

# Relationship between Packing Structure and Monomer Reactivity in the Photoinduced Solid-State Polymerizations of Muconic Diesters with Different Side Groups

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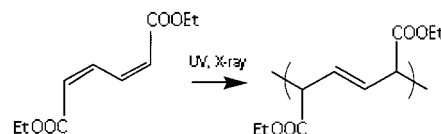
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To clarify the relation between packing structure and reactivity of monomer molecules in the photoinduced solid-state polymerization, we analyzed crystal structures by X-ray diffraction for a series of dialkyl muconates with various types of side group. Single crystal of diethyl (Z,Z)-muconate (diethyl (Z,Z)-2,4-hexadiendioate) changed into the stereoregular polymer crystal by irradiating visible or ultraviolet light at room temperature. The dicyclohexyl (Z,Z)-muconate and the dibenzyl (Z,Z)-muconate showed the isomerization reactions from (Z,Z) form to (E,E) form. The bisdecyl (Z,Z)-muconate and bis(2,2,2-trichloroethyl) (Z,Z)-muconate changed into amorphous polymers. All the compounds used in this study have the columnar structures. The distance of the butadiene carbon atoms of the neighboring molecules along the columnar axis was 3.5–6.4 Å; almost no correlation could be found with the reactivity. The tilt angle of molecular axis from the columnar axis was estimated to be 38–78°, which could not be assumed as a good index to represent the reactivity of monomer molecules. Rather, a set of the distance and the tilting angle seems to be better index, but it could not necessarily explain the difference in the reactivity for all the substances. The free volume or the cavity between molecules is also not a proper measure. The degree of overlap of  $\pi$ -electron orbitals between the butadiene carbon atoms of the neighboring molecules was found to work as a relatively good measure of their reactivity. The systematic study of the molecular packing geometry for a series of muconate derivatives brought up a very important warning about the conventionally made discussion on the factors governing the solid-state polymerization reaction based on only the interatomic distance, the tilting angle of the molecules, etc.

## Introduction

Solid-state polymerization reactions induced by irradiation of UV light, X-ray, or  $\gamma$ -ray have been reported for several kinds of monomer crystals. For example, polyoxymethylene crystal is synthesized from trioxane or tetraoxane single crystal by irradiating  $\gamma$ -rays at a controlled temperature.<sup>1,2</sup> Light-induced polymerizations of 2,5-distyrylpyrazine and diacetylene derivatives are another well-known examples.<sup>3–7</sup> These photoinduced polymerization reactions are one branch of the so-called topochemical reactions, which were reported for a variety of organic and inorganic substances.<sup>8,9</sup> In the topochemical reaction, the geometrical relation between the compounds existing before and after the reaction is very important for speculation of the reaction mechanism from the molecular level. In particular the symmetrical relationship is important in the discussion of the spatial restriction of the molecules during the solid-state chemical reactions. As to the monomers mentioned above, the cases of 2,5-distyrylpyrazine and diacetylenes are typical examples where the symmetry of the molecular packing is unchanged before and after the reaction. In these cases, the reactions proceed homogeneously through the bulk materials, and the single crystalline polymeric materials are obtained. This special case of topochemical reaction is called the “topotactic” reaction.<sup>10</sup>

Several years ago, Matsumoto et al. found that the single crystal of diethyl (Z,Z)-muconate (EMU: diethyl (Z,Z)-2,4-hexadiendioate) yielded polymer single crystal by irradiation of UV light, X-ray, or  $\gamma$ -ray at room temperature.<sup>11–13</sup> The obtained polymer is almost perfectly stereoregular and has the ultrahigh molecular weight.



This reaction is important because the butadiene ester of simple and popular chemical structure can exhibit the highly controlled solid-state polymerization reaction. This gives us a possibility of developing a new field of morphology-controlled polymerization reaction to produce the highly regular polymer materials with ultrahigh molecular weight. The time-resolved measurements of FTIR and FT-Raman spectra, X-ray powder diffraction, ESR, and so on were reported to reveal the microscopic mechanism of this reaction.<sup>14</sup> One of the best methods of investigating the symmetric relation between monomer and polymer in the crystal lattice is the X-ray structure analysis. Yet the structural change in this reaction occurs quite rapidly on a time scale of several tens of minutes under the irradiation of a powerful X-ray beam. Therefore, the automatic four-circle diffractometer (AFC) and even the highly sensitive

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**TABLE 1: Photoinduced Solid-State Reactions of Muconate Derivatives with Various Side Groups**

reaction	side group
( <i>Z,Z</i> )-form → tritactic polymer (stereoregular polymerization)	ethyl, 4-bromobenzyl, 4-chlorobenzyl
( <i>Z,Z</i> )-form → ( <i>E,E</i> )-form (isomerization)	cyclohexyl, benzyl
( <i>Z,Z</i> )-form → atactic polymer	octyl, decyl, 2,2,2-trichloroethyl, 2,2,2-trifluoroethyl
( <i>E,E</i> )-form → atactic polymer	ethyl, methyl, cyclohexyl, benzyl, octyl, decyl, 2,2,2-trichloroethyl, 2,2,2-trifluoroethyl

X-ray imaging plate system (IP) could not give us the answer because the structure changed rapidly during the collection of the reflection data. The rapid-scan-type X-ray CCD camera system was applied to the collection of the diffraction data of the EMU monomer single crystal.<sup>15</sup> The CCD camera system allowed us to collect a set of two-dimensional diffraction patterns consisting of ca. 5000 reflections every 13 min till the polymerization reaction was completed. Then the crystal structure of both the monomer and polymer could be clarified successfully. EMU single crystal has been found to be the fourth example of the topotactic polymerization reaction with the space group symmetry unchanged through the reaction process.

Matsumoto et al. substituted the ethyl groups of EMU molecule by other kinds of chemical groups such as methyl, cyclohexyl, benzyl, etc. and investigated the reaction behaviors of these compounds. The photoinduced reactions were observed for most of these compounds, but the reaction modes were found to be quite different, depending on the type of side groups. In the previous papers,<sup>16,17</sup> we measured the time dependence of the infrared spectra for these compounds and could classify the reactions into the three types as listed in Table 1. The vibrational spectroscopic study gave us useful information about the kinetics of the chemical reactions, but no detailed discussion could be made about the concrete structural change in these photoinduced reactions. To discuss the difference in the characteristic features of these reactions and to reveal the essential factors governing these reaction modes, we must clarify the packing structure of the molecules in the crystal lattices by X-ray diffraction. In the present paper, the structural analysis was made for a series of muconate derivatives, and the factors which are essentially significant for the photoinduced solid-state reactions were extracted through the geometrical consideration of the packing structures.

## Experimental Section

**Samples.** A series of muconic acid derivatives with various types of side groups were synthesized from (*Z,Z*)-muconic acid [(*Z,Z*)-2,4-hexadienedioic acid], supplied from Mitsubishi Chemicals Co. Ltd., Japan, by the method described in reference.<sup>12</sup> Single crystals for the X-ray structural analyses were grown from the solutions by solvent evaporation at room temperature. Chemical formulas and the solvents used for preparation of the single crystals are listed in Table 2. To avoid an occurrence of light-induced reaction during the preparation of the samples, we ran all the processes under a weak red lamp in the dark room.

**X-ray Diffraction Measurements.** The X-ray diffraction measurements were carried out by using the CCD camera system for the rapidly reacting species and the IP system for the species of low reactivity.

**A. Measurements by CCD Camera System.** For single crystals of EMU, dicyclohexyl (*Z,Z*)-muconate, and dibenzyl (*Z,Z*)-

**TABLE 2: Muconate Derivatives Used in the Present Study and the Solvents for Preparation of Single Crystals**

monomer configuration	side group	solvent
(Z,Z)	ethyl (EMU)	hexane
	methyl	acetone/water = 1/1
	cyclohexyl	hexane
	benzyl	hexane
	2,2,2-trichloroethyl	methanol
(E,E)	<i>n</i> -decyl	acetone
	ethyl	methanol
	methyl	methanol
	cyclohexyl	ethanol
	benzyl	ethanol
	2,2,2-trichloroethyl	methanol

muconate, the rapid-scan-type CCD camera system, Kappa-CCD (Nonius BV, Delft, The Netherlands), was used. The graphite-monochromatized and finely focused Mo-K  $\alpha$  line ( $\lambda = 0.71073$  Å) were used as an incident source at a power of 40 kV and 45 mA. A single crystal was set to the goniometer head under a weak red lamp. The collection of reflection data was made under the following conditions: oscillating angle, 3°; rotation angle around  $\omega$  axis, 0–180°; exposure time, 10 s for 1 shot. It took about 13 min in total to measure the 60 shots, where the read-out time, ca. 3 s for 1 shot, was included. The collected data were analyzed by using the HKL Package developed by Nonius BV, which consisted of a set of software DENZO and SCALEPACK.<sup>18,19</sup> The software DENZO is for indexing the observed reflections and refining the lattice and geometrical parameters of the measurement system such as the rotational axis of the sample, the center position of the oscillation, etc. The SCALEPACK refines the lattice parameters and adjusts the intensity scale between the successive images, from which the exact structure factors are obtained. The crystal structure was solved by using the software maXus developed by Nonius BV, which consisted of a set of software necessary for the determination of the space group symmetry and the least-squares refinement of initial models, etc. The direct method was used to find out the initial models, where the software SIR92 developed by Altmar et al.<sup>20</sup> was used. Least squares refinement was made on the basis of the full matrix method by using the quantity  $\sum w(|F_o|^2 - |F_c|^2)^2$  as a minimized function with the weight  $w = \exp[FA \sin^2 \theta / \lambda^2] / [\sigma^2(F_o) + FBF_o^2]$ , where  $\sigma^2(F_o)$  was the squared standard deviation of the observed structure factor  $F_o$  and the coefficients  $FA$  and  $FB$  were set to the values 0.0 and 0.03, respectively. The reflections satisfying the cutoff condition of  $|F_o| > 3\sigma(|F_o|)$  were used in the least squares refinement, where  $|F_o|$  and  $\sigma(|F_o|)$  were the observed structure factor and its standard deviation, respectively. Because no detectable effect was found, the absorption correction for the observed intensity was not included in the structural refinement. The reliability factors  $R$  and  $R_w$  were defined, respectively, by the following equations:

$$R = \frac{\sum ||F_o|^2 - |F_c|^2|}{\sum |F_o|^2} \quad \text{and} \quad R_w = \left[ \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^2} \right]^{1/2}$$

**B. Measurements by Imaging Plate System.** For the single crystals of diethyl (*E,E*)-muconate, dimethyl (*Z,Z*)-muconate, dimethyl (*E,E*)-muconate, dicyclohexyl (*E,E*)-muconate, dibenzyl (*E,E*)-muconate, bis(2,2,2-trichloroethyl) (*E,E*)-muconate, bis(2,2,2-trichloroethyl) (*E,E*)-muconate, and bisdecyl (*Z,Z*)-muconate, an X-ray imaging plate system DIP3000 (MAC Science Co. Ltd., Japan) was used. As an incident X-ray source the graphite-monochromatized Mo-K $\alpha$  line ( $\lambda = 0.71073$  Å)

TABLE 3: Crystallographic Data of Muconate Derivatives

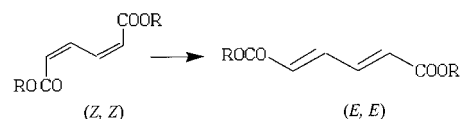
(a) Dialkyl (Z,Z)-Muconate						
side group	ethyl(EMU)	methyl	cyclohexyl	benzyl	trichloroethyl	<i>n</i> -decyl
formula	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>18</sub> H <sub>28</sub> O <sub>4</sub>	C <sub>20</sub> H <sub>18</sub> O <sub>4</sub>	C <sub>10</sub> H <sub>8</sub> O <sub>4</sub> Cl <sub>6</sub>	C <sub>26</sub> H <sub>46</sub> O <sub>4</sub>
mw	198.22	170.16	308.42	322.36	404.89	422.72
crystal system	monoclinic	triclinic	triclinic	monoclinic	orthorhombic	triclinic
space Group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 1
<i>a</i> /Å	10.2320(24)	5.788(7)	5.6200(1)	10.3610(39)	5.860(4)	5.486(14)
<i>b</i> /Å	4.9310(6)	5.722(10)	6.3670(27)	5.6900(10)	10.053(4)	5.498(7)
<i>c</i> /Å	11.4970(28)	6.991(10)	12.8940(54)	14.8380(60)	27.213(48)	22.127(27)
$\alpha$ /deg	90.00	93.081(40)	91.310(20)	90.000	90.000	92.637(20)
$\beta$ /deg	107.146(10)	109.559(20)	92.510(30)	106.083(20)	90.000	91.880(60)
$\gamma$ /deg	90.000	94.794(30)	109.736(20)	90.000	90.000	95.942(60)
<i>V</i> /Å <sup>3</sup>	554.29(22)	216.59(56)	433.51(18)	840.52(29)	1603.19(48)	662.63(26)
<i>Z</i>	2	1	1	2	4	1
<i>R</i>	0.0426	0.0682	0.0309	0.0460	0.0387	0.0628
<i>R<sub>w</sub></i>	0.0432	0.1017	0.0319	0.0586	0.0409	0.0691
(b) Dialkyl (E,E)-muconate						
side group	ethyl	methyl	cyclohexyl	benzyl	trichloroethyl	
formula	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>4</sub>	C <sub>18</sub> H <sub>28</sub> O <sub>4</sub>	C <sub>20</sub> H <sub>18</sub> O <sub>4</sub>	C <sub>10</sub> H <sub>8</sub> O <sub>4</sub> Cl <sub>6</sub>	
mw	198.22	170.16	308.42	322.36	404.89	
crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic	
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	
<i>a</i> /Å	7.849(13)	5.810(8)	5.651(7)	9.152(22)	10.1479(9)	
<i>b</i> /Å	17.080(50)	5.820(6)	9.348(19)	5.706(6)	6.067(30)	
<i>c</i> /Å	8.457(13)	6.804(13)	9.276(20)	16.959(24)	13.433(17)	
$\alpha$ /deg	90.000	105.091(40)	103.701(60)	90.000	90.000	
$\beta$ /deg	91.218(40)	106.335(7)	97.520(20)	104.683(60)	107.357(40)	
$\gamma$ /deg	90.000	92.146(30)	107.409(20)	90.000	90.000	
<i>V</i> /Å <sup>3</sup>	1133.50(47)	211.64(55)	433.37(43)	856.70(56)	789.30(29)	
<i>Z</i>	4	1	1	2	4	
<i>R</i>	0.0511	0.0391	0.0463	0.0385	0.0399	
<i>R<sub>w</sub></i>	0.0521	0.0525	0.0489	0.0402	0.0418	

was used, which was generated from the SRA-M18XHF rotating anode X-ray generator (50 kV and 200 mA). The data collection was performed by the XDIP software (Mac Science). The sample was oscillated in a range of 5° over a total rotation angle of 0–120° around the  $\omega$  axis. The exposure time was 30 min for one image. It took about 12 h to collect the 24 images in total. The data were analyzed by using the software DENZO and SCALEPACK. The crystal structure was solved by using maXus (Nonius BV, Delft). The concrete procedures were essentially the same as those described in the above section for CCD camera system.

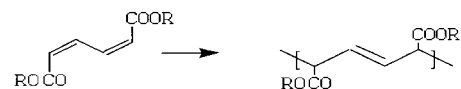
## Results and Discussions

**Crystal Structure of Muconate Derivatives.** The obtained crystallographic data are listed in Table 3. The packing structures of monomer molecules are shown in Figure 1. The fractional coordinates of atoms in the unit cells are given in the Appendix. In the previous study, it was clarified that the EMU molecules form the columnar structure in the crystal lattice.<sup>15</sup> The molecules are stacked along the *b*-axis with the distance of about 3.8 Å between the carbon atoms of the butadiene groups of the neighboring molecules. The polymerization reaction occurs along the columnar axis, as shown in Figure 2, where the structures of monomer and polymer molecules are compared with each other. By forming new bonds between the carbon atoms of the adjacent butadiene groups, the monomer molecules change into the monomeric units of the polymer chain without any remarkable displacement of their centers of mass. The other kinds of monomers are found to show the similar columnar structures. In most cases, the distance between the butadiene carbon atoms of the neighboring molecules along the columnar axis is in the range of 3.5–6.4 Å. 3.5 Å is the distance allowable for the polymerization reaction. Yet some kinds of the muconate monomers experience only the transformation from the (Z,Z)

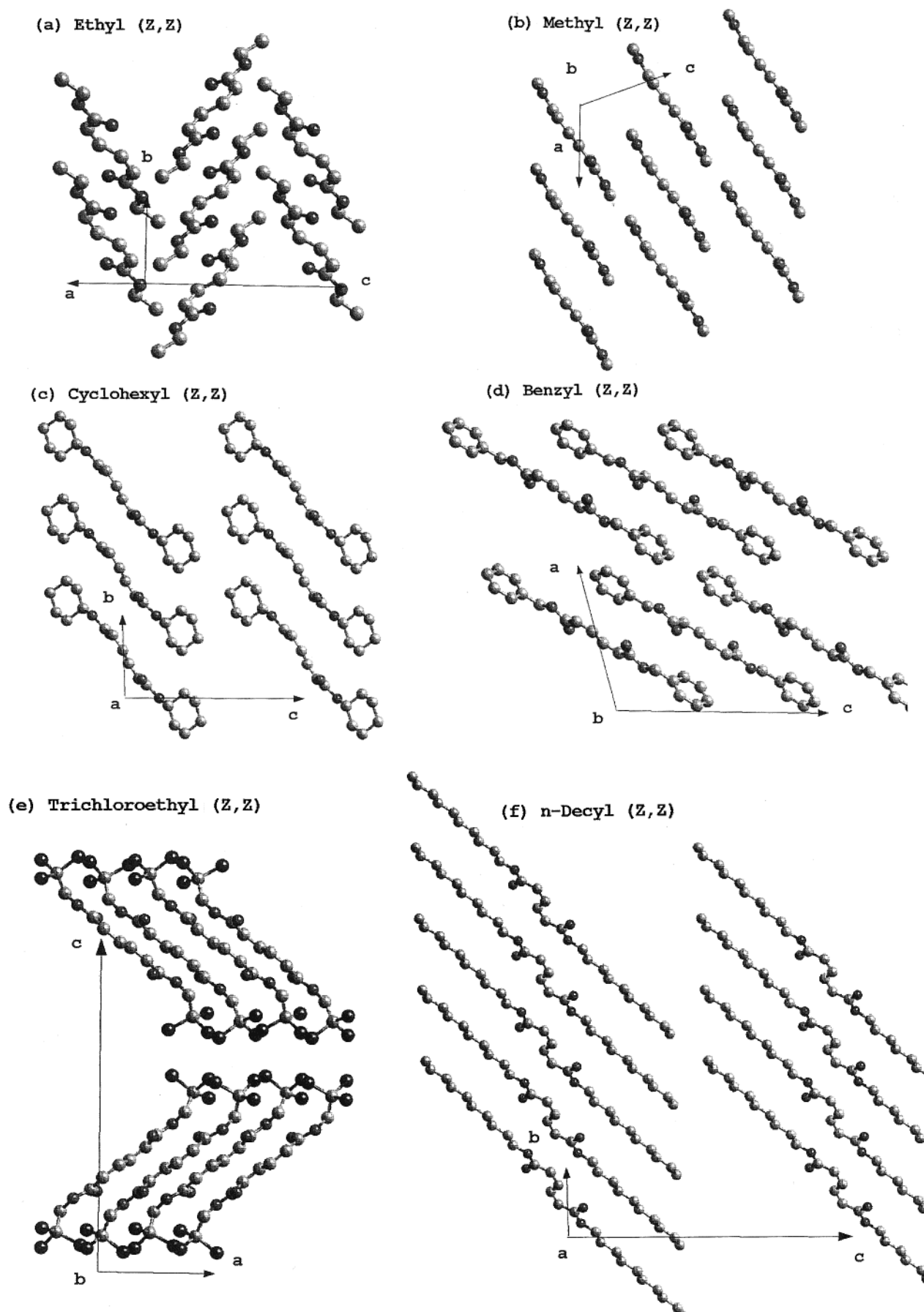
form to the (E,E) form (R = cyclohexyl, benzyl):



and some others show the polymerization reaction without any control of the stereoregularity (R = *n*-octyl, *n*-decyl, etc.).

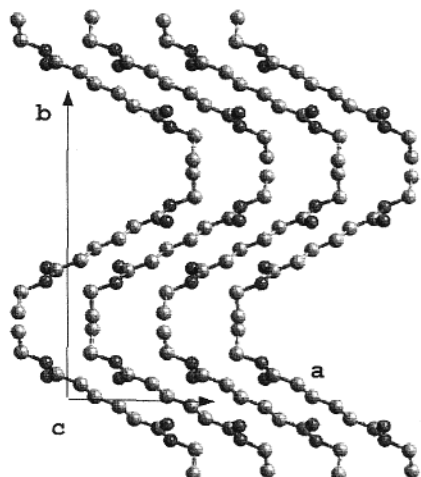


That is to say, the intermolecular carbon-to-carbon distance is not a unique factor for giving a stereospecific polymerization reaction such as the case of EMU. In the case of polydiacetylene derivatives, the two parameters, the intermolecular carbon-to-carbon distance between the diacetylene units and the tilt angle of the skeletal bond of the diacetylene group from the columnar axis, show relatively good correlation with the polymerization reactivity, although some exceptions were pointed out as seen in the case of carbazolyl side group. In the present cases of the muconate esters, we investigated the various other factors in addition to the above-mentioned butadiene carbon–carbon distance. The candidates might be the tilt angle  $\phi$  of the molecular axis from the columnar axis, the distance *d* between the centers of mass of the neighboring molecules, and so on. Table 4 gives the concrete numerical values of these parameters. Figure 3 shows the plot of the two parameters *d* and  $\phi$  evaluated for the various muconates, where new members of muconate with R = *p*-bromobenzyl and *p*-chlorobenzyl, which show the photoinduced polymerization reactions, are also added.<sup>21</sup> As indicated by solid circles, the muconates locating in the (*d*,  $\phi$ ) region around (5 Å, 45°) are polymerized by irradiation of the light. Yet we cannot give rational reasons why the muconates

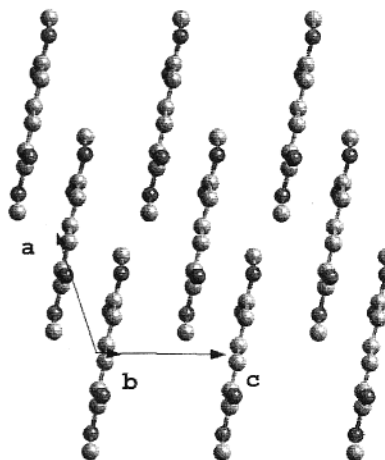


**Figure 1.** Packing structures of a series of muconate derivatives analyzed by X-ray diffraction: (a) diethyl (Z,Z) muconate, (b) dimethyl (Z,Z) muconate, (c) biscyclohexyl (Z,Z) muconate, (d) bisbenzyl (Z,Z) muconate, (e) bistrichloroethyl (Z,Z) muconate, (f) bis-*n*-decyl (Z,Z) muconate, (g) diethyl (E,E) muconate, (h) dimethyl (E,E) muconate, (i) biscyclohexyl (E,E) muconate, (j) bisbenzyl (E,E) muconate, and (k) bistrichloroethyl (E,E) muconate.

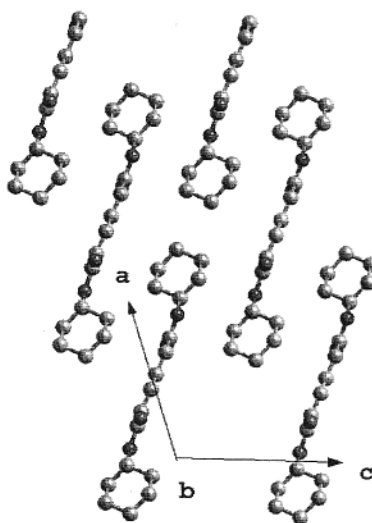
(g) Ethyl (E,E)



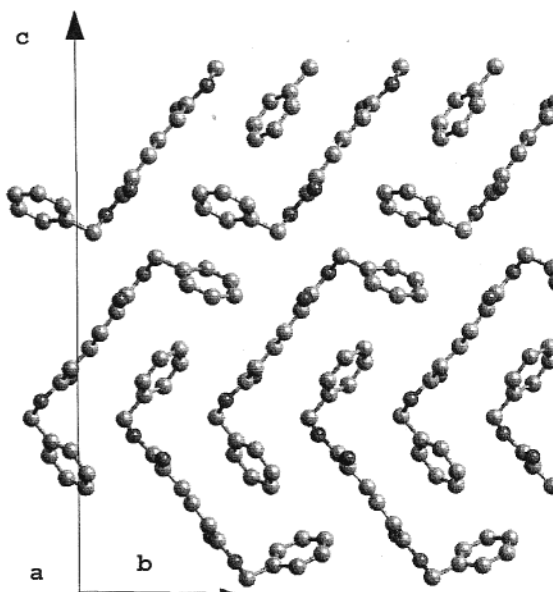
(h) Methyl (E,E)



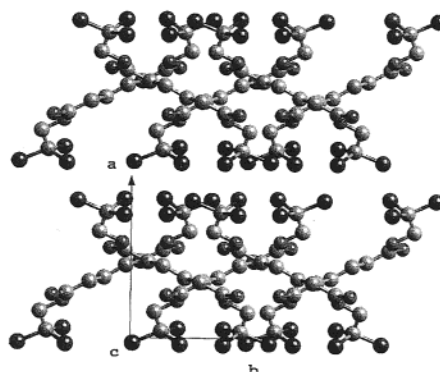
(i) Cyclohexyl (E,E)



(j) Benzyl (E,E)



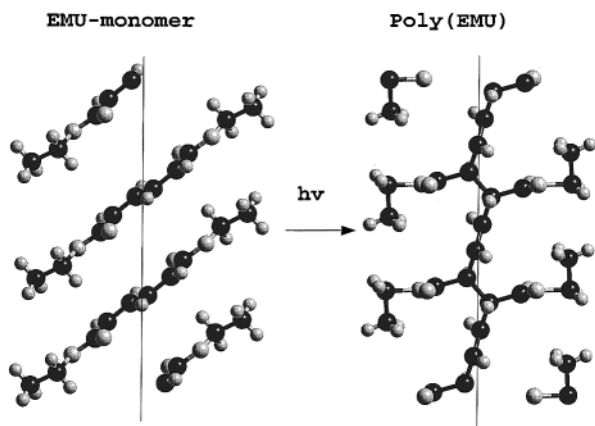
(k) Trichloroethyl (E,E)



having these ( $d$ ,  $\phi$ ) sets can polymerize by photoirradiation. Besides, the compounds exhibiting the isomerization reaction do not show any correlation. The compounds showing the irregular polymerization reaction also are in the similar situation. Larger cavity around the molecules might make the molecular

motion more easy, and so, it could be one factor causing the photoisomerization from the ( $Z,Z$ ) form to the ( $E,E$ ) form.<sup>22</sup> The cavity was calculated for the present cases by using the standard values for the van der Waals radii of the atoms, but no good correlation with the reactivity could be found.



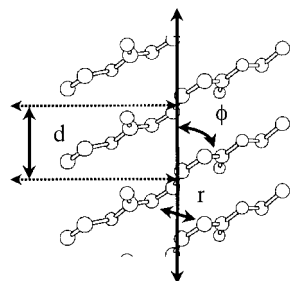


**Figure 2.** Comparison of molecular structure between monomer and polymer of diethyl (Z,Z)-muconate.

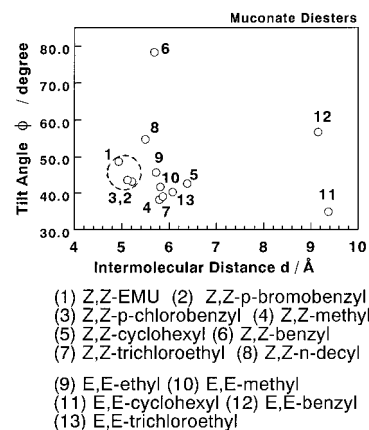
**TABLE 4: Molecular Orientation and Intermolecular Distance along the Columnar Axis of the Various Kinds of Muconate Derivatives<sup>a</sup>**

monomer					
configuration	side group		$r/\text{\AA}$	$d/\text{\AA}$	$\phi/^\circ$
(Z,Z)	1 ethyl (EMU)		3.79	4.93	48.7
	2 bromobenzyl		3.89	5.21	43.2
	3 chlorobenzyl		3.57	5.12	43.6
	4 methyl		3.79	5.79	38.2
	5 cyclohexyl		3.63	6.38	42.6
	6 benzyl		6.42	5.68	78.3
	7 2,2,2-trichloroethyl		4.02	5.86	39.1
(E,E)	8 <i>n</i> -decyl		3.70	5.49	54.8
	9 ethyl		3.64	5.72	45.7
	10 methyl		3.54	5.81	41.7
	11 cyclohexyl		6.76	9.37	34.0
	12 benzyl		7.59	9.15	56.7
	13 2,2,2-trichloroethyl		4.51	6.07	40.3

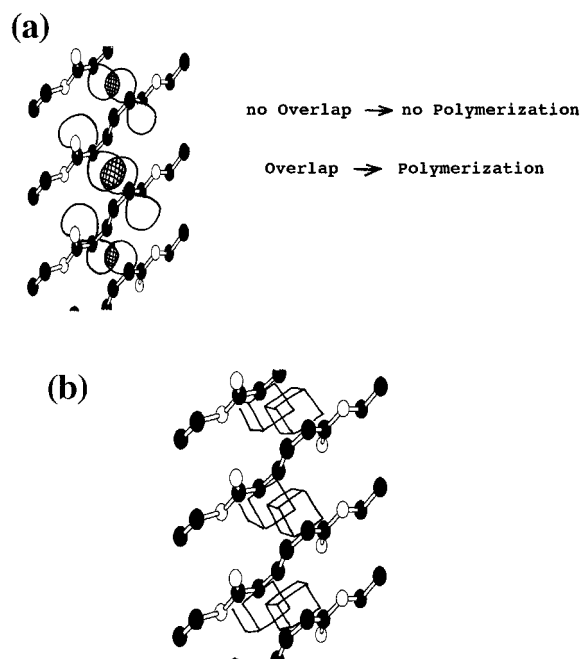
<sup>a</sup>  $r$ , carbon-to-carbon distance between butadiene groups of the adjacent molecules along the columnar axis;  $d$ , distance between centers of mass of the adjacent molecules;  $\phi$ , tilt angle of the molecular axis from the columnar axis.



As an another plausible factor, we focused on the degree of overlap of the  $\pi$ -electron orbitals between the butadiene groups of the adjacent molecules. Larger overlap of the  $\pi$ -electron clouds suggests more effective interchange of the  $\pi$ -electrons, resulting in the smooth formation of the covalent bond in the overlapped  $\pi$ -electron orbitals, as illustrated in Figure 4a. Then we calculated the overlap volume of the  $\pi$ -electron clouds between the butadiene carbon atoms. The  $\pi$ -electron orbitals have the complicated shape because of the conjugation between the adjacent  $\pi$ -electrons in the butadiene group. It is now very difficult to calculate the exact overlap volume of  $\pi$ -electron orbitals. Therefore, to make the calculation easier but in a good approximation, we assumed the  $\pi$ -electron orbital to have a rectangular box shape, as shown in Figure 4b. The size of the box was needed to choice properly so that this box could imitate



**Figure 3.** Plot of  $d$  (distance between the center of masses of the adjacent molecules) and  $\phi$  (tilt angle of the molecular axis from the columnar axis) made for a series of muconate derivatives.

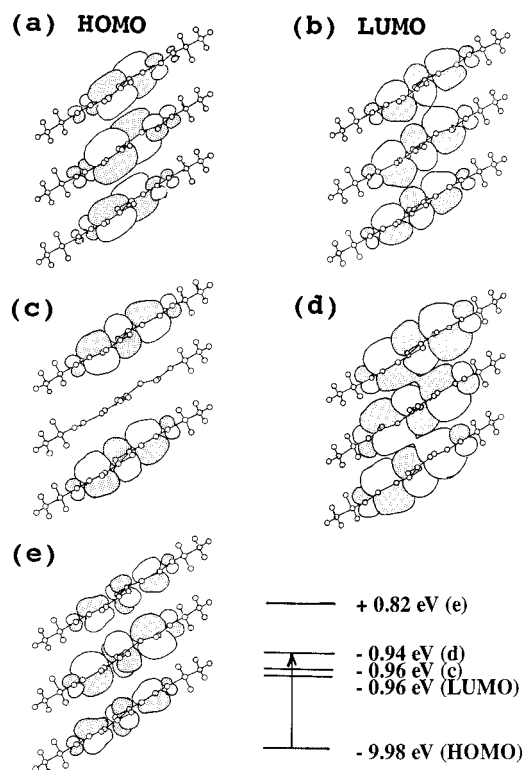


**Figure 4.** (a) Illustration of  $\pi$ -orbital overlapping between the adjacent muconate molecules and the corresponding reactivity. (b) Model for the calculation of  $\pi$ -orbital overlapping by using orthogonal boxes attached to the carbon atoms of the butadiene groups.

**TABLE 5: Calculated Overlapping Volume of the  $\pi$ -Orbitals of (Z,Z)-Muconate Derivatives**

$R$	$V/\text{\AA}^3$	reaction
ethyl	20.7	stereoregular polymerization
<i>n</i> -decyl	17.5	irregular polymerization
2,2,2-trichloroethyl	15.6	irregular polymerization
methyl	16.9	isomerization to (E,E)-type + irregular polymerization
cyclohexyl	14.3	isomerization to (E,E)-type
benzyl	6.2	isomerization to (E,E)-type

the  $\pi$ -orbital as reasonably as possible and the evaluated overlapping volume was as physically acceptable as possible. Yet, of course, we do not have to adhere the "correct" box size because our purpose was to find a suitable measure to express the degree of the  $\pi$ -electron overlap. The box size chosen here was  $4 \times 4 \times 4 \text{\AA}^3$ . The calculated overlapping volume between the adjacent boxes is listed in Table 5. The muconate esters investigated in the present study were classified into three groups: (a) the group of monomers which react rapidly to give

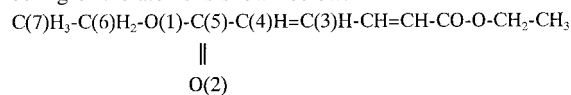


**Figure 5.** Molecular orbitals of the excited states of diethyl (Z,Z)-muconate molecules arrayed along the columnar axes, which were calculated by a semiempirical method (MOPAC, PM3). The MO energies are (a) HOMO (−9.98 eV), (b) LUMO (−0.96 eV), (c) −0.96 eV, (d) −0.94 eV, and (e) +0.82 eV. The shaded and white parts of an individual orbital cloud are of the opposite sign of the wave function.

**TABLE A1: Fractional Atomic Coordinates of Diethyl (Z,Z)-Muconate<sup>a</sup>**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	0.7117(1)	−0.0178(2)	0.2402(1)	0.0882(8)
O(2)	0.7570(1)	0.2180(3)	0.0920(1)	0.1147(9)
C(3)	0.4746(2)	0.4353(4)	0.0445(2)	0.078(1)
C(4)	0.5400(2)	0.2570(4)	0.1283(2)	0.082(1)
C(5)	0.6787(2)	0.1556(3)	0.1469(2)	0.077(1)
C(6)	0.8492(3)	−0.1322(7)	0.2717(3)	0.110(2)
C(7)	0.8704(4)	−0.287(1)	0.3832(4)	0.142(3)
H(3)	0.387(2)	0.493(2)	0.037(1)	0.074(5)
H(4)	0.491(2)	0.185(3)	0.179(1)	0.090(6)
H(6A)	0.851(2)	−0.249(4)	0.201(2)	0.16(1)
H(6B)	0.911(2)	0.014(4)	0.279(2)	0.14(1)
H(7A)	0.962(2)	−0.356(4)	0.406(2)	0.112(7)
H(7B)	0.791(3)	−0.399(6)	0.379(2)	0.22(2)
H(7C)	0.864(3)	−0.167(5)	0.444(2)	0.18(2)

<sup>a</sup> Temperature factor of the form:  $\exp[-2\pi^2 U(ij)]$ , where  $U(\text{eqv}) = \frac{1}{3} \sum \sum [U(ij) a^*(i) a^*(j) a(i) a(j) \cos(tij)]$ , where  $U_{ij}$  is the component of an isotropic thermal parameter tensor.  $a^*$  and  $a$  are, respectively, the unit cell vectors of the reciprocal lattice and the real lattice. The numbering of the atoms is shown below.

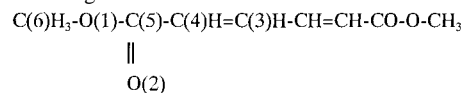


the stereoregular polymer crystal, (b) the group to show the transformation from (Z,Z) to (E,E) isomers, and (c) the group in which the (Z,Z) monomers react to give atactic polymers. As shown in Table 5, EMU shows the largest overlapping volume among these three groups, corresponding well to the high reactivity of this monomer crystal. Group c shows the smallest overlapping volume corresponding to the low reactivity.

**TABLE A2: Fractional Atomic Coordinates of Dimethyl (Z,Z)-Muconate<sup>a</sup>**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	−0.17060(9)	0.10430(8)	0.66510(8)	0.0615(3)
O(2)	0.1710(1)	0.34380(9)	0.8173(1)	0.0867(3)
C(3)	0.4067(1)	−0.0942(1)	0.94650(9)	0.0532(3)
C(4)	0.1789(1)	−0.0734(1)	0.8257(1)	0.0554(3)
C(5)	0.0694(1)	0.1488(1)	0.7734(1)	0.0531(3)
C(6)	−0.3040(2)	0.3073(2)	0.6115(2)	0.0745(5)
H(3)	0.438(2)	−0.254(2)	0.952(1)	0.062(2)
H(4)	0.076(2)	−0.204(2)	0.760(1)	0.060(2)
H(6A)	−0.256(2)	0.401(2)	0.507(2)	0.085(3)
H(6B)	−0.293(2)	0.379(2)	0.744(2)	0.089(3)
H(6C)	−0.481(4)	0.220(4)	0.576(3)	0.154(6)

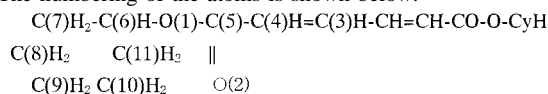
<sup>a</sup> The numbering of the atoms is shown below.



**TABLE A3: Fractional Atomic Coordinates of Biscyclohexyl (Z,Z)-Muconate<sup>a</sup>**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	−0.1795(4)	−0.0020(4)	0.3233(2)	0.064(2)
O(2)	−0.0317(4)	−0.2299(4)	0.4164(2)	0.085(2)
C(3)	−0.5593(7)	−0.4207(7)	0.4851(3)	0.059(2)
C(4)	−0.4572(6)	−0.2377(8)	0.4332(3)	0.061(2)
C(5)	−0.2018(7)	−0.1636(7)	0.3918(3)	0.064(3)
C(6)	0.0608(7)	0.0836(7)	0.2740(3)	0.056(3)
C(7)	0.0619(8)	−0.0646(8)	0.1817(3)	0.068(3)
C(8)	0.304(1)	0.033(1)	0.1244(5)	0.088(4)
C(9)	0.351(1)	0.271(1)	0.0965(5)	0.092(4)
C(10)	0.3356(9)	0.416(1)	0.1879(5)	0.088(4)
C(11)	0.0889(7)	0.3170(8)	0.2432(4)	0.072(3)
H(3)	−0.759(6)	−0.467(5)	0.507(2)	0.09(1)
H(4)	−0.555(5)	−0.152(5)	0.414(2)	0.051(9)
H(6)	0.190(6)	0.078(5)	0.331(2)	0.08(1)
H(7A)	−0.101(6)	−0.079(5)	0.140(2)	0.09(1)
H(7B)	0.028(5)	−0.232(6)	0.209(2)	0.08(1)
H(8A)	0.295(8)	−0.078(9)	0.068(4)	0.18(3)
H(8B)	0.431(6)	0.037(5)	0.165(3)	0.06(1)
H(9A)	0.514(7)	0.345(6)	0.058(3)	0.10(1)
H(9B)	0.225(6)	0.279(5)	0.047(2)	0.07(1)
H(10A)	0.469(6)	0.420(5)	0.235(2)	0.06(1)
H(10B)	0.353(8)	0.582(9)	0.162(3)	0.17(2)
H(11A)	0.070(6)	0.408(6)	0.299(3)	0.10(2)
H(11B)	−0.066(7)	0.290(5)	0.188(2)	0.09(1)

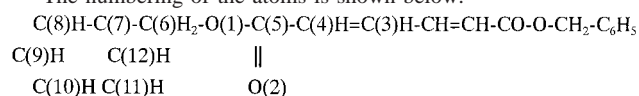
<sup>a</sup> The numbering of the atoms is shown below.



In the actual experiments, the part of the crystal irradiated by an X-ray beam was melted, and the sticky atactic polymers were formed on this damaged part. It is speculated that the crystal lattice is broken by the X-ray irradiation and the polymerization reaction is induced from the monomer species activated as radicals. Group b shows the overlapping volume intermediate between the groups a and c. Unfortunately, however, at the present stage, we cannot give the rational reasons why the monomers of group b experience the (Z,Z)–(E,E) isomerization reaction. In the previous paper,<sup>23</sup> we analyzed the crystal structures of the low- and high-temperature phases of (Z,Z)-EMU compound. The high-temperature phase exhibits a quite rapid polymerization reaction by irradiation of light, while the low-temperature phase below −45 °C does not react at all. These two phases show in common the columnar structures with slightly different geometrical parameters concerning the distance *d* and the tilting angle *φ*. Yet such a small difference cannot give any answer for the very large difference in the reactivity

**TABLE A4: Fractional Atomic Coordinates of Bisbenzyl (Z,Z)-Muconate<sup>a</sup>**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	0.7961(6)	0.322(1)	0.6759(4)	0.060(4)
O(2)	0.9485(6)	0.1342(9)	0.6223(4)	0.089(5)
C(3)	0.9615(9)	0.583(2)	0.5188(7)	0.065(7)
C(4)	0.894(1)	0.536(2)	0.5799(7)	0.073(7)
C(5)	0.887(1)	0.308(2)	0.6264(6)	0.057(7)
C(6)	0.782(1)	0.113(2)	0.7281(9)	0.069(9)
C(7)	0.707(1)	0.172(2)	0.7976(6)	0.050(6)
C(8)	0.610(1)	0.022(2)	0.8111(8)	0.055(7)
C(9)	0.545(1)	0.071(2)	0.8782(9)	0.071(8)
C(10)	0.576(1)	0.268(2)	0.9320(8)	0.068(8)
C(11)	0.670(1)	0.420(2)	0.9181(8)	0.068(7)
C(12)	0.737(1)	0.372(2)	0.8526(7)	0.063(7)
H(3)	0.967(7)	0.75(1)	0.494(5)	0.08(3)
H(4)	0.855(7)	0.64(1)	0.600(5)	0.05(3)
H(6A)	0.883(9)	0.06(1)	0.763(5)	0.09(4)
H(6B)	0.732(7)	0.00(1)	0.682(5)	0.06(3)
H(8)	0.582(7)	−0.12(1)	0.767(4)	0.07(3)
H(9)	0.477(8)	−0.022(9)	0.880(5)	0.05(3)
H(10)	0.530(7)	0.31(1)	0.974(5)	0.05(3)
H(11)	0.693(6)	0.55(1)	0.957(5)	0.05(3)
H(12)	0.803(7)	0.465(9)	0.843(5)	0.05(3)

<sup>a</sup> The numbering of the atoms is shown below.

between the high- and low-temperature phases of the same chemical compounds. The temperature effect was considered as an origin of this difference, but the bis-*p*-bromobenzyl (Z,Z)-muconate crystal gives the polymerization reaction even at such a low temperature as −80 °C. In this way, as long as we take only the packing geometry of these compounds into consideration, we cannot know the essentially important factors which systematically control the reactivity of these crystals induced by an irradiation of light.

We have to consider another point here. So far, we discussed the light-induced reactions on the basis of the structure of the stable ground state without any photoinduced excitation of molecules. In the actual reaction, however, the monomer molecules are speculated to be excited by a photoirradiation from the ground state to the energetically excited state. Then the excited molecules react each other to give an intermediate state, which goes back to the ground-state again but with a different chemical structure. If the  $\pi$ -electron orbitals overlap effectively in this intermediate state over many monomeric molecules, then the propagation of radicals may be made smoothly, and the polymer product may grow rapidly along the columnar axis. Therefore, the most important point for the study of the solid-state polymerization reaction seems to investigate the stability of the intermediate state consisting of a group of the excited molecules. As a trial, we calculated the molecular orbitals for the various energy levels of EMU and searched the configuration with the widely developed  $\pi$ -electron orbitals, which might relate well with the formation of polymer chain. The preliminary calculation was made on the basis of semiempirical method (PM3) by using the MOPAC (version 6) software. The models used in the calculation were clusters consisting of three molecules arrayed along the columnar axis, which were extracted from the crystal structures determined by the X-ray analyses. Some of the MOs are shown in Figure 5, which illustrate concretely the situation of the excited states of EMU crystal. Among the many excited states, the configuration of energetically relatively low and well-developed  $\pi$ -electron overlapping structure could be found as seen in Figure 5d. In the cases of dimethyl (Z,Z)-muconate, diethyl (*E,E*)-muconate, and dicyclohexyl (Z,Z)-muconate, the overlapping of the  $\pi$ -electron orbital was found to be very poor for all the possible excited states. For further discussion about the relation between the reactivity and the packing structure, the detailed MO calculation is needed along the reaction path from the original

**TABLE A5: Fractional Atomic Coordinates of Bistrichloroethyl (Z,Z)-Muconate<sup>a</sup>**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
Cl(1)	0.1329(1)	−0.24760(4)	0.05510(1)	0.0658(3)
Cl(2)	0.1261(1)	0.01240(5)	0.09970(2)	0.0688(3)
Cl(3)	−0.2861(1)	−0.10030(5)	0.06080(2)	0.0734(3)
Cl(4)	−1.6486(1)	0.00330(5)	0.44840(2)	0.0739(4)
Cl(5)	−1.6496(1)	−0.25840(5)	0.40490(2)	0.0859(4)
Cl(6)	−1.2575(1)	−0.16550(7)	0.45580(2)	0.1099(5)
O(7)	−0.2070(2)	−0.1146(1)	0.16960(4)	0.0562(8)
O(8)	−0.4558(3)	−0.2769(1)	0.18690(5)	0.087(1)
O(9)	−1.2671(3)	−0.1522(1)	0.34460(4)	0.0711(8)
O(10)	−1.0523(3)	0.0122(1)	0.31520(6)	0.099(1)
C(11)	−0.6936(4)	−0.0742(2)	0.24790(5)	0.054(1)
C(12)	−0.5175(5)	−0.0577(2)	0.21830(6)	0.060(1)
C(13)	−0.3954(4)	−0.1640(2)	0.19050(5)	0.050(1)
C(14)	−0.0735(4)	−0.2039(2)	0.13980(6)	0.056(1)
C(15)	−0.0283(3)	−0.1357(2)	0.09120(5)	0.0437(9)
C(16)	−0.8056(4)	−0.1980(2)	0.25970(5)	0.049(1)
C(17)	−0.9805(4)	−0.2122(2)	0.29030(5)	0.055(1)
C(18)	−1.0961(4)	−0.1034(2)	0.31720(5)	0.054(1)
C(19)	−1.4001(6)	−0.0542(2)	0.37110(8)	0.074(2)
C(20)	−1.4831(3)	−0.1190(1)	0.41820(5)	0.048(1)
H(11)	−0.757(3)	−0.005(2)	0.2586(6)	0.076(6)
H(12)	−0.462(3)	0.028(2)	0.2109(5)	0.058(5)
H(14A)	−0.162(3)	−0.287(2)	0.1355(5)	0.082(4)
H(14B)	0.074(3)	−0.229(2)	0.1583(5)	0.117(5)
H(16)	−0.727(4)	−0.274(2)	0.2458(6)	0.054(6)
H(17)	−1.032(4)	−0.308(2)	0.2976(7)	0.062(9)
H(19A)	−1.547(6)	−0.027(3)	0.348(1)	0.19(2)
H(19B)	−1.308(4)	0.010(2)	0.3783(7)	0.092(8)

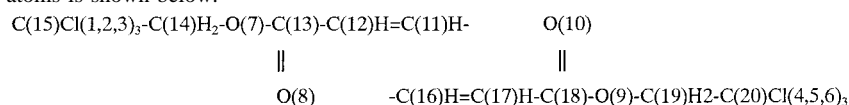
<sup>a</sup> The numbering of the atoms is shown below.



TABLE A6: Fractional Atomic Coordinates of Bis-*n*-decyl (*Z,Z*)-Muconate<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	0.396(1)	0.326(1)	0.1250(3)	0.064(2)	H(11A)	0.92660	-0.11280	0.26380	0.10(1)
O(2)	0.0722(7)	0.5306(6)	0.1444(2)	0.082(2)	H(11B)	0.75630	-0.33270	0.23640	0.10(2)
O(3)	-0.2490(3)	1.3246(3)	-0.04500(8)	0.066(2)	H(12A)	0.59390	-0.45190	0.32630	0.10(1)
O(4)	0.0722(7)	1.1227(7)	-0.0643(2)	0.091(2)	H(12B)	0.66530	-0.23550	0.34780	0.10(1)
C(5)	0.1789(9)	0.7700(8)	0.0294(2)	0.061(2)	H(13A)	0.93840	-0.60440	0.30480	0.10(1)
C(6)	0.2974(9)	0.5977(8)	0.0546(2)	0.064(2)	H(13B)	1.10870	-0.37090	0.33540	0.100(9)
C(7)	0.2335(8)	0.5000(6)	0.1127(2)	0.055(2)	H(14A)	0.77580	-0.71750	0.40120	0.100(9)
C(8)	0.3530(8)	0.2057(9)	0.1817(2)	0.063(2)	H(14B)	0.88360	-0.54700	0.42810	0.10(1)
C(9)	0.5762(9)	0.0678(8)	0.1957(2)	0.070(2)	H(15A)	1.29590	-0.62560	0.42140	0.10(2)
C(10)	0.5434(9)	-0.0656(9)	0.2493(2)	0.059(2)	H(15B)	1.21150	-0.85210	0.37780	0.10(3)
C(11)	0.7671(9)	-0.2007(8)	0.2667(2)	0.067(2)	H(16A)	1.08550	-0.79970	0.50260	0.100(7)
C(12)	0.7440(9)	-0.348(1)	0.3226(2)	0.064(2)	H(16B)	1.00800	-1.03030	0.45860	0.10(4)
C(13)	0.9627(9)	-0.4825(8)	0.3375(2)	0.066(2)	H(17A)	1.33330	-1.10960	0.52200	0.100(8)
C(14)	0.9343(9)	-0.6373(8)	0.3934(2)	0.070(2)	H(17B)	1.49330	-0.88590	0.49800	0.10(3)
C(15)	1.1659(9)	-0.7540(8)	0.4119(2)	0.082(2)	H(17C)	1.41670	-1.11140	0.45440	0.10(6)
C(16)	1.132(1)	-0.897(1)	0.4687(3)	0.134(3)	H(18)	-0.08810	0.81010	0.08880	0.100(6)
C(17)	1.363(1)	-1.013(1)	0.4874(3)	0.136(4)	H(19)	-0.27350	1.10760	0.05070	0.100(6)
C(18)	-0.0315(9)	0.8781(8)	0.0519(2)	0.058(2)	H(21A)	-0.19750	1.34450	-0.13380	0.10(1)
C(19)	-0.1476(8)	1.0512(8)	0.0260(2)	0.061(2)	H(21B)	-0.07270	1.56990	-0.09530	0.10(2)
C(20)	-0.0910(8)	1.1814(8)	-0.0316(2)	0.062(2)	H(22A)	-0.44650	1.69870	-0.07680	0.10(2)
C(21)	-0.2170(9)	1.4561(9)	-0.1001(2)	0.074(2)	H(22B)	-0.57310	1.47210	-0.11470	0.100(9)
C(22)	-0.4284(9)	1.5877(7)	-0.1108(2)	0.056(2)	H(23A)	-0.39240	1.62090	-0.20420	0.100(9)
C(23)	-0.4147(9)	1.7366(7)	-0.1716(2)	0.063(2)	H(23B)	-0.27780	1.85870	-0.16530	0.10(1)
C(24)	-0.6333(9)	1.8608(8)	-0.1857(2)	0.064(2)	H(24A)	-0.67010	1.95810	-0.15060	0.100(5)
C(25)	-0.6069(9)	2.0137(8)	-0.2407(2)	0.077(2)	H(24B)	-0.76830	1.73510	-0.19290	0.100(9)
C(26)	-0.836(1)	2.1330(8)	-0.2592(3)	0.083(3)	H(25A)	-0.57450	1.90850	-0.27460	0.100(5)
C(27)	-0.805(1)	2.2828(8)	-0.3134(2)	0.076(2)	H(25B)	-0.47390	2.13800	-0.23170	0.10(1)
C(28)	-1.028(1)	2.4034(9)	-0.3318(2)	0.091(3)	H(26A)	-0.87150	2.23780	-0.22540	0.100(8)
C(29)	-0.9945(8)	2.5745(8)	-0.3825(2)	0.065(2)	H(26B)	-0.97260	2.00960	-0.26690	0.10(1)
C(30)	-1.222(1)	2.672(1)	-0.4046(2)	0.137(4)	H(27A)	-0.78340	2.17030	-0.34670	0.100(7)
H(5)	0.23860	0.81520	-0.00920	0.10(2)	H(27B)	-0.69440	2.41860	-0.29760	0.100(8)
H(6)	0.43660	0.55350	0.03310	0.10(2)	H(28A)	-1.06350	2.51510	-0.29930	0.10(2)
H(8A)	0.20560	0.09450	0.17920	0.10(1)	H(28B)	-1.16130	2.27700	-0.34050	0.10(1)
H(8B)	0.34080	0.32870	0.21340	0.10(1)	H(29A)	-0.96850	2.46380	-0.41590	0.1(1)
H(9A)	0.71990	0.18330	0.20090	0.10(2)	H(29B)	-0.87640	2.70780	-0.36920	0.100(9)
H(9B)	0.59480	-0.04330	0.16180	0.100(4)	H(30A)	-1.18240	2.76920	-0.43860	0.10(4)
H(10A)	0.40200	-0.17950	0.24220	0.10(1)	H(30B)	-1.28010	2.77700	-0.37330	0.10(4)
H(10B)	0.51520	0.04960	0.28160	0.10(1)	H(30C)	-1.34940	2.54340	-0.41680	0.10(3)

<sup>a</sup> The numbering of the atoms is shown below. C(17)H<sub>3</sub>-C(16)H<sub>2</sub>-C(15)H<sub>2</sub>-C(14)H<sub>2</sub>-C(13)H<sub>2</sub>-C(12)H<sub>2</sub>-C(11)H<sub>2</sub>-C(10)H<sub>2</sub>-C(9)H<sub>2</sub>-C(8)H<sub>2</sub>-O(1)-C(7)O(2)-C(6)H=C(5)H-C(18)H=C(19)H-C(20)O(4)-O(3)-C(20)H<sub>2</sub>-C(21)H<sub>2</sub>-C(22)H<sub>2</sub>-C(23)H<sub>2</sub>-C(24)H<sub>2</sub>-C(25)H<sub>2</sub>-C(26)H<sub>2</sub>-C(27)H<sub>2</sub>-C(28)H<sub>2</sub>-C(29)H<sub>2</sub>-C(30)H<sub>3</sub>

TABLE A7: Fractional Atomic Coordinates of Diethyl (*E,E*)-Muconate<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	0.1867(2)	0.37600(8)	0.1218(2)	0.083(1)
O(2)	0.1626(2)	0.42780(9)	0.3635(2)	0.098(1)
C(3)	-0.1633(3)	0.4837(1)	0.2668(3)	0.064(2)
C(4)	-0.0620(3)	0.4442(1)	0.1732(3)	0.063(2)
C(5)	0.1052(3)	0.4158(1)	0.2332(3)	0.068(2)
C(6)	0.3573(3)	0.3480(2)	0.1638(5)	0.107(2)
C(7)	0.3455(7)	0.2713(3)	0.2417(7)	0.152(3)
O(8)	-0.6671(2)	0.62140(8)	0.3904(2)	0.074(1)
O(9)	-0.6602(2)	0.57710(8)	0.1422(2)	0.096(1)
C(10)	-0.3299(3)	0.5147(1)	0.2214(3)	0.060(2)
C(11)	-0.4270(3)	0.5535(1)	0.3189(3)	0.065(2)
C(12)	-0.5950(3)	0.5843(1)	0.2714(3)	0.064(2)
C(13)	-0.8368(3)	0.6541(2)	0.3610(4)	0.088(2)
C(14)	-0.8564(6)	0.7189(3)	0.4766(6)	0.128(3)
H(3)	-0.132(2)	0.4948(8)	0.369(2)	0.064(6)
H(4)	-0.088(3)	0.428(1)	0.067(3)	0.099(8)
H(6A)	0.429(4)	0.331(2)	0.067(4)	0.16(1)
H(6B)	0.415(3)	0.382(1)	0.233(3)	0.12(1)
H(7A)	0.472(4)	0.259(2)	0.270(4)	0.19(1)
H(7B)	0.297(4)	0.242(2)	0.126(5)	0.18(1)
H(7C)	0.260(6)	0.260(3)	0.319(7)	0.34(4)
H(10)	-0.362(2)	0.502(1)	0.120(2)	0.081(8)
H(11)	-0.390(2)	0.5649(9)	0.419(2)	0.068(7)
H(13A)	-0.827(3)	0.675(2)	0.241(4)	0.19(1)
H(13B)	-0.920(4)	0.608(2)	0.381(3)	0.16(1)
H(14A)	-0.966(4)	0.741(2)	0.456(4)	0.17(1)
H(14B)	-0.781(4)	0.756(2)	0.414(4)	0.17(2)
H(14C)	-0.820(4)	0.702(2)	0.587(5)	0.21(2)

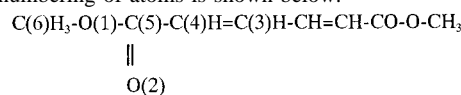
<sup>a</sup> The numbering of atoms is as follows.  
C(14)H<sub>3</sub>-C(13)H<sub>2</sub>-O(8)-C(12)-C(11)H=C(10)H-C(5)H=C(5)-O(1)-C(6)H<sub>2</sub>-C(7)H<sub>2</sub>  
 $\parallel$   $\parallel$   
O(9) O(2)

ground state to the newly constructed ground state via the photonic excited intermediate state with the symmetry relation taken into consideration.

TABLE A8: Fractional Atomic Coordinates of Dimethyl (*E,E*)-Muconate<sup>a</sup>

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	0.16860(6)	0.84990(7)	0.82370(9)	0.0446(2)
O(2)	-0.14930(7)	0.56660(8)	0.6949(1)	0.0609(3)
C(3)	-0.4305(1)	0.9106(1)	0.5379(1)	0.0376(3)
C(4)	-0.1970(1)	0.9567(1)	0.6478(1)	0.0377(3)
C(5)	-0.06520(9)	0.7664(1)	0.7209(1)	0.0371(3)
C(6)	0.3177(1)	0.6751(1)	0.8973(2)	0.0541(4)
H(3)	-0.514(1)	0.763(1)	0.512(1)	0.039(2)
H(4)	-0.106(1)	1.104(1)	0.679(1)	0.043(2)
H(6A)	0.322(1)	0.551(1)	0.770(2)	0.066(2)
H(6B)	0.260(1)	0.605(1)	0.989(2)	0.066(2)
H(6C)	0.477(1)	0.768(2)	0.960(2)	0.078(3)

<sup>a</sup> The numbering of atoms is shown below.

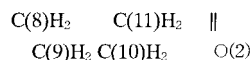
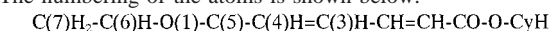


## Conclusions

In the present paper, we analyzed the crystal structures of a series of dialkyl muconates with different side groups in order to clarify the relation between packing structure and reactivity of monomer molecules in the photoinduced solid-state polymerization. The photoinduced reactions of dialkyl muconates are classified into three categories. One is the smooth solid-state polymerization reaction of diethyl (*Z,Z*)-muconate to give the stereoregular polymer crystal by irradiating visible or ultraviolet light at room temperature. The second reaction is an isomerization from the (*Z,Z*) form to the (*E,E*) form. The third reaction is the production of amorphous polymer. All the compounds analyzed in the present paper have the columnar structures. The

**TABLE A9: Fractional Atomic Coordinates of Biscyclohexyl (*E,E*)-Muconate<sup>a</sup>**

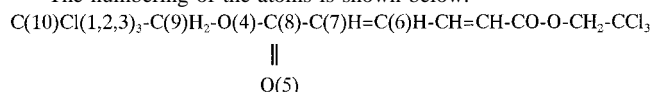
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	0.52990(5)	−0.06760(3)	0.25250(4)	0.0533(2)
O(2)	0.65400(6)	−0.26380(4)	0.13870(4)	0.0710(2)
C(3)	0.13300(7)	−0.45130(6)	0.02810(6)	0.0511(2)
C(4)	0.21450(8)	−0.30830(6)	0.12150(5)	0.0513(2)
C(5)	0.48650(8)	−0.21500(5)	0.16990(5)	0.0494(2)
C(6)	0.79360(8)	0.03910(5)	0.29540(5)	0.0488(2)
C(7)	0.85980(9)	0.10520(7)	0.16710(6)	0.0598(3)
C(8)	1.1322(1)	0.21950(7)	0.21310(7)	0.0704(3)
C(9)	1.1707(1)	0.34780(7)	0.35680(8)	0.0808(4)
C(10)	1.0952(1)	0.28070(8)	0.48480(7)	0.0777(4)
C(11)	0.8220(1)	0.16540(7)	0.43810(7)	0.0672(3)
H(3)	0.2522(9)	−0.4967(5)	−0.0077(5)	0.059(1)
H(4)	0.1093(8)	−0.2602(5)	0.1604(5)	0.047(1)
H(6)	0.8988(8)	−0.0235(5)	0.3161(5)	0.050(1)
H(7A)	0.741(1)	0.1646(7)	0.1444(7)	0.088(2)
H(7B)	0.834(1)	0.0129(7)	0.0748(7)	0.080(2)
H(8A)	1.182(1)	0.2654(6)	0.1269(7)	0.084(2)
H(8B)	1.246(1)	0.1581(6)	0.2304(6)	0.074(2)
H(9A)	1.063(1)	0.4100(8)	0.3393(8)	0.107(2)
H(9B)	1.352(1)	0.4171(7)	0.3921(7)	0.099(2)
H(10A)	1.219(1)	0.2217(7)	0.5115(7)	0.095(2)
H(10B)	1.119(1)	0.3589(8)	0.5711(9)	0.111(2)
H(11A)	0.771(1)	0.1139(7)	0.5154(7)	0.089(2)
H(11B)	0.707(1)	0.2189(6)	0.4156(6)	0.076(2)

<sup>a</sup> The numbering of the atoms is shown below.

distance of the butadiene carbon atoms of the neighboring molecules along the columnar axis ranges from 3.5 to 6.4 Å.

**TABLE A11: Fractional Atomic Coordinates of Bistrichloroethyl (*E,E*)-Muconate<sup>a</sup>**

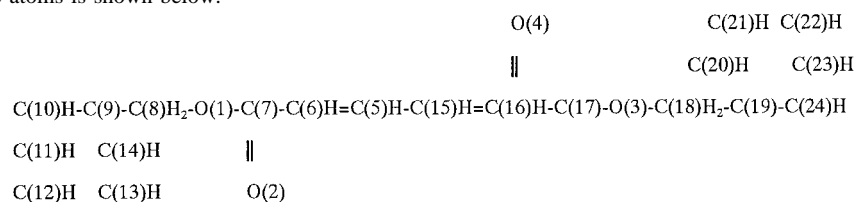
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
Cl(1)	0.81450(1)	0.55610(2)	−0.13390(1)	0.05845(7)
Cl(2)	0.90060(1)	0.56750(3)	0.16080(2)	0.06571(8)
Cl(3)	0.89290(1)	0.15690(2)	0.01570(2)	0.06272(7)
O(4)	0.66250(3)	0.54450(5)	0.03250(4)	0.0459(2)
O(5)	0.63030(3)	0.44600(6)	0.22950(4)	0.0550(2)
C(6)	0.53420(3)	0.90510(7)	0.00820(5)	0.0341(2)
C(7)	0.55590(3)	0.77490(8)	0.11810(5)	0.0382(2)
C(8)	0.62020(3)	0.57360(7)	0.13610(5)	0.0358(2)
C(9)	0.72200(4)	0.34810(8)	0.03440(6)	0.0435(2)
C(10)	0.82760(3)	0.40860(7)	0.02010(5)	0.0358(2)
H(6)	0.5607(4)	0.8768(8)	−0.0631(5)	0.031(1)
H(7)	0.5261(4)	0.7988(9)	0.1940(5)	0.046(1)
H(9A)	0.6825(5)	0.259(1)	−0.0477(7)	0.067(2)
H(9B)	0.7341(5)	0.275(1)	0.1178(6)	0.050(2)

<sup>a</sup> The numbering of the atoms is shown below.

The tilting angle of the molecular axis from the columnar axis is from 38 to 78°. The distance between the centers of mass of the adjacent two molecules was also calculated. These parameters are difficult to be assumed as the good measures for the classification of these three reaction categories. Rather the degree of overlap of  $\pi$ -electron orbitals between the butadiene carbon atoms of the neighboring molecules might be one of the reasonable measures of their reactivity. In fact, the case of (*Z,Z*)-EMU was found to give the largest  $\pi$ -electron overlap. Yet it

**TABLE A10: Fractional Atomic Coordinates of Bisbenzyl (*E,E*)-Muconate<sup>a</sup>**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv)
O(1)	0.85920(8)	0.2(2)	0.41980(5)	0.0607(4)
O(2)	0.9563(1)	−0.0460(2)	0.34940(6)	0.0775(5)
O(3)	1.21650(9)	0.6854(2)	0.04600(5)	0.0632(4)
O(4)	1.1152(1)	0.9339(2)	0.11890(6)	0.0911(6)
C(5)	1.0178(1)	0.3403(2)	0.25300(7)	0.0509(5)
C(6)	0.9583(1)	0.3587(3)	0.31600(7)	0.0516(5)
C(7)	0.9267(1)	0.1550(2)	0.36130(7)	0.0514(5)
C(8)	0.8085(1)	0.0330(3)	0.46650(8)	0.0672(7)
C(9)	0.6479(1)	−0.0287(2)	0.42690(6)	0.0508(5)
C(10)	0.6084(2)	−0.2396(2)	0.38500(8)	0.0692(7)
C(11)	0.4572(2)	−0.2875(3)	0.34820(8)	0.0754(8)
C(12)	0.3470(2)	−0.1324(3)	0.35350(8)	0.0718(8)
C(13)	0.3849(1)	0.0730(3)	0.39430(8)	0.0677(7)
C(14)	0.5334(1)	0.1242(2)	0.43100(7)	0.0549(6)
C(15)	1.0484(1)	0.5395(3)	0.20710(7)	0.0523(5)
C(16)	1.1143(1)	0.5268(2)	0.14640(7)	0.0567(6)
C(17)	1.1463(1)	0.7368(2)	0.10380(7)	0.0547(6)
C(18)	1.2550(2)	0.8797(3)	0.00080(8)	0.0631(7)
C(19)	1.3163(1)	0.7891(2)	−0.06700(6)	0.0508(5)
C(20)	1.4189(1)	0.9228(3)	−0.09380(8)	0.0684(7)
C(21)	1.4745(2)	0.8505(3)	−0.15810(9)	0.0862(9)
C(22)	1.4288(2)	0.6438(3)	−0.19690(8)	0.0783(9)
C(23)	1.3276(2)	0.5068(2)	−0.17020(8)	0.0718(7)
C(24)	1.2710(2)	0.5777(3)	−0.10640(8)	0.0650(7)
H(5)	1.043(1)	0.194(3)	0.2379(7)	0.067(3)
H(6)	0.935(1)	0.483(2)	0.3316(7)	0.051(3)
H(8A)	0.811(1)	0.123(2)	0.5242(8)	0.075(4)
H(8B)	0.876(1)	−0.100(2)	0.4694(7)	0.063(3)
H(10)	0.689(2)	−0.338(3)	0.3811(9)	0.092(4)
H(11)	0.424(2)	−0.427(3)	0.318(1)	0.110(5)
H(12)	0.231(2)	−0.177(2)	0.3315(9)	0.095(4)
H(13)	0.301(1)	0.198(3)	0.3958(8)	0.085(4)
H(14)	0.559(1)	0.274(2)	0.4612(7)	0.067(3)
H(15)	1.015(1)	0.691(3)	0.2238(7)	0.070(4)
H(16)	1.146(1)	0.387(3)	0.1294(8)	0.081(4)
H(18A)	1.331(1)	0.986(3)	0.0406(9)	0.095(4)
H(18B)	1.161(2)	0.955(3)	−0.017(1)	0.096(5)
H(20)	1.443(2)	1.077(3)	−0.0685(9)	0.097(4)
H(21)	1.543(2)	0.962(4)	−0.181(1)	0.140(7)
H(22)	1.465(1)	0.609(3)	−0.2425(9)	0.090(4)
H(23)	1.291(2)	0.353(3)	−0.199(1)	0.106(4)
H(24)	1.202(1)	0.491(3)	−0.0848(9)	0.090(5)

<sup>a</sup> The numbering of the atoms is shown below.

is still difficult to explain the different behavior between the (Z,Z)-to-(E,E) isomerization and the irregular polymerization in terms of such  $\pi$ -orbital overlapping only. In the previous paper, we analyzed the crystal structures of the low- and high-temperature phases of (Z,Z)-EMU compound. The high-temperature phase exhibits a quite rapid polymerization reaction by irradiation of light, while the low-temperature phase does not react at all. These two phases show the columnar structures with only slightly different geometrical parameters concerning the distance  $d$  and the tilting angle  $\phi$ , making it impossible to explain the reason the reactivity is quite different between these two phases of the same chemical compounds. The temperature effect was considered as an origin of this difference, but the case of bis-*p*-bromobenzyl (Z,Z)-muconate crystal gives the polymerization reaction even at such a low temperature as  $-80\text{ }^{\circ}\text{C}$ . In this way, as long as we see only the packing geometry of these compounds, we cannot know the essentially important factors which control the reactivity of these crystals induced by an irradiation of light. In other words, the systematic study of the molecular packing geometry for a series of muconate derivatives is considered to bring up a very important warning about the conventionally made discussion on the factors governing the solid-state polymerization reaction based on only the interatomic distance, the tilting angle of the molecules, etc.

## Appendix

The fractional coordinates of the constituent atoms are given in this Appendix for a series of muconate derivatives. The details of molecular geometry etc. are listed in the the footnotes to the tables.

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