2)	0.077(1)
C(6)	0.8491(3)	−0.1323(7)	0.2717(3)	0.109(2)
C(7)	0.8704(4)	−0.286(1)	0.3835(4)	0.141(3)
H(3)	0.387(2)	0.494(2)	0.037(1)	0.076(5)
H(4)	0.491(2)	0.187(3)	0.178(1)	0.089(6)
H(6A)	0.851(2)	−0.250(4)	0.201(2)	0.16(1)
H(6B)	0.911(2)	0.013(4)	0.280(2)	0.14(1)
H(7A)	0.962(2)	−0.355(4)	0.406(2)	0.110(7)
H(7B)	0.791(3)	−0.400(6)	0.378(2)	0.22(2)
H(7C)	0.865(3)	−0.162(6)	0.444(3)	0.19(2)

[a] $U_{eq} = (^1/_3)\sum_i\sum_j U_{ij}a_ia_j\, \mathbf{a}_i\mathbf{a}_j$. [b] The numbering of the atoms is shown below.

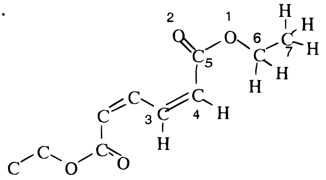

Table 2. Selected Geometry Parameters (Å, deg) for Ethyl *cis,cis*-Muconate

(A) Intramolecular Bond Length[a]			
O(1)−C(5)	1.335(3)	O(1)−C(6)	1.458(3)
O(2)−C(5)	1.196(3)	C(3)−C(3′)	1.428(3)
C(3)−C(4)	1.330(3)	C(4)−C(5)	1.461(3)
C(6)−C(7)	1.453(6)		
(B) Intramolecular Bond Angles			
C(5)−O(1)−C(6)	116.3(2)	C(3′)−C(3)−C(4)	127.1(2)
C(3)−C(4)−C(5)	126.3(2)	O(1)−C(5)−O(2)	122.6(2)
O(1)−C(5)−C(4)	109.9(2)	O(2)−C(5)−C(4)	127.4(2)
O(1)−C(6)−C(7)	107.7(3)		
(C) Intramolecular Torsional Angles			
C(6)−O(1)−C(5)−O(2)	−0.8(2)	C(6)−O(1)−C(5)−C(4)	−178.7(3)
C(5)−O(1)−C(6)−C(7)	172.9(4)	C(3′)−C(3)−C(4)−C(5)	0.0(2)
C(3)−C(4)−C(5)−O(1)	179.1(3)	C(3)−C(4)−C(5)−O(2)	1.3(3)
(D) Intermolecular Interatomic Distances			
C(3)−C(4′)	3.930(3)	C(3)−C(5′)	3.709(3)
C(4)−C(4′)	3.791(3)	C(4)−C(5′)	3.871(3)
C(5)−C(6′)	3.994(4)	C(5)−C(7′)	3.959(5)

[a] The atomic numbering is referred to in Table 1.

Crystal Structure of the Polymer. In the previous paper,[4] we stated that the polymer sample obtained by irradiating the sunlight or the "unfiltered" ultraviolet beam onto the monomer single crystal was not a perfect single crystal. In that experiment, the quality of the monomer crystal itself was not high. Later, it was found that irradiation by a higher energy beam such as X-ray or γ-ray could produce a single crystal of polymer when a qualified monomer single crystal was used. For the purpose of the structure analysis, the almost perfect polymer single crystal, polyEMU, was used. Depending on the irradiation conditions such as temperature, light source, and so on, the obtained sample was not purely the polymer but sometimes contained the monomer residue more or less. But the present polymer sample was almost pure, as checked by the infrared and Raman spectral measurements. The unit cell is of monoclinic type with parameters $a = 10.4030(12)$ Å, b (chain axis) $= 4.8410(3)$ Å, $c = 10.9920(13)$ Å, and $\beta = 107.627(10)°$. The space group was the same with that of the monomer, $P2_1/c{-}C_{2h}{}^5$, and two chains are included in this

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Poly(ethyl *cis,cis*-muconate)

	x	y	z	U_{eq} (Å^2)[a]
O(1)[b]	0.7360(2)	0.0302(3)	0.9278(2)	0.107(1)
C(2)	0.9702(2)	0.3883(4)	1.0115(2)	0.072(2)
O(3)	0.8123(2)	−0.0467(4)	0.7632(2)	0.112(1)
C(4)	0.9692(2)	0.1198(5)	0.9495(2)	0.070(1)
C(5)	0.8243(2)	0.0290(5)	0.8792(2)	0.077(1)
C(6)	0.6519(6)	−0.081(1)	0.6609(5)	0.232(5)
C(7)	0.6599(5)	−0.340(1)	0.6965(5)	0.193(4)
H(2)	0.930(2)	0.392(4)	1.074(2)	0.064(6)
H(4)	1.011(2)	0.129(4)	0.871(2)	0.077(6)
H(6A)	0.594(2)	0.042(4)	0.688(2)	0.090(7)
H(6B)	0.651(2)	−0.035(5)	0.576(2)	0.14(1)
H(7A)	0.579(2)	−0.441(6)	0.656(2)	0.17(1)
H(7B)	0.677(2)	−0.344(4)	0.787(2)	0.31(3)
H(7C)	0.734(3)	−0.422(5)	0.675(2)	0.26(2)

[a] $U_{eq} = (^1/_3)\sum_i\sum_j U_{ij}a_i a_j\, \mathbf{a}_i\mathbf{a}_j$. [b] The numbering of the atoms is shown below.

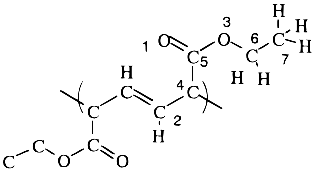

Table 4. Selected Geometry Parameters (Å, deg) for Poly(ethyl *cis,cis*-muconate)

(A) Intramolecular Bond Length[a]			
O(1)−C(5)	1.194(3)	C(2)−C(2′)	1.309(3)
C(2)−C(4)	1.466(4)	O(3)−C(5)	1.296(3)
C(4)−C(4′)	1.599(4)	C(4)−C(5)	1.535(4)
C(6)−C(7)	1.305(9)		
(B) Intramolecular Bond Angles			
C(2′)−C(2)−C(4)	125.4(4)	C(2)−C(4)−C(4′)	112.0(2)
C(2)−C(4)−C(5)	110.8(5)	C(4)−C(4′)−C(5)	105.5(2)
O(1)−C(5)−O(3)	125.7(3)	O(1)−C(5)−O(4)	123.0(3)
O(3)−C(5)−C(4)	111.3(4)	O(3)−C(6)−C(7)	86.3(4)
(C) Intramolecular Torsional Angles			
C(2′)−C(2)−C(4)−C(5)	−120.2(3)	C(2)−C(4)−C(5)−O(1)	−49.7(3)
C(2)−C(4)−C(5)−O(3)	130.4(3)	C(4′)−C(4)−C(5)−O(1)	71.8(3)
C(4′)−C(4)−C(5)−C(3)	−108.1(3)		
(D) Intermolecular Interatomic Distances			
O(1)−C(4′)	3.041(3)	C(2)−C(2′)	3.831(3)
C(2)−O(3′)	3.225(3)	C(2)−C(5′)	3.564(3)
O(3)−C(4′)	3.304(3)	C(5)−C(5′)	3.823(3)

[a] The atomic numbering is referred to in Table 3.

cell. The lack of change in the space group symmetry before and after the reaction indicates that this reaction may be the "topochemical (and topotactic) polymerization reaction". Table 3 shows the fractional coordinates of the atoms consisting of an asymmetric unit. Table 4 shows the geometry of the polymer chain. The intensity data of diffraction are available as Supporting Information.

In Figure 2 the molecular structures of the monomer and polymer are shown together. As pointed out already, the monomer molecules form a column structure. The polymerization occurs along this column axis, where almost no large displacement of the center of mass is detected before and after the polymerization reaction: the monomers are linked together through the formation of covalent bondings between the butadiene carbon atoms of the adjacent monomer molecules separated by ca. 3.8 Å. The angle between the column axis and the long axis of the monomer molecule is about 49°. These distance and angle might be associated intimately with the trigger of the topotactic polymerization reaction, as already seen in the case of polydiacetylenes.[15−17] To discuss the mechanism of this reaction in more detail, we are now investigating the relation between the packing geometry and the reactivity for a series of muconate crystals with different kinds of side groups. Anyway, from Figure 2, we may recognize visually why this polymerization reaction occurs quite smoothly and rapidly. The effective cross-sectional area was decreased by 3% in the process from the monomer to the polymer.

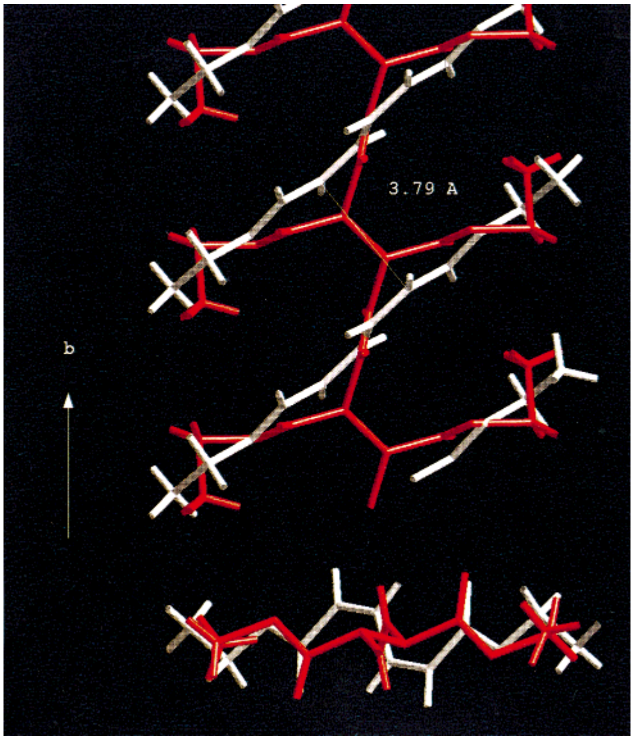

Figure 2. Crystal structure of polyEMU obtained after long exposure of X-ray beam to the monomer crystal at room temperature. Key: red, polymer chain; white, monomer molecules forming a column structure. The distance between the butadiene carbon atoms of the neighboring monomer molecules is ca. 3.79 Å.

As seen in Table 4, the ethyl side group has an abnormal C−C length, ca. 1.31 Å, much shorter than the normal distance of 1.54 Å. The C−C−O angle of ethyl ester group is also abnormal, ca. 86°. At the present stage, we cannot know the reasons for this geometrical abnormality in the polymer chain. A disordering in the crystal structure, which is generated during the polymerization reaction process,[4] might be related with such an apparently abnormal geometry of the side chains, as suggested by the relatively large thermal parameters U_{eq} shown in Tables 1 and 3. A detailed study is required to clarify the origin of this abnormality.

Structural Change in Polymerization Process. Figure 3 shows a series of contour maps obtained by calculating $F_o - F_c$, where F_o is the structure factor observed at a particular time and F_c is the structure factor calculated for the initial monomer structure. With passage of time, the electron density corresponding to the polymer chain (solid lines) begins to increase, and the peak position gradually changes. In this way the conformation of the skeletal chain is seen to change in the early stage of the reaction at 65−143 min. The orientation of the ethyl side groups is found to change from the horizontal direction to the perpendicular direction (parallel to the chain axis) in the time region

Table 5. Comparison of Cell Constants of Cytidine Crystal Analyzed by CCD Camera System

(a) Oscillation Angle $\Delta\phi = 1°$ (Constant), $\phi = 0-180°$

measurement	(time/shot)/s	total time/min	a/Å	b/Å	c/Å
dezinger[a]	30	180	5.1180(1)	13.9940(7)	14.7821(7)
dezinger	10	60	5.1160(3)	13.9890(20)	14.7810(11)
no dezinger	3	18	5.1170(3)	13.9880(20)	14.7740(21)
no dezinger	2	12	5.1170(4)	13.9940(21)	14.7830(23)

(b) Oscillation Angle $\Delta\phi$ Varied, $\phi = 0-120°$, 1 s/Shot, No Dezinger

$\Delta\phi$/deg	total time/s	a/Å	b/Å	c/Å
2	306	5.1150(10)	13.9910(54)	14.7760(64)
5	125	5.1150(31)	13.9940(191)	14.7830(200)
6	105	5.1140(39)	13.9790(255)	14.7740(287)
8	81	5.1140(62)	14.0350(449)	14.8160(525)
10	66	5.1120(93)	13.9930(687)	14.7760(704)

[a] Dezinger: The measurements were made twice in order to check whether the observed reflection spots come from the crystal or from the cosmic ray. [b] In part a, the exposure time to the X-ray beam was changed with the oscillation angle constant (1°), and the total rotation angle of the sample was 180°. In part b, the exposure time was fixed to 1 s, and the oscillation angle was varied in the range 0−120°. [c] The standard errors are indicated by parentheses behind the corresponding cell parameters. For example, 5.1150(31) means 5.1150 ± 0.0031 Å.

Table 6. Comparison of Internal Parameters of Cytidine Molecule

(a) $\Delta\phi = 1°$ (Constant), $\phi = 0-180°$

	(time/shot)/s (total time/min)	total no. of reflections	R_{merg}/%	R/%	r/Å	θ/deg	τ/deg
dezinger	30 (180)	6492	3.6	2.42	1.240(2)	101.3(2)	47.4(2)
dezinger	10 (60)	6528	5.8	3.88	1.221(6)	100.2(4)	46.9(4)
no dezinger	3 (18)	6489	10.4	3.26	1.25(2)	99.7(8)	43.9(8)
no dezinger	2 (12)	6398	10.1	3.05	1.26(2)	100.3(10)	44.7(10)

(b) $\Delta\phi$ Varied, $\phi = 0-120°$, 1 s/Shot, No Dezinger

$\Delta\phi$/deg	total time/s	total no. of reflections	R_{merg}/%	R/%	r/Å	θ/deg	τ/deg
2	306	6966	16.1	3.97	1.19(3)	103.3(14)	48.9(15)
5	125	5692	26.6	3.28	1.25(8)	98.9(32)	43.8(40)
6	105	5403	23.3	1.97	1.23(7)	99.2(37)	45.2(44)
8	81	4983	29.1	2.16	1.23(28)	102.7(139)	44.4(155)
10	66	4706	25.4	1.79	1.35(52)	93.8(306)	42.3(296)

[a] Dezinger: The measurements were made twice in order to check whether the observed reflection spots come from the crystal or from the cosmic ray. [b] In part a, the exposure time to the X-ray beam was changed with the oscillation angle constant (1°), and the total rotation angle of the sample was 180°. In part b, the exposure time was fixed to 1 s, and the oscillation angle was varied in the range 0−120°.

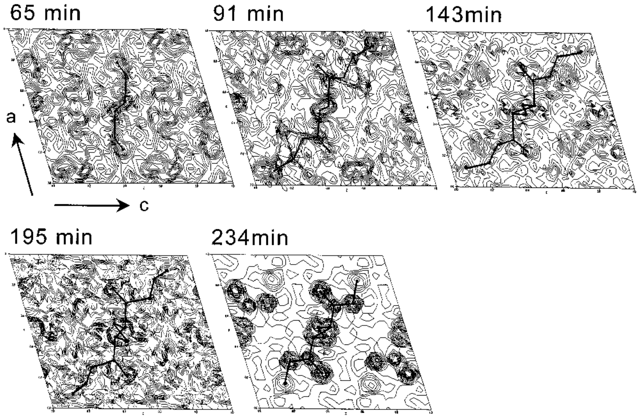

Figure 3. Time evolution of contour maps showing the generation of polymer chain structure during the photoinduced polymerization of the EMU monomer single crystal, which was obtained by calculating the $F_o - F_c$ maps. As time passes, the electron density corresponding to the polymer chain increases and allows us to identify the atomic positions of atoms.

between 195 and 234 min. As stated in Figure 2, the carbon atoms of the adjacent butadiene groups are linked covalently and are shifted to form the skeletal chain of the polymer, but the carbon atoms of the ethyl groups interact with those belonging to the neighboring chains. The change in the ethyl group orientation might come from a compromise between these two factors.

Figure 3 shows a preliminary result of the data collected by the rapid-scan X-ray measurement. However, this figure may illustrate the possibility of tracing the structural change, which occurs rapidly in the solid-state polymerization reaction. We are now trying to analyze the detailed change in the atomic positions in order to reveal the stereochemical mechanism of the polymerization reaction.

Appendix. Structure Analysis of Cytidine Single-Crystal Based on the X-ray Data Collected by a Rapid-Scan Measurement. To clarify to what extent the reflection data collected by a rapid measurement are useful for the 3-dimensional structural analysis, we checked the data of a standard sample cytidine by using a rapid-scan-type CCD camera system. The CCD camera used was a Nonius Kappa CCD system. The CCD detector was made of 1152 × 1242 pixels (56 × 56 μm^2/pixel) with a total area of 65 × 65 mm^2. The readout time was ca. 3 s for 1 frame of the collected 2-dimensional data. The Mo Kα beam from the sealed tube (λ = 0.710 73 Å) was irradiated at a power of 40 kV and 45 mA. The collection of reflections was made by oscillating the cytidine single crystal around the ϕ axis at a predetermined rate for a fixed exposure time.

Table 5 shows the comparison of the cell parameters obtained under the different collection conditions. Table 5a shows the influence of changing the exposure time on the accuracy of the cell parameters under the condition of oscillation angle $\Delta\phi = 1°$ in the full range of $\phi = 0-180°$, where in some cases the measurement at every ϕ angle was repeated twice in order to carry out the so-called dezinger, i.e., to remove the accidentally incident cosmic rays. Even when the exposure time was only 2 s and the total experimental time was only 12 min, the 6398 reflections could be collected (refer to Table 6) and the independent 908 reflections were transferred to the structure analysis. In general, the standard deviations of the cell parameters $\sigma(a)$ were about several thousandths of the averaged values $\langle a\rangle$, i.e., $\sigma(a)/\langle a\rangle \approx 10^{-3}$ when various X-ray diffraction systems, such as AFC and IP, were used, where the reflection data were collected for a long enough time to increase the signal-to-noise ratio as high as possible. Table 5a shows that the cell parameters obtained by the rapid CCD system show almost the same ratio of $\sigma(a)/\langle a\rangle \approx 10^{-3}$ and are acceptable. More rapid collection of reflections was made by oscillating the crystal more quickly, where no dezinger was made but only one shot was taken for one oscillation angle. Table 5b shows the cell constants thus obtained. For example, in the case of the oscillation angle range of $\Delta\phi = 10°$, it took only 66 s to collect the 4706 reflections in total. In this case the standard error of the cell constants is one order worse than the case of Table 5a, although the averaged cell parameters are not that far from the exact values.

In Table 6 are compared the molecular parameters such as bond lengths, bond angles, or torsional angles among the data collected under the above-mentioned various conditions. For example, in Table 6a, where the dezinger was performed, the standard deviations of the molecular parameters are enough small, allowing us to have a discussion about the geometry of molecules, even when the total experimental time was only 12 min. On the other hand, in Table 6b, where more rapid measurement was made, the standard deviations are extremely large. In particular, the standard deviations increased rapidly when the total collection time was shorter than 80 s. However, the molecular geometrical parameters themselves, which were obtained from the analysis of ca. 5000 reflections collected for such a short time as 1−2 min, are not deformed very much and may be used in the discussion of the structure *as long as we recognize that the standard deviations are about one order larger than the normal case*. In fact, the molecular shape obtained by such rapidly collected data was found to be essentially the same as that obtained by the normal analysis, although the atomic positions are observed to deviate more or less from the standard positions. In this way, as long as the limitations of the accuracy of cell parameters and molecular geometry are recognized carefully enough, the discussion about the molecular structure and molecular packing in the crystal cell may be meaningful even when all the reflection data are collected in only a few minutes. This is quite important and useful when we want to obtain any rough information about the molecular shape and packing in the research of rapidly occurring structural changes in the solid-state reaction process, for example, which has never been solved so far by conventional X-ray diffraction experiments.

Supporting Information Available: Tables of collected X-ray data, anisotropic thermal parameters, and observed and calculated structure factors and CIF files for the monomer and polymer crystals of EMU. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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