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Generation and relaxation of large stress in the photoinduced solid-state polymerization reaction of diethyl muconate detected by simultaneous time-resolved measurement of X-ray diffraction and Raman spectra

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Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

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Abstract

Simultaneous measurement of X-ray diffraction and Raman spectra has been performed for studying the structural changes in the photoinduced solid-state polymerization reaction of diethyl *Z*,*Z*-muconate (EMU) single crystal. As the reaction proceeded, the X-ray reflections coming from the polymer species started to appear and shifted the positions toward those of the finally attained polymer product. The Raman bands of the polymer species were also found to shift their frequencies toward those of the final polymer. From these experimental data, combined with the previously reported information on crystal structure and Raman shift data collected for stressed polymer single crystal, it was deduced reasonably that the polymer chains generated in the initial stage of reaction were strongly stressed because of the geometrical constraints coming from the surrounding monomer matrix and that the stress was gradually relaxed as the reaction proceeded.

Keywords: Photoinduced solid-state polymerization; Diethyl *Z*,*Z*-muconate; Raman spectra

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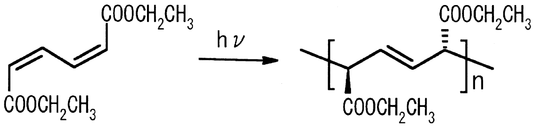
1. Introduction

Photoinduced solid-state polymerization reaction has attracted much attention because of its distinguished selectivity in the reaction and specific regularity of the product. The bulk single crystal of trioxane or tetraoxane, for example, changes to polyoxymethylene by the γ-ray irradiation at elevated temperature [1–4]. But the obtained polymer product was polycrystal, not single crystal. Among the various types of monomer crystal, there have been reported some specific cases, in which the polymer product keeps the morphology of the initial monomer crystal and the giant single crystal is obtained. The reaction occurs without any loss of lattice symmetry. Some examples are seen for 2,5-distyrylpyradine [5–8], diacetylene derivatives [9–11] and *Z*,*Z*-muconate derivatives [12–17]. In the last case, in particular, diethyl *Z*,*Z*-muconate (EMU) is polymerized by an irradiation of γ-ray, X-ray or ultraviolet light to give a giant polymer single crystal [12–15]. We call this polymer polyEMU in this paper.



In the previous paper [18], we analyzed the crystal structures of EMU monomer and polyEMU by carrying out the rapid-scan X-ray diffraction measurement in the course of solid-state polymerization reaction by means of 2-dimensional CCD camera detector. Fig. 1 shows a comparison of crystal structure between the initial monomer and the final polyEMU. The carbon atoms of *Z*,*Z*-butadiene part of an EMU molecule are connected, as indicated by

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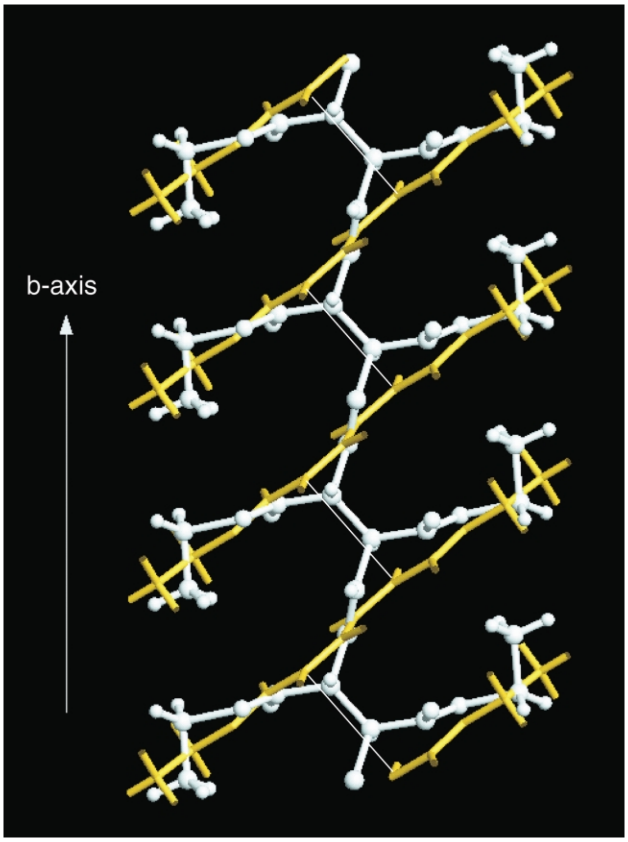

Fig. 1. Crystal structures of EMU monomer and polyEMU [18].

white lines, covalently with those of the adjacent molecules arrayed along the *b*-axis to give a polymer chain. When the cross section of the molecule is viewed along the *b*-axis, the center of cross section is not changed and the space group symmetry is preserved before and after the reaction. The morphology of the sample is also kept and a polymer single crystal is obtained in large size. This photoinduced solid-state polymerization is a typical topotactic reaction, a special case of topochemical reactions.

The sensitive X-ray CCD detector allowed us to continuously collect a set of about 5000 reflections for every 13 min and to analyze the structural change in the EMU monomer single crystal on the way of polymerization reaction. In the previous paper [18], we stated the thus-obtained structural change only briefly. It might be useful to describe that result in more detail in order to make the problem to be solved in the present paper clearer. The relative intensity and position of the observed X-ray reflections changed gradually, and the structure parameters changed as shown in Fig. 2, where the unit cell parameters and the molecular geometry (C–C and C=C bond lengths) are plotted against irradiation time of X-ray beam. It should be noticed that the information shown in this figure was obtained from the reflection data of the monomer species, but these data contained the contribution from the polymer species to some extent. Therefore the structure parameters shown here are considered to have some influences from the polymer molecules generated on the way of reaction. The *b* axial length parallel to the chain direction was decreased, while the *a*- and *c*-axes perpendicular to the chain direction were increased. Although the total experimental time was not long enough because of a limited computer memory, these parameters look to approach the values of the polymer crystal at a final stage. The *c* axial length did not change at first but should be shortened on the way of reaction. The C=C bond length of *Z*,*Z*-butadiene part became longer and approached the length of C–C bond in the skeletal chain of polymer. At the same time the C–C bond length of the monomer was shortened and changed toward the length of the C=C bond of the polymer skeleton. In this way the X-ray structure analysis gave us information on the *averaged* structural change from the monomer to the polymer. By calculating the so-called F_o–F_c Fourier transform based on the observed (F_o) and calculated (F_c) structural factors, information on the structural evolution of the polymer species could be obtained also as a function of time, but unfortunately the accuracy was not high enough to allow us the detailed discussion about the structural change.

In order to know more detailed information on the structural change in the polymerization reaction, other such method as vibrational spectroscopy may be useful because it is sensitive to the slight change in local structure. Of course the X-ray diffraction method cannot be ignored for the structural investigation. Therefore it is desirable to combine the experimental data given by these two methods. But these different types of experiments are usually performed separately for the different samples, and therefore we do not have any confidence about the identity of the experimental condition. More ideal experiment is to carry out the simultaneous measurement of X-ray diffraction and Raman scattering for a single crystal in the course of polymerization reaction under the irradiation of X-ray beam, which works as a source for the photoinduced reaction. We applied this simultaneous measurment technique to the study of photoinduced polymerization reaction of EMU.

Some of the data were already reported briefly in the previous paper concerning the development of the simultaneous measurement system [19]. In the present paper more detailed discussion will be made about the structural change in the photoinduced solid-state polymerization reaction from the microscopic point of view. As described in this paper, not only the intensity but also the position of the X-ray reflections and Raman bands changed as the reaction proceeded. These data can be used for evaluating the strain (and stress) generated in the crystal state during the transformation from monomer to polymer species.

Detection of stress in the photoinduced polymerization reaction was reported for polydiacetylene [20,21]. In this case, however, the Raman spectra were measured for the different samples with various degrees of polymerization, which had been obtained by quitting the polymerization

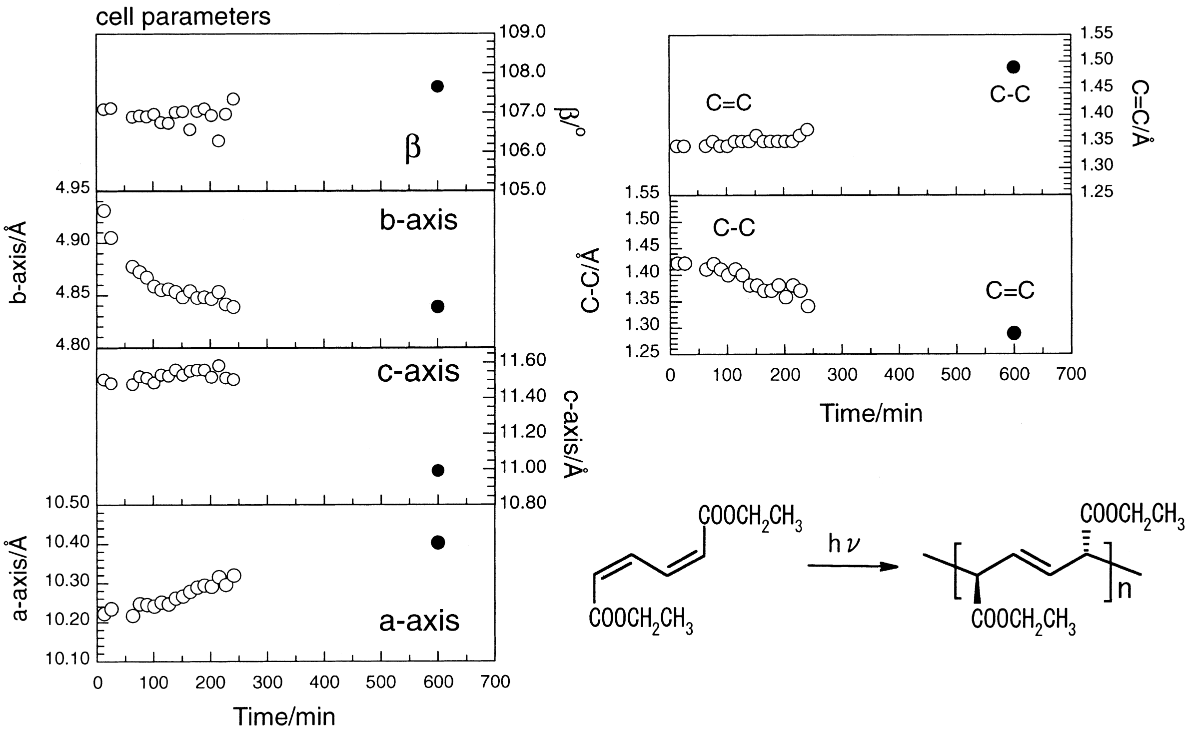

Fig. 2. Time dependence of crystal lattice parameters and CC bond lengths of EMU obtained from the analysis of X-ray reflection data collected in the photoinduced polymerization reaction process [18].

reaction after irradiating a light for a fixed time, not an in situ measurement. In such a sense, the present study is considered to be the first trial to directly trace the structural change during the solid-state polymerization reaction about the EMU monomer.

2. Experimental

2.1. Samples

The needle like single crystals of EMU were prepared from a hexane solution at room temperature. The high-quality sample was chosen and was set on the X-ray goniometer head. The sample was rotated around the needle axis during the measurement in order to get as many reflections as possible. The Raman signals were also averaged by rotating the sample to erase the effect of polarization. These operations were performed in the dark room so that the monomer did not polymerize by an external light.

2.2. Simultaneous measurement system

Fig. 3 shows an illustration of our simultaneous measurement system of X-ray diffraction and Raman spectra [19]. In this system, a miniature Raman spectrometer and X-ray CCD detector were set around the sample. A graphite monochromatized Cu Kα ($\lambda = 1.5418$ Å) line generated from a MAC Science SRA18A rotating anode X-ray generator was used as an X-ray source. The X-ray beam was used as an excitation light source of the photoinduced solid-state polymerization reaction as well as an incident beam for X-ray diffraction measurement. The scattered X-ray signal was detected using a CCD camera (Hamamatsu Photonics Co. Ltd). The Raman spectra were measured by Chromex Raman 2000 spectrometer system at a resolution of 2 cm^{-1}. A semiconductor laser of 785 nm wavelength was used as an excitation light source. The details of this system are described in Ref. [19]. The Raman and X-ray diffraction measurements were synchronized and both were performed for every 3 min.

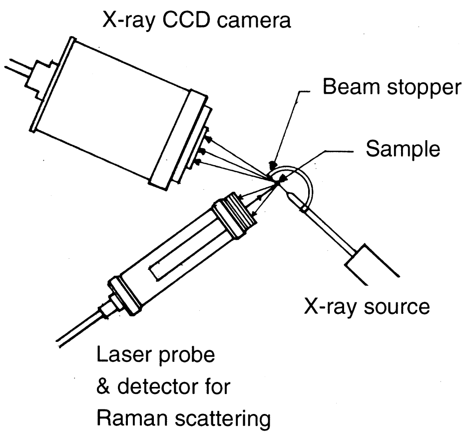

Fig. 3. A system of simultaneous measurement of X-ray diffraction and Raman spectra [19].

3. Results and discussion

Fig. 4 shows the change in the 2-dimensional X-ray diffraction pattern detected by CCD camera. The reflections were observed upward and downward from the exact equatorial line, coming from the slight misalignment of the sample axis. As the reaction time passed, new reflections started to appear, which were considered to come from the generated polymer species. The reflection indices shown in this figure are for the monomer crystal at 0 min and for the polymer crystal at 60 min. Fig. 5 shows the X-ray diffraction profile obtained by integrating the reflection intensity of Fig. 4. As the X-ray irradiation time increased the reflections originated from monomer species decreased in intensity. Correspondingly the new reflections of polymer appeared and increased in intensity. Many reflections of polymer species overlapped with those of monomer in the limited scattering angle region of the experiment, but the (102) reflection of polymer showed the peak clearly and was found to shift the position as the reaction proceeded. This shift of reflections was already reported in the previous paper [15].

Similar phenomenon was observed in the Raman spectra. The time dependence of Raman spectra is shown in Fig. 6. As the polymerization started under the irradiation of X-ray beam, the Raman bands of monomer species began to decrease in intensity and the bands characteristic of polymer species appeared and increased in intensity. More detailed spectral change in the frequency range of 1020–990 cm^{-1} and 900–850 cm^{-1} are shown in Fig. 7(a) and (b), respectively. These spectral profiles were deconvoluted to the components by a computer software (WinIR Pro, Digilab) in order to erase the effect of band overlap. The 1010 cm^{-1} band assigned to the anti-symmetric stretching mode [ν (C–C)] of skeletal C–C bond of polymer species increased in intensity and shifted its peak position to higher frequency side as the reaction proceeded. In Fig. 7(b), the polymer band at 869 cm^{-1}, assigned to the CH_3 rocking mode of the side chain [r (CH_3)], increased in intensity and shifted to lower frequency side. The 889 cm^{-1} band of

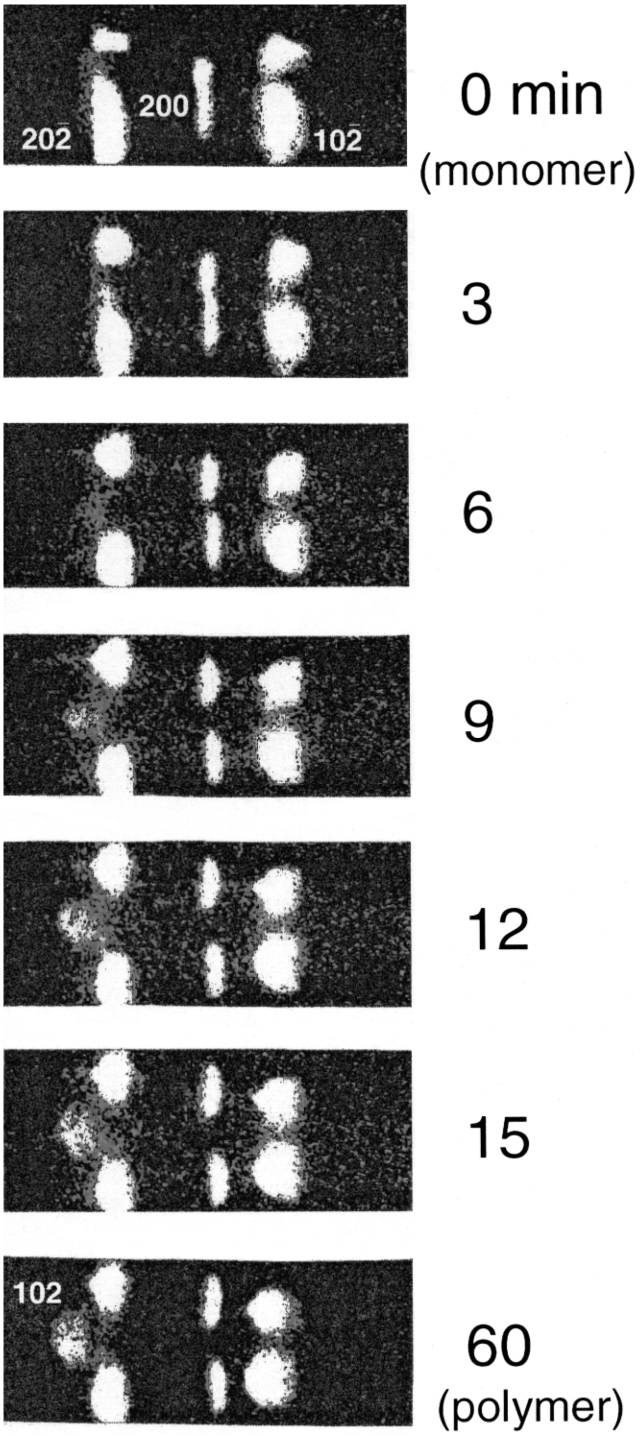

Fig. 4. Time dependence of 2-dimensional X-ray reflection pattern taken in the photoinduced polymerization reaction of EMU single crystal. The ($20\bar{2}$), (200) and ($10\bar{2}$) at the top are indices of monomer crystal and (102) at the bottom is that of polymer crystal.

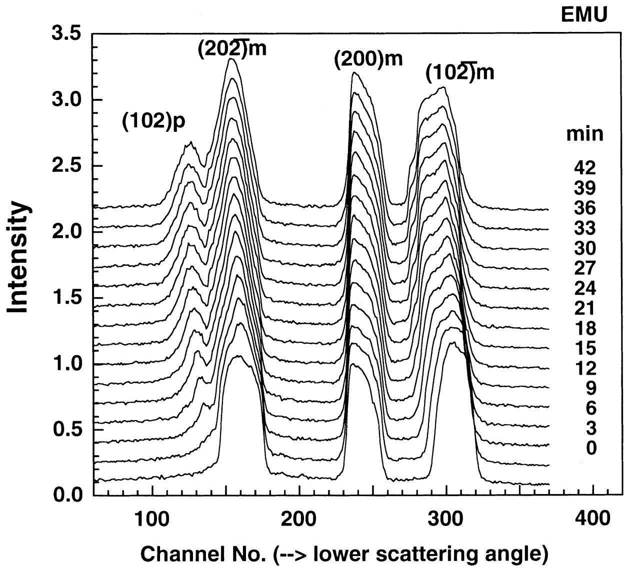

Fig. 5. Time dependence of X-ray diffraction profile of EMU single crystal in the photoinduced polymerization reaction (p: polymer and m: monomer). Larger channel number corresponds to lower scattering angles.

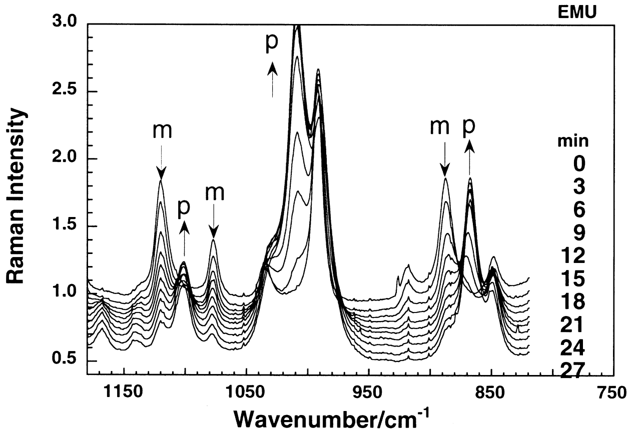

Fig. 6. Time dependence of Raman spectra in the photoinduced polymerization process of EMU single crystal (p: polymer and m: monomer).

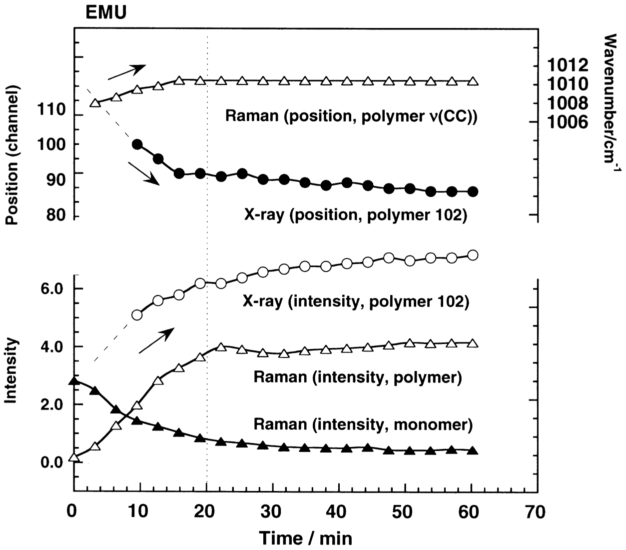

Fig. 8. Time dependence of the intensity and peak position evaluated for the X-ray (102) reflection (polymer) and the Raman bands at 1010 cm^{-1} (polymer) and 889 cm^{-1} (monomer).

monomer species decreased in intensity and shifted to lower frequency side, although the magnitude of peak shift was dependent on the band.

The time dependence of the intensity and peak position is shown in Fig. 8 for the X-ray (102) reflection and the Raman bands characteristic of the polymer [ν (C–C) at 1010 cm^{-1}] and monomer (889 cm^{-1}) species. The intensity of Raman band of the polymer species increased as the reaction proceeded under the irradiation. After 20 min the increasing rate of the intensity became lower for both the Raman bands and the X-ray reflections, indicating an approach of the reaction to the end. The shift of X-ray reflection position indicates a generation of strain in the crystal lattice of polymer during the reaction. Because the time scale is different between Figs. 2 and 8 due to the differences in the sample size, X-ray beam intensity, measurement conditions, etc., it may be difficult to compare the time dependence of (102) reflection in Fig. 8 with the changes in the unit cell parameters indicated in Fig. 2. According to the result of Fig. 2 the *a*-axial length increased and the *c*-axial length decreased in the process from the monomer to the polymer. The observation of the lattice spacing contraction in the 102 direction (Fig. 8) is consistent with this change in the unit cell parameters. The shift of the Raman band of polymer skeletal chain indicates the generation of strain on the molecular chain. These strains of crystal lattice and molecular chain were released gradually as the reaction time reached around 20 min.

In the previous study we reported the tensile stress dependence of Raman band frequency measured for the polyEMU giant single crystal [22]. The bands related to the skeletal vibrational modes were found to show relatively

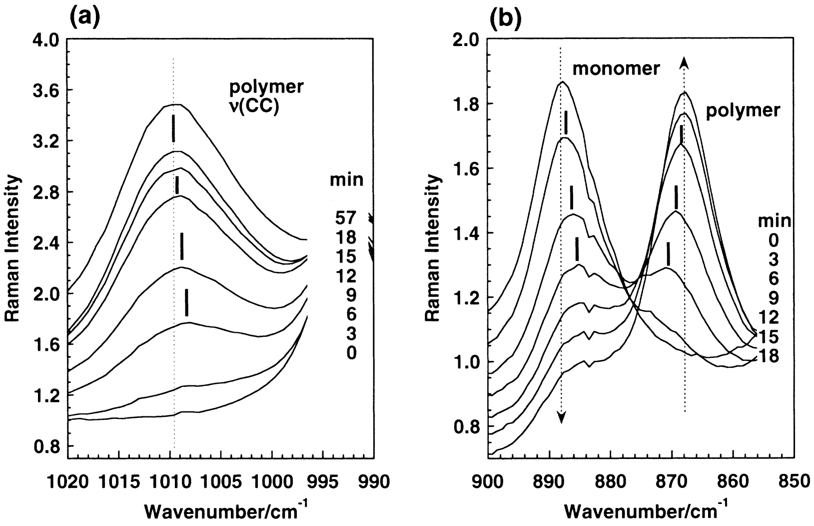

Fig. 7. Time dependence of Raman spectra measured for (a) the skeletal C–C stretching band [ν (C–C)] and (b) the methyl rocking mode [r (CH_3)] of polyEMU in the photoinduced polymerization process.

large low-frequency shift when the tensile stress was applied to the polymer crystal, while the other bands related with the vibrations of side groups did not shift or shifted rather to higher frequency side. For example, the C–C skeletal stretching mode [ν (C–C)] showed a shift of $-2.0\ \mathrm{cm}^{-1}$/GPa, while methyl rocking mode [r (CH_3)] gave a shift of $+1.2\ \mathrm{cm}^{-1}$/GPa. As shown in Fig. 7(a), the ν (C–C) band of the polymer species shifted by about $2\ \mathrm{cm}^{-1}$ toward *higher* frequency in a progress of reaction. Thus the polymer chain generated at the initial stage of reaction was thought to be highly tensioned. The shift of this Raman band toward higher frequency side indicates a relaxation of the tensioned polymer chain during the reaction. The low-frequency shift of r (CH_3) band is also consistent with this idea because the band has a positive shift factor. Since the shift factor of ν (C–C) band is $-2.0\ \mathrm{cm}^{-1}$/GPa, the $2\ \mathrm{cm}^{-1}$ shift at the initial stage of the reaction corresponds to the tensile stress of about 1 GPa, which worked positively along the polymer chain axis. The Young's modulus of polyEMU single crystal is 47.1 GPa [22]. Therefore the tensile stress of 1 GPa corresponds to the strain of about 2%, if this modulus is applied as it is. As seen in Figs. 1 and 2, the repeating period of monomer molecules along the b-axis is 4.93 Å, which is longer than the repeating period of polymer chain 4.84 Å by 1.86%, which is in good agreement with the strain value estimated above. That is to say, the polymer species created in the early stage of reaction is considered to have almost the same repeating period with that of the monomer crystal.

From these data the polymerization mechanism of polyEMU may be illustrated as shown in Fig. 9. At the initial stage of the reaction the neighboring monomer molecules start to be combined together covalently along the b-axis to form a polymer chain segment. But the geometrical constraint from the surrounding monomers prohibits the polymer chain to transform to more stable structure and the repeating period is fixed to the value almost equal to that of the original monomer lattice. As a result a large tensile force works on the polymer chain. This stress is estimated as high as 1 GPa from the shift of Raman frequency (Unfortunately because of the apparatus problem, the observed Raman bands of polymer were limited. More exact evaluation of stress may be possible when more number of Raman bands can be measured in the experiment). As the reaction proceeds the polymer component becomes dominant and the stress relaxation occurs. As a result the b-axis approaches gradually to that of stable polymer.

As another possibility to interpret the band shifts of polymer in the reaction process, we may consider the dependence of vibrational frequency on the length of growing polymer chain. The so-called progression bands of n-alkane chains are one typical example [23]. An alkane chain shows a series of bands depending on the phase relation between the adjacent methylene units or on the chain length. As the chain length increases toward the infinite polyethylene chain, the relative intensity of the most-in-phase band becomes prominent. In the present case of EMU, we did not detect any progression bands coming from the oligomers of polyEMU, because the intensities of the progression bands must have been weak due to the low population of short polyEMU chains at the initial stage of reaction and also because the most-in-phase band should have become main when the polymer chain length grew to some extent. Besides these oligomer components are stressed more or less by the surrounding matrix as known from the X-ray data, making the situation complicated. That is to say, we need to take these two contributions (stress and chain length) into consideration for more detailed interpretation of the Raman data. In order to make these situations clearer, we will have to perform the time-resolved experiment in more detail, although it will be quite difficult to collect the bands with higher signal-to-noise ratio at higher time resolution. In the present paper, therefore, we discussed the important effect of stress as given in the preceding sections which was one of the most plausible interpretation ways of the experimental data.

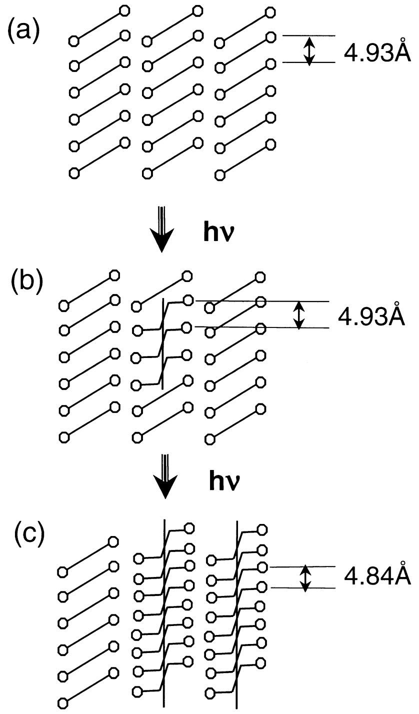

Fig. 9. Schematic illustration of photoinduced polymerization process of EMU. Starting from a monomeric crystal (a), the polymer chains are created (b) and grow to form the crystal domain (c). At the stage (b) the repeating period of polymer species is the same with that of the monomer matrix, generating a high stress along the chain axis.

4. Conclusions

In the present study, the simultaneous X-ray and Raman measurement was carried out in order to clarify the structural change in the photoinduced solid-state reaction of EMU. The peak positions of X-ray reflections and Raman bands of the polymer species were found to shift as the reaction proceeded, indicating that the initial polymer was appreciably tensioned along the chain axis in the monomer matrix. The stress working on the polymer chain was estimated as high as 1 GPa. This strain was relaxed as the total number of polymer chains increased in the sample. Similar observation was made for diacetylene case, where the strain of ca. 3% or the stress of 1.2 GPa was generated along the chain axis (The Young's modulus 40 GPa) [21]. In the case of polyEMU, generation of 1 GPa is equivalent to the application of about 3.2 kg if we stretch a thin fiber of 200 μm diameter by loading a weight along the chain axis. This is a quite heavy weight for the polymer!

In this way it has been suggested that a quite high stress is generated in the photoinduced solid-state polymerization reaction of EMU. This high stress is considered to come from the difference in repeating period between the monomer and the polymer (see Fig. 9). Therefore, if the repeating period of monomer molecules in the crystal lattice is largely different from that of polymer lattice, an extremely large stress should be generated and the single crystal will be broken. In such a case only the polycrystalline product will be obtained. If the crystal structure of polymer produced on the way of reaction can overcome this large stress, then the giant single crystal of polymer can be obtained. The solid-state polymerization reaction in a large monomer single crystal is one good idea to obtain a giant polymer single crystal with highly ordered aggregation structure of chains. If such a giant single crystal can be produced for any kind of monomer, many unsolved problems in the research field of polymer solids might be erased away. Such a large polymer crystal may have many possibilities for industrial application. But, in such a trial of molecular design of new monomer, we need to consider not only the geometrical factors of the monomer crystals [24, 25] but also the mechanical factors as discussed in the present paper.

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