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Structural Change in the Topochemical Solid-State Polymerization Process of Diethyl *cis,cis*-Muconate Crystal. 1. Investigation of Polymerization Process by Means of X-ray Diffraction, Infrared/Raman Spectra, and DSC

Kohji Tashiro,*,† Toshiya Kamae,† Masamichi Kobayashi,† Akikazu Matsumoto,‡ Katsutaka Yokoi,‡ and Shuzo Aoki‡

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, and Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Osaka 558-8585, Japan

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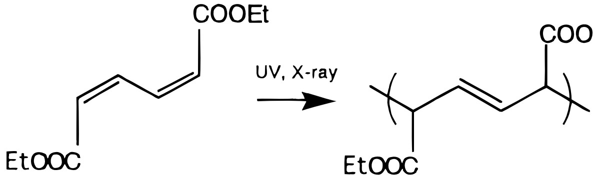
ABSTRACT: Structural change occurring in the light-induced solid-state polymerization of diethyl *cis,-cis*-muconate crystal has been investigated by means of the X-ray diffraction, infrared and Raman spectra, and DSC. The infrared and Raman spectral changes during this polymerization reaction could be interpreted on the basis of a simple two-component system consisting of monomer and polymer molecules. This apparent observation may originate from the high sensitivity of the vibrational spectra to the local structure. The time-resolved X-ray diffraction measurement, however, showed that the lattice spacings changed continuously in the process of polymerization, indicating that the strain to the crystal lattice, due to the coexistence of the different chemical species of monomer and polymer with various lengths or volumes, changed in this reaction. But this strain was quite small, and the crystal lattice could be maintained more or less during the polymerization reaction. It was also found that the polymerization did not occur at a low temperature below −40 °C, where the phase transition occurred and the packing structure of monomer molecules changed, as indicated by the large change in the X-ray diffraction pattern. This good correlation between the reactivity and the crystal structure indicates that the polymerization reaction is governed sensitively by the packing structure of monomer molecules; i.e., this reaction is just the lattice-controlled polymerization.

Introduction

Many examples have been reported about the monomer crystals which give the highly crystalline polymer solids by irradiating visible light, UV light, X-ray, or γ-ray or by heating.[1−3] For example, the poly(oxymethylene) crystal is obtained by γ-ray irradiation on trioxane or tetraoxane crystal.[4] Generally speaking, the symmetry of the resultant polymer crystal is usually different from that of the original monomer crystal. However, special cases are known in which the symmetry of the crystal lattice of monomers is preserved even after the polymerization reaction. We call it “the topochemical polymerization”.[5,6] In the topochemical polymerization, the reaction’s progress is under the structural restraint of the crystal lattice, and thus the resultant polymers have highly controlled chemical structure and/or morphology.

For the topochemical polymerizations, only a few papers have been reported so far: for example, the solid-state polymerizations of diacetylenes[7−9] and those of 2,5-distyrylpyrazine.[6] Recently, Matsumoto et al. discovered the crystals of diethyl *cis,cis*-muconate (EMU) polymerize topochemically in the solid state by exposing the monomer crystals under UV light, X-ray, or γ-ray.[10−12] Although the mixture of poly(*trans*-1,4-diethyl muconate) and poly(*cis*-1,4-diethyl muconate) is obtained by the polymerization in solution, the solid-state topochemical polymerization of EMU crystal gives only one kind of polymer crystal, poly(*trans*-1,4-diethyl muconate), with high regularity. Before their finding of EMU, the study of the topochemical polymerization was limited to the cases of some special chemical structure, for example, diacethylene derivatives.[7−9] The discovery of topochemical polymerization of EMU crystal seems to be a trigger to develop a possibility that even such usual chemical compounds as muconate may give the highly regulated polymers through the solid-state polymerization. From such a viewpoint of “controlled polymerization”, therefore, it is very important to clarify the mechanism of the topochemical polymerization of this EMU crystal.



Matsumoto et al. also reported that EMU monomer crystal does not polymerize at low temperature even under an irradiation of strong light.[10−12] This makes us speculate the existence of some phase transition at low temperature, where the EMU monomer crystal might have a structure that cannot cause the polymerization reaction. By clarifying the details of the structural changes in these transitions, we may obtain the essential features of the topochemical polymerization from the molecular level. In this paper we investigate the structural changes of EMU during the polymerization process by means of X-ray diffraction, vibrational spectroscopy, and thermal analysis.

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* Corresponding author.
† Osaka University.
‡ Osaka City University.

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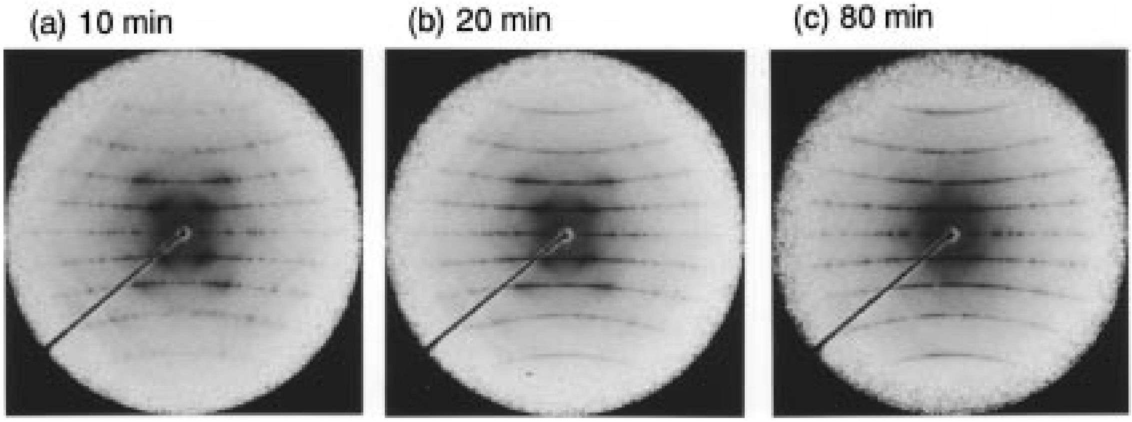

Figure 1. Time dependence of X-ray diffraction patterns of the EMU single crystal measured by an imaging plate system at room temperature. The relative intensity of the reflections can be detected to change. At the same time the streaks can be detected more intensely as the polymerization time is increased.

Experimental Section

Samples. EMU molecules were synthesized from (*Z,Z*)-2,4-hexadienedioic acid (*cis,cis*-muconic acid), supplied from Mitsubishi Chemical Co., Ltd., Japan, by the method described in refs 10−12. The needle-shaped single crystals of EMU were prepared from the methanol−water solution at room temperature. We paid much attention not to irradiate the light on the EMU crystals as carefully as possible during preparation of samples and setting them on the measurement apparatus because the EMU polymerized quite easily by visible and UV light irradiation. All the processes were made under a weak red lamp in the dark room.

Measurements. *1. X-ray Diffraction Measurement by Imaging Plate System.* Single crystals of EMU were set to the goniometer head under a red lamp. The X-ray diffraction measurement was carried out by using a DIP1000 X-ray imaging plate system (MAC Science Co. Ltd., Japan). The graphite-monochromatized Mo−Kα line ($\lambda = 0.710\ 73$ Å) was used as an incident source at the power of the X-ray generator (SRA 18, MAC Science Co. Ltd.), 50 kV and 100 mA. The sample-to-imaging plate distance was 150 mm, and the exposure time was 600 s for one shot. The sample was oscillated over a rotation angle of 0°−100° around the needle axis. The measurements were carried out repeatedly with constant time interval.

2. X-ray Diffraction Measurement by Powder Diffractometer. The powdered EMU crystals were pasted on an aluminum holder in the dark room, and the measurements were carried out by using a Rigaku RAD-ROC X-ray diffractometer also in the dark room. The graphite-monochromatized Cu−Kα line ($\lambda = 1.541\ 78$ Å) was used with the power of the X-ray generator 40 kV and 100 mA, just when the X-ray power was decreased in order to reduce the polymerization rate. The scan speed was 2°/min with a step width of 0.010°. The measurements were carried out repeatedly with a constant time interval in the 2θ range from 5° to 40°.

For the measurement of the X-ray diffraction profiles at low temperature, the cryostat (RIGAKU Co. Ltd.) was used. The temperature of the sample was monitored by a thermocouple attached on the back of the sample holder. The measurements were carried out in the temperature range from −80 to 60 °C at the 2θ range from 5° to 40°.

3. FT-Raman and FT-IR Measurements. In the FT-Raman measurement, the powder samples were packed into glass capillaries and set to the sample holder. The Raman measurements were carried out with a 180° scattering geometry. The spectra were taken by using a BIO RAD FT-Raman spectrometer FTS-60A/896 FT-Raman system, where a 1064 nm line from a Nd:YAG laser was used as an excitation source. The data were taken at a resolution of 2 cm^{-1}. The near-infrared laser beam was useful for the EMU sample because no polymerization reaction was induced during the Raman measurement.

In the case of FT-IR measurement, the KBr disks of powdered EMU crystals were prepared. The spectra were measured by using a Japan Spectroscopic Co. FT-IR 8300 spectrometer at a resolution of 2 cm^{-1}.

The IR and Raman spectra were measured for the samples irradiated repeatedly by UV light for a constant period (30 s for one cycle). The UV light from a medium-pressure Hg lamp was used for irradiation, which was not filtered so that the wavelength range was wide. The Hg lamp was warmed for several hours to stabilize the UV light power.

4. DSC Measurement. The EMU crystals were packed in an aluminum pan for the thermal analysis by using a Seiko SSC5200 differential scanning calorimeter. The DSC thermograms were measured in the temperature range of −120 to 100 °C at a scan rate of 3 °C/min.

Results and Discussion

Structural Changes during Polymerization. *1. X-ray Diffraction.* The X-ray diffractions of the EMU single crystal were measured at constant time interval by an imaging plate system as shown in Figure 1. The sample had a needlelike shape and was set to a goniometer head vertically in this figure. The sample was found to change to the polymer during the measurement under the irradiation of an X-ray beam. Only small changes were observed for the reflection positions, but the relative intensity changed remarkably. The reflections were still relatively sharp even after the completion of polymerization. An amorphous halo was not observed in these X-ray diffraction patterns, indicating the sample contained almost purely crystalline region. The streaks along the layer lines began to appear and increased the intensity, suggesting the appearance of disorder in the relative height along the chain axis during polymerization.

These observations are more obvious in the measurements of the X-ray diffraction profiles as shown in Figure 2. The reflections were found to shift continuously during the polymerization and approached the reflection position of the polymer (see Figure 3). The continuous shift of reflections is important to suggest that the polymerization occurs gradually but continuously with generating some strains in the crystal lattice, where both the monomer and polymer species are coexistent. In other words, the X-ray diffraction may occur coherently from both the domains of monomers and polymers.

2. FT-Raman and FT-IR Spectra. The FT-Raman and FT-IR spectra of EMU and poly-EMU were obtained as

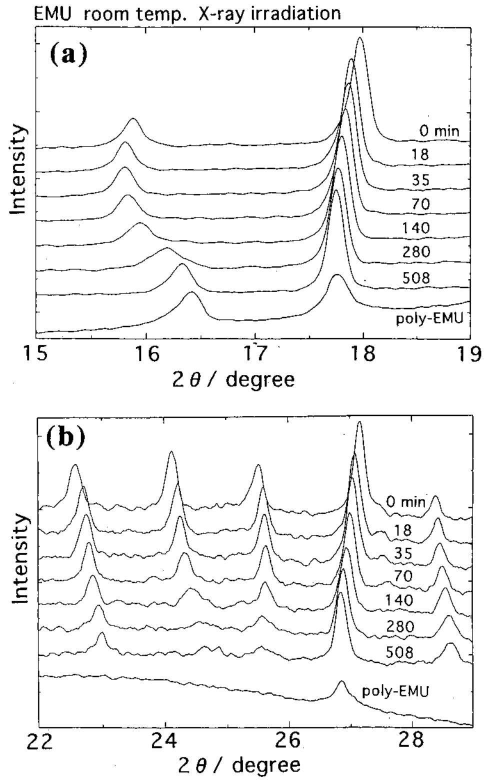

Figure 2. Time dependence of X-ray diffraction profiles measured for the EMU powder crystal at room temperature. (a) The 2θ range is from 15.0° to 19.0°. (b) The 2θ range is from 22.0° to 28.5°.

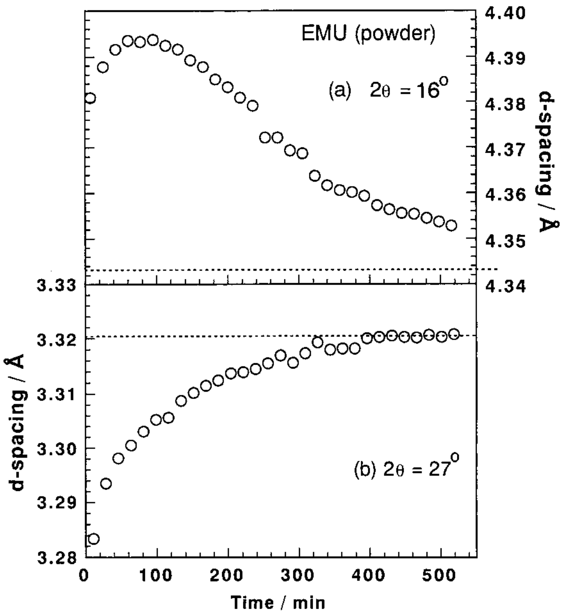

Figure 3. Lattice spacing changes of the EMU powder crystal as a function of X-ray irradiation time (room temperature). The broken line in the figure shows the position of the lattice spacing of polymer crystal. (a) The reflection around $2\theta = 20°$ (see Figure 2), and (b) the reflection around $2\theta = 27°$.

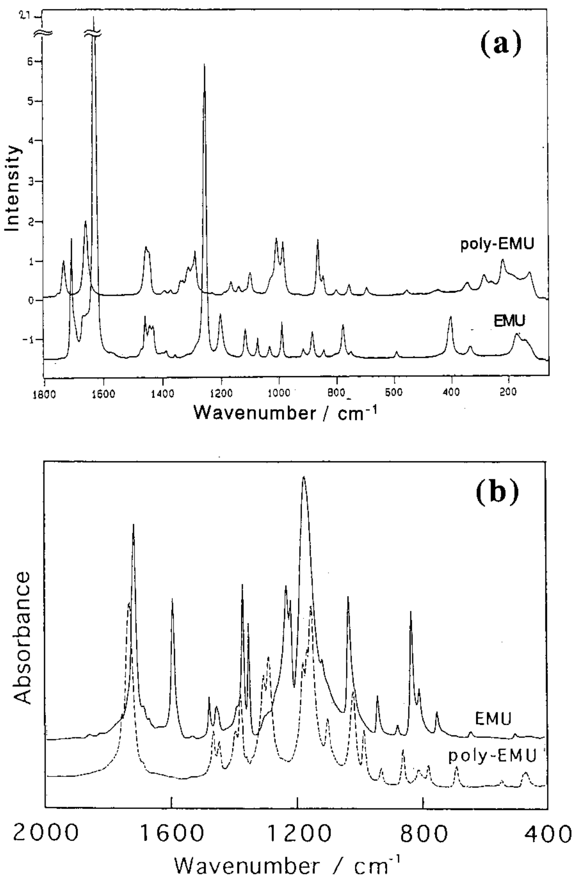

Figure 4. (a) FT-Raman and (b) FT-IR spectra taken for the EMU monomer and polymer.

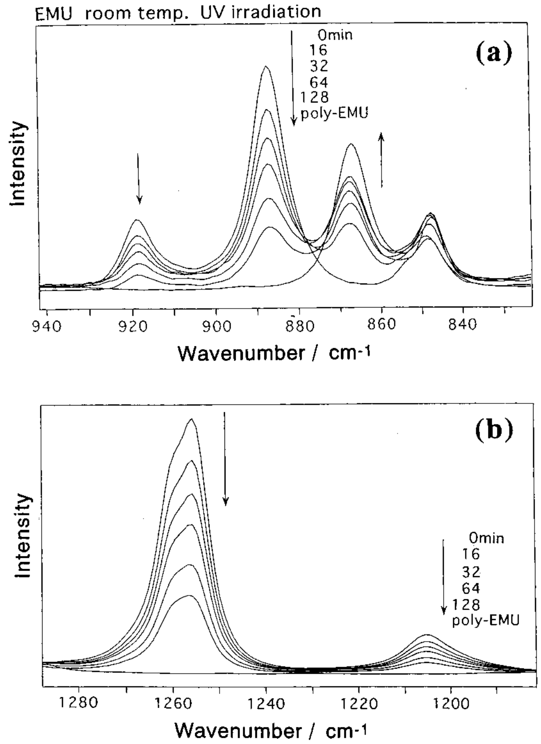

Figure 5. FT-Raman spectral change of the EMU monomer (powder) as a function of UV light irradiation time (room temperature): (a) the frequency region of 830−940 cm^{-1} and (b) the frequency region of 1180−1290 cm^{-1}.

shown in Figure 4, a and b, respectively. In these spectra, the positions of monomer bands are different from those of polymer bands. Therefore, it is possible to investigate the structural changes of polymerization process by observing the changes of these bands separately. The changes of FT-Raman spectra of EMU irradiated by UV light periodically are shown in Figure 5. The intensity of monomer bands decreases with increasing the irradiation time of UV light, and the intensity of polymer bands increases. As shown in

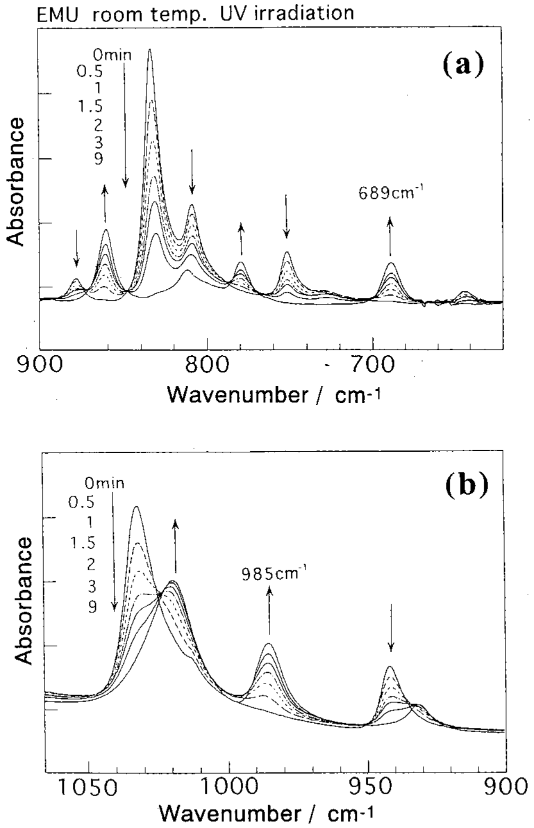

Figure 6. FT-IR spectral change of EMU monomer (powder) as a function of UV light irradiation time (room temperature): (a) the frequency region of 620−900 cm^{-1} and (b) the frequency region of 900−1065 cm^{-1}.

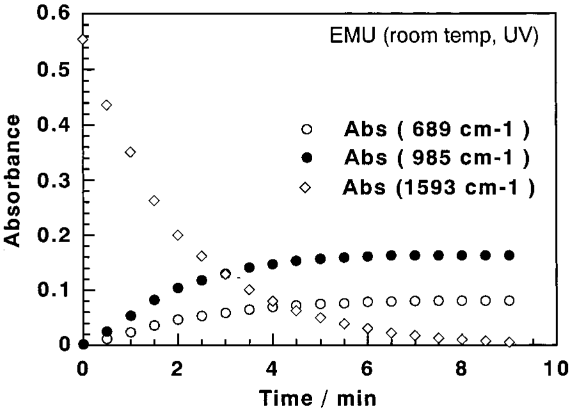

Figure 7. Dependence of IR absorbance of the various bands on the UV light irradiation time (room temperature). The bands investigated are at the frequencies 689, 985, and 1593 cm^{-1} (refer to Figure 6).

Figure 6, the FT-IR spectra show a similar change as that of the FT-Raman spectra. Isosbestic points were observed between the IR bands of monomer and polymer, suggesting that the IR spectra can detect only the two chemical components of monomer and polymer molecules in the crystal during polymerization. That is, the intermediate chemical species such as the oligomers of various chain lengths could not be extracted from these vibrational spectra.

The peak heights of the monomer band at 1593 cm^{-1} and the two polymer bands at 689 and 985 cm^{-1} were measured and plotted against the UV light irradiation time, as shown in Figure 7. The concentration of the EMU crystal in the KBr disk used for the IR measurement was low, allowing us to assume Lambert−Beer's law.

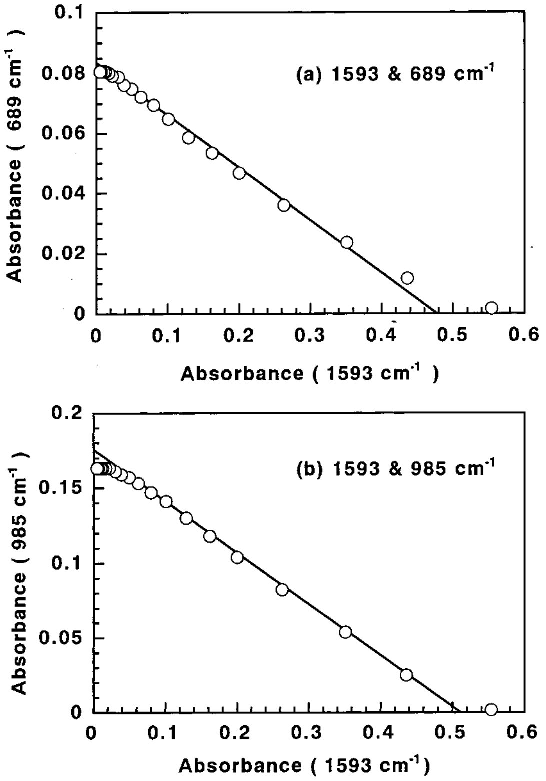

Figure 8. (a) The IR absorbance of the 689 cm^{-1} band plotted against that of the 1593 cm^{-1} band (room temperature). (b) The IR absorbance of the 985 cm^{-1} band plotted against that of the 1593 cm^{-1} band.

$$A_1 = \epsilon_1 b X_1 \tag{1}$$

$$A_2 = \epsilon_2 b X_2 \tag{2}$$

where A is an IR absorbance, ϵ is an absorption coefficient, b is a path length, and X_1 is the fraction of the ith component ($i = 1$ for the monomer and $i = 2$ the polymer). If the equation $X_1 + X_2 = 1$ is assumed to be satisfied, then the following equation is obtained from eqs 1 and 2.

$$A_2 = -\frac{\epsilon_2}{\epsilon_1}A_1 + \epsilon_2 b \tag{3}$$

From eqs 1−3, the X_1 can be evaluated in the following way.

$$X_1 = \frac{1}{(A_2/A_1)(\epsilon_1/\epsilon_2) + 1} \tag{4}$$

The absorbances A_2 of the 689 and 985 cm^{-1} bands were plotted against the A_1 of the 1593 cm^{-1} band, as shown in Figure 8, a and b, respectively. In these figures the data points are approximately on linear straight lines, indicating our assumption is reasonable; that is, during polymerization only the two chemical components of monomer and polymer can be detected by infrared (and Raman) spectroscopy. From the slopes of these linear straight lines, the values of ϵ_1/ϵ_2 were obtained, and the fraction of the monomer component X_1 was obtained on the basis of eq 4. The result is shown in Figure 9 as a function of UV light irradiation time. The X_1 values

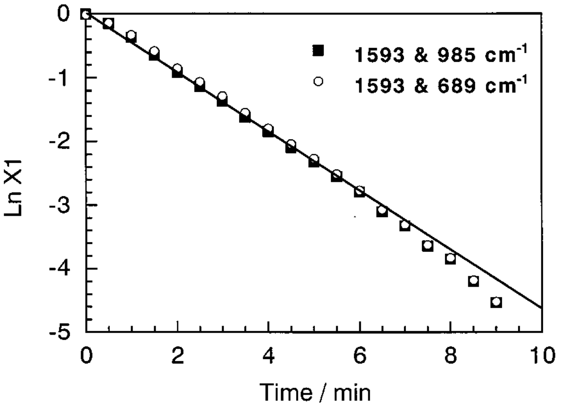

Figure 9. Semilogarithmic plot of monomer fraction X_1 against the UV light irradiation time. The X_1 was evaluated from the plots shown in Figure 8: (●) for the pair of bands at 1593 and 985 cm^{-1}, (○) for the pair of bands at 1593 and 689 cm^{-1}.

evaluated from different pairs of bands shown in Figure 8 are almost coincident with each other, indicating the reasonableness of the present data treatment. As seen in this figure, the logarithm X_1 is linearly proportional to the irradiation time in the range 0–6 min.

$$\ln X_1 = -kt \tag{5}$$

or

$$-\frac{dX_1}{dt} = kX_1 \tag{6}$$

where k is the rate constant and t is the UV light irradiation time. That is to say, the solid-state polymerization of EMU may obey approximately the equation of the first-order reaction. The rate constant was estimated as $k = 7.93 \times 10^{-3}$ s^{-1}. It should be noticed that this k value is not absolute but only relative. To clarify the quantum efficiency of the reaction, the absolute number of photons must be known by clarifying the absolute intensity of the used mercury lamp, which will be a future problem.

3. Relation between X-ray Diffraction and Vibrational Spectra. From the observation of isosbestic points in the IR and Raman spectral change during the polymerization, the vibrational spectra were found to detect the system as a mixture of only two chemical components of monomer and polymer molecules existing in the crystals. The X-ray data clarified, however, that the continuous change in the position and relative intensity of the reflections is observed during this polymerization reaction. The EMU monomers are speculated to react with the adjacent molecules rapidly and give a mixture of monomer and polymer. Because the effective sizes of monomer and polymer molecules are different from each other, as judged from the difference in the X-ray reflectional positions, the mixture of monomer and polymer is speculated to cause some degree of lattice mismatching or the strain in the crystal lattice. This strain changes continuously with the progress of polymerization reaction, and then the whole crystal approaches the structure of polymer molecules. The vibrational spectra see only the local structural change, and so the change in the crystal lattice of larger scale is difficult to detect. Of course, strictly speaking, depending on the degree of strain charged to the crystal lattice, the vibrational frequencies of the monomer and polymer molecules should change because of the change in the geometry and the intra- and intermolecular interactions. The detailed investigation of the spectra from such a type of viewpoint is now being tried.

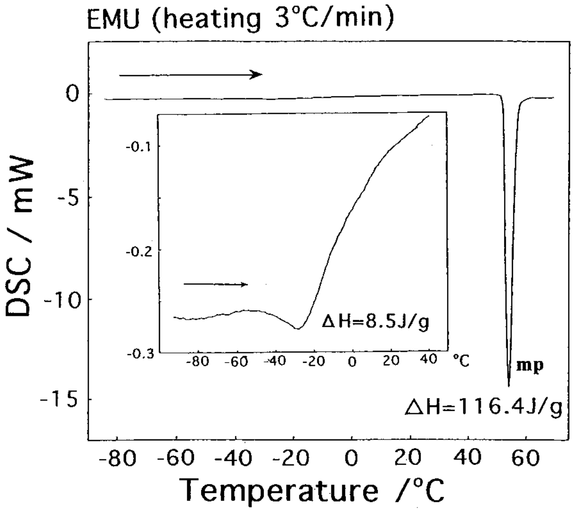

Figure 10. DSC thermogram measured for EMU monomer in the heating process from −80 to 65 °C at a rate of 3 °C/min. The inset is the zoomed-in part in the region of −80 to 45 °C.

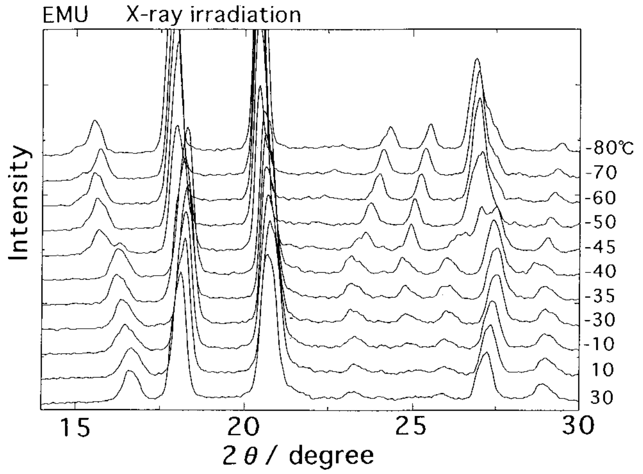

Figure 11. Temperature dependence of the X-ray diffraction profile measured for the powdered EMU crystal in the dark room.

Structural Changes at Low Temperature. Matsumoto et al. revealed that the EMU crystal does not polymerize at low temperature even when a high enough amount of light is irradiated.[10,11] We speculated this low reactivity at low temperature may come from the structural change of monomer crystal. To check this possibility, the DSC measurement was carried out, as shown in Figure 10. The endothermic peak was observed at about 55 °C, corresponding to the melting point of EMU crystal. The broad and very small endothermic peak of $\Delta H = 8.5$ J/g could be detected in the temperature range from −45 to −20 °C, suggesting a possibility of crystal structural change.

To investigate the structural change in this temperature range in more detail, the X-ray diffraction measurement of the powdered EMU crystal was carried out at the various temperatures. As shown in Figure 11, the X-ray diffraction profiles change drastically at about −45 °C. The new reflections began to appear around −45 °C and coexisted with the original reflections

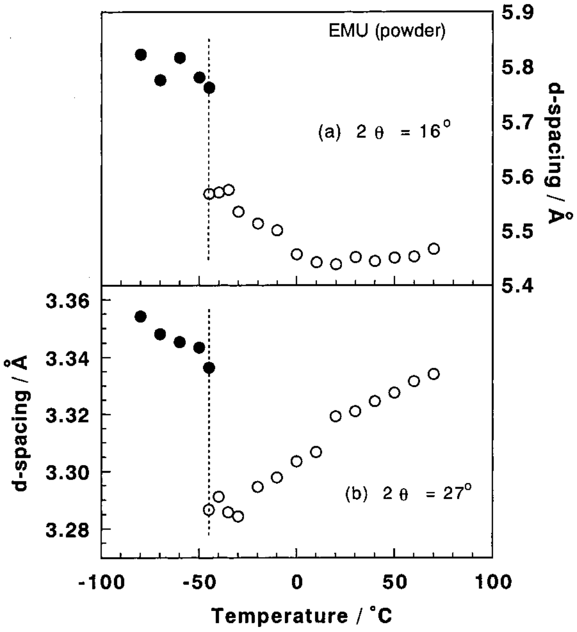

Figure 12. Temperature dependence of lattice spacings of the EMU crystal evaluated for the reflections at (a) 16° and (b) 27°. The X-ray diffraction data shown in Figure 11 were used.

observed at lower temperature. The temperature dependence of the lattice spacings of the two reflections located near $2\theta = 15.8°$ and 27.0° are shown in Figure 12, a and b, respectively. Below −45 °C, the reflection positions shift continuously with temperature due to the thermal expansion of the crystal. Around −45 °C the X-ray reflections change both their position and intensity discontinuously, indicating the thermodynamically first-order phase transition from the low-temperature phase to the high-temperature phase of the monomer crystal. As the temperature increases furthermore, the reflections behave in a similar way to that observed in Figure 2 due to the combined effect of polymerization reaction and thermal expansion.

To confirm that the EMU crystal does not polymerize at such a low temperature below −45 °C, the X-ray diffraction profiles were measured repeatedly at −80 °C for about 2 h. Different from the measurement at room temperature (Figure 2), the X-ray profile did not change at all as shown in Figure 13.

That is, the crystal structure of the EMU monomer at room temperature can be polymerized by light beam irradiation, while the crystal structure obtained by the phase transition below − 45 °C cannot cause the polymerization reaction. This experimental result is quite important to realize that the activity of the solid-state polymerization is governed by the packing mode of monomer molecules in the crystal lattice. To confirm it, we have to carry out the structural analysis of monomer crystals at low temperature as well as at room temperature.

Conclusions

As described in this paper, the EMU crystals polymerize by light irradiation and give the highly regular crystalline polymer, although this crystalline polymer contains the disorder along the chain direction. The X-ray diffraction and the IR and Raman spectra measured during the polymerization reaction could show us clearly the occurrence of structural change from the monomer crystal to the polymer crystal. To clarify the polymerization mechanism from the molecular level, we have to carry out the structure analysis of the initial monomer crystal and that of the resultant polymer crystal and also investigate the concrete structural change in the course of the polymerization reaction. At the present stage, unfortunately, it is actually quite difficult to carry out the crystal structure analysis because the polymerization reaction of the EMU crystal occurs too rapidly under the irradiation of X-ray beams to collect the X-ray reflections necessary for the structure analysis by using the conventional X-ray diffraction system. We are now trying to carry out the X-ray diffraction measurements of this sample by utilizing the X-ray CCD camera. The results will be reported as soon as possible.

The EMU crystals do not polymerize at low temperature below −45 °C. The DSC and powdered X-ray diffraction measurements revealed that this change in the reaction activity comes from the structural change in the phase transition at the low temperature. In other words, the intimate relation between the polymerization reactivity and the packing mode of molecules could be detected clearly for the EMU crystal system. A detailed structural analysis is needed to clarify what occurs at the transition temperature of ca. −45 °C.

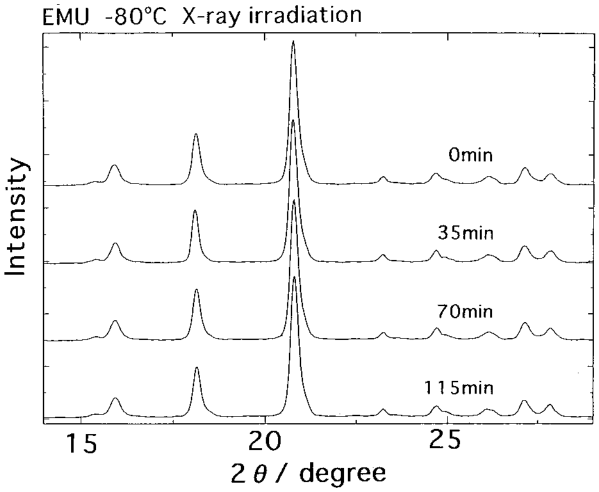

Figure 13. X-ray diffraction profiles measured for the powdered EMU crystal at −80 °C as a function of X-ray irradiation time.

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