

Title	Radiation-Induced Phase Transition of Paraffins (Special Issue on Polymer Chemistry, XVI)
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Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1981), 59(4): 284-292
Issue Date	1981-11-30
URL	<a href="http://hdl.handle.net/2433/76951">http://hdl.handle.net/2433/76951</a>
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Type	Departmental Bulletin Paper
Textversion	publisher

## Radiation-Induced Phase Transition of Paraffins

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*Received September 10, 1981*

When irradiated by the 500 kV electron at a dose of about  $1.5 \times 10^{-8}$  C/cm<sup>2</sup>, normal paraffins exhibit a solid-solid phase transition; a transition from a triclinic form to an orthorhombic one in *n*-C<sub>22</sub>H<sub>46</sub> and *n*-C<sub>24</sub>H<sub>50</sub> and from a monoclinic form to an orthorhombic one in *n*-C<sub>28</sub>H<sub>58</sub>, *n*-C<sub>36</sub>H<sub>74</sub> and *n*-C<sub>44</sub>H<sub>90</sub>. The transition to a phase with high energy (orthorhombic phase) accommodates the radiation-induced stresses. The excess strain energy produced by cross-links in crystals is assumed to be equal to the enthalpy change of the phase transition, and the number of cross-links required to induce the phase transition is estimated at one per volume of about ten molecular chains. To compare with irradiated crystals, mixed crystals are prepared from solutions of binary mixtures of *n*-C<sub>23</sub>H<sub>48</sub> and *n*-C<sub>24</sub>H<sub>50</sub> and of *n*-C<sub>24</sub>H<sub>50</sub> and *n*-C<sub>25</sub>H<sub>52</sub>. When the content of impurities (*n*-C<sub>23</sub>H<sub>48</sub> or *n*-C<sub>25</sub>H<sub>52</sub>) reaches 10% in molar fraction, the crystal form of mixed crystals changes from the stable triclinic one to the unstable orthorhombic one. Thus, the number of lattice imperfections of mixed lattice is also estimated at one per volume of ten molecules. It is concluded from the above two estimations that the phase transition occurs when the content of lattice imperfections reaches the value of one per ten molecular chains and the value does not depend on the type of imperfections in these paraffins.

KEY WORDS: Paraffins/ Phase transition/ Electron irradiation/ Mixed crystal/

### INTRODUCTION

Polymers are more or less damaged by electron irradiation. In connection with electron microscopy, the radiation damage of various polymer crystals have been investigated<sup>1)</sup>. Paraffins have been studied as a model substance of polyethylene.<sup>2,3)</sup> Their radiation damage is, however, quite different from that of polyethylene. The lattice spacings of polyethylene crystals increase with the irradiation dose and their crystallinity is lost rapidly, while the spacings of paraffins are independent of the irradiation dose and the segregated domains are observed as the crystalline and the rest as the amorphous. The scission of and cross-linkage between chain molecules are produced by an electron exposure, and the crystal lattice is strained or distorted by these structural irregularities or defects. Stem segments of polyethylene single crystals are connected with one another by folds at the surface, while those of paraffins have no connection with their neighbors by chemical bonds. This structural difference between two substances causes the difference in the mobility of stem segments and consequently the degree of stress recovery of disordered crystals. This may result in their different irradiation behavior. In the inorganic substances and metals with many crystallographic modifications, for example zirconia<sup>4)</sup> and barium titanate,<sup>5)</sup> the stress associated with the radiation-induced point defects or disorders is known to be accommodated by a phase transition to a high energy phase. In the case of polyethylene and paraffins, the radiation-induced phase transition of the orthorhombic form to the

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hexagonal one has been observed.<sup>6,7)</sup> In this paper, the phase transition of paraffins from the monoclinic form to an orthorhombic one will be discussed. The transition is induced by a small exposure of specimen to electron beams and closely associated with the stress-relaxation of disordered lattice.

### EXPERIMENTAL

Normal paraffins used in the present work are docosane  $n\text{-C}_{22}\text{H}_{46}$ , tricosane  $n\text{-C}_{23}\text{H}_{48}$ , tetracosane  $n\text{-C}_{24}\text{H}_{50}$ , pentacosane  $n\text{-C}_{25}\text{H}_{52}$ , octacosane  $n\text{-C}_{28}\text{H}_{58}$ , pentatriacontane  $n\text{-C}_{35}\text{H}_{72}$ , hexatriacontane  $n\text{-C}_{36}\text{H}_{74}$ , tetracontane  $n\text{-C}_{40}\text{H}_{82}$ , and tetratetracontane  $n\text{-C}_{44}\text{H}_{90}$  which are commercially available (these are hereinafter abbreviated to  $n\text{-C}_{22}$ ,  $n\text{-C}_{23}$ ,  $n\text{-C}_{24}$ ,  $n\text{-C}_{25}$ ,  $n\text{-C}_{28}$ ,  $n\text{-C}_{35}$ ,  $n\text{-C}_{36}$ ,  $n\text{-C}_{40}$  and  $n\text{-C}_{44}$ ) and their purity is more than 95%. Lamellar single crystals or platelets of these paraffins were precipitated from dilute solutions. Two paraffins with different chain length ( $n\text{-C}_{23}$  and  $n\text{-C}_{24}$ ,  $n\text{-C}_{24}$  and  $n\text{-C}_{25}$ ) were co-crystallized from solution to form a mixed crystal. Then, since the fractionation or segregation takes place because of the difference in solubility in the solvent between the two paraffins, the composition of obtained crystals was determined by gas chromatography.

Electron irradiation was carried out using a high voltage electron microscope (JEM-500) at an accelerating voltage of 500 kV and the irradiation dose was measured with a Faraday cage. X-ray films (Kodak AA) were used for taking the electron diffraction patterns. They are sensitive to the electron beam so that the exposure to take the patterns is reduced to  $6 \times 10^{-4}$  C/cm<sup>2</sup>. The irradiation dose described below includes this value. The irradiation experiment to prepare the specimen for X-ray diffraction was carried out using an electron microscope of an accelerating voltage of 80 kV, JEM-7A. The Ni-filtered Cu-K $\alpha$  radiation was used for X-ray diffraction and the calorimetric measurements were performed with DSC.

### RESULTS

Figures 1(a) and (b) show the electron diffraction patterns of  $n\text{-C}_{36}$  crystals taken at 500 kV after exposures of  $0.11 \times 10^{-2}$  and  $1.95 \times 10^{-2}$  C/cm<sup>2</sup>, respectively. In  $n\text{-C}_{36}$  paraffin, two crystal modifications, monoclinic and orthorhombic forms, are known and their precise structure analysis has been carried out.<sup>8,9)</sup> Models of both crystal structures are shown in Fig. 2 with a model of the triclinic form. The molecular axis ( $c$ -axis) of monoclinic form makes an angle of about 120° with the  $b$ -axis, that is, molecular chains are inclined to the basal plane at an angle of tilt of 60°. Generally, the surface of lamellar single crystals or platelets, which are grown from a dilute solution, is identical to the basal plane of the unit cell. In other words, paraffin chains within platelets of the monoclinic form are tilted to their surface at the angle of tilt, and in the case of the orthorhombic form they are perpendicularly arranged to the platelet surface. Furthermore, the subcell of the crystal structure, that is, the mode of the packing of methylene groups, is the same for both forms. When platelets themselves have the orientation in which molecular chains are parallel to the incident direction of electron beams, the electron diffraction pattern is the same for both monoclinic and orthorhombic forms. Therefore, in principle, it may be difficult on the basis of the electron diffraction to know which modification the platelets

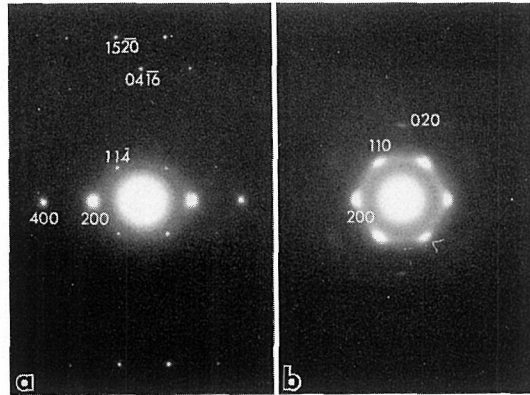


Fig. 1. Electron diffraction patterns of  $n$ -C<sub>36</sub> crystals taken after exposures of (a)  $0.11 \times 10^{-2} \text{C/cm}^2$  and (b)  $1.95 \times 10^{-2} \text{C/cm}^2$ . Diffraction spots of patterns are indexed on the basis of (a) the monoclinic and (b) orthorhombic forms. The orientation of a platelet for each pattern is identical.

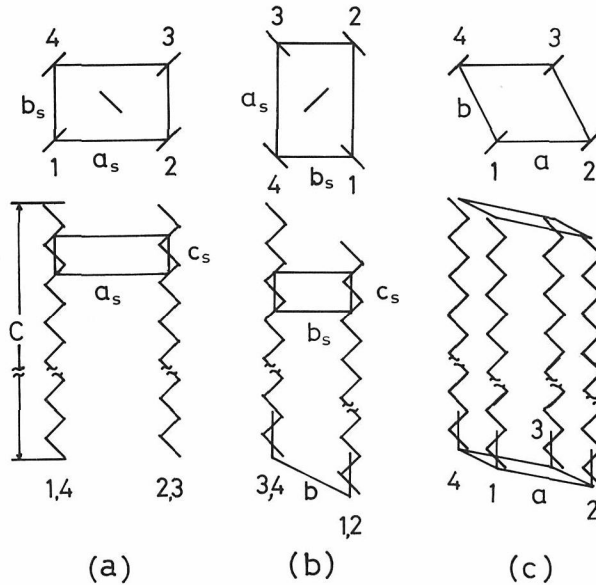


Fig. 2. The schematic representation of (a) the orthorhombic, (b) monoclinic and (c) triclinic unit cells. The dimension of c-axis changes with the molecular length of paraffins. The triclinic form is observed as a stable form in paraffins shorter than  $n$ -C<sub>24</sub>. The small cell suffixed with s in (a) and (b) is the subcell. The cell dimensions  $a_s$ ,  $b_s$  and  $b$  of the monoclinic form are equivalent to  $b_s$ ,  $a_s$  and  $a$  in the Ref. (8). This notation is adopted to index the electron diffraction patterns of Fig. 1 on the same crystallographic basis, since the subcell is same for both forms.

take. The platelets of the monoclinic form must rotate about a-axis by about  $30^\circ$  in order that they have the above orientation with respect to the incident beam originally normal to the surface of platelets. Such a large change in their orientation, however, hardly occurs during exposure to electron beams. In consideration of the molecular inclination in the platelets, electron diffraction patterns are justly indexed with the monoclinic and orthorhombic forms as shown in Fig. 1(a) and (b). This shows that the change of electron diffraction pattern due to electron irradiation results from the transformation of the crystalline modification from the monoclinic form to the orthorhombic, that is, the orientational change of molecular chains in a platelet from their oblique arrangement to the normal.

In order to ascertain the result, X-ray measurement was done about the paraffin ( $n\text{-C}_{36}$ ) irradiated with 80 kV electrons. Figure 3 shows the X-ray diffraction pattern of  $n\text{-C}_{36}$  crystals after an electron exposure of  $6.3 \times 10^{-4} \text{ C/cm}^2$ . This value of exposure corresponds to about  $3 \times 10^{-3} \text{ C/cm}^2$  in the case of 500 kV electrons. The crystal form of the original sample before irradiation is entirely monoclinic, but after irradiation the peaks corresponding to  $(00l)$  reflections of the orthorhombic form appear. Some molecular chains stand normally to the surface of platelet. Thus, it is assured from the measurement by X-ray diffraction that the phase transition is induced by electron irradiation.

In other paraffins such as  $n\text{-C}_{22}$ ,  $n\text{-C}_{24}$ ,  $n\text{-C}_{28}$  and  $n\text{-C}_{44}$ , a phase transition due to electron irradiation was also observed from the change in electron diffraction pattern. The phase is transformed from the triclinic form<sup>10)</sup> to the orthorhombic in  $n\text{-C}_{22}$  and  $n\text{-C}_{24}$ , and from the monoclinic to the orthorhombic in  $n\text{-C}_{28}$  and  $n\text{-C}_{44}$ , though the transition phenomenon in  $n\text{-C}_{44}$  is not so clear-cut as in the others. For example, Fig. 4 shows the change in the electron diffraction pattern of  $n\text{-C}_{22}$ . This paraffin usually crystallizes in the triclinic form and its electron diffraction pattern is shown in Fig. 4(a). After an exposure of more than  $1.5 \times 10^{-3} \text{ C/cm}^2$ , this pattern changes into Fig. 4(b). In consideration of the mole-

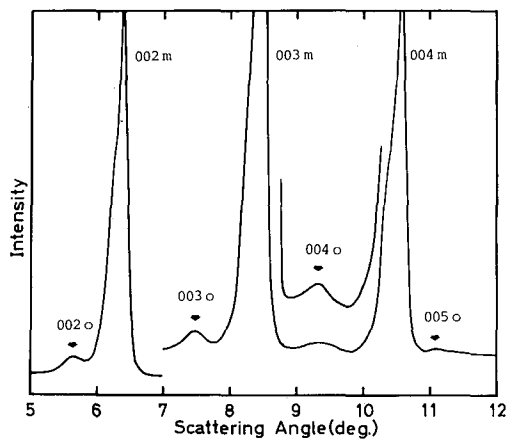


Fig. 3. The X-ray diffraction patterns of the specimen exposed to electron beams accelerated at a voltage of 80 kV. The exposure dose is  $6.3 \times 10^{-4} \text{ C/cm}^2$ . The arrowed peaks are characteristic of the orthorhombic form. Suffixes o and m of reflections denote the orthorhombic and monoclinic forms, respectively.

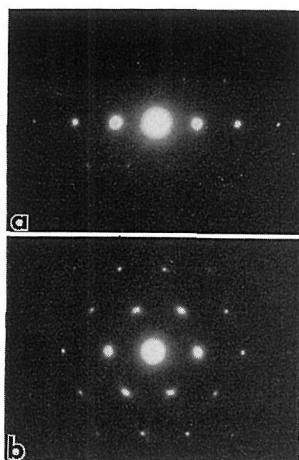


Fig. 4. Electron diffraction patterns of  $n$ -C<sub>22</sub> crystals taken after exposures of (a)  $0.11 \times 10^{-2}$  C/cm<sup>2</sup> and (b)  $1.95 \times 10^{-2}$  C/cm<sup>2</sup>. The patterns (a) and (b) correspond to those of the triclinic and orthorhombic forms, respectively. The orientation of a platelet for each pattern is identical.

cular orientation in platelets, the electron diffraction pattern of Fig. 4(b) is interpreted in terms of the orthorhombic form as in the case of  $n$ -C<sub>36</sub>, and this form is not observed at any temperature in crystals prepared from the solution and melt. The electron irradiation dose required to produce these phase transitions is almost constant in the present range of molecular length, and is  $1.5 \times 10^{-3}$  C/cm<sup>2</sup>.

There are other two factors to induce the phase transition of paraffins, *i.e.* temperature and impurities. To compare with the effect of electron beams, the effect of these factors on the phase transition was examined. The transition temperatures and heats of transition of the monoclinic form to the orthorhombic were measured with DSC and the results are listed in Table I together with data reported.<sup>11)</sup> The phase transition of the triclinic form to the monoclinic form never occurs thermally.

An addition of a slight amount of impurities, for example homologs with different molecular length, causes the crystal transformation when a paraffin exists in various modifications.<sup>12)</sup> The binary mixtures of  $n$ -C<sub>23</sub> and  $n$ -C<sub>24</sub> and of  $n$ -C<sub>24</sub> and  $n$ -C<sub>25</sub> were crystallized from 0.1% solutions in methanol and the long periods of crystals thus obtained were measured by X-ray diffraction. Figure 5 shows the results. Pure  $n$ -C<sub>24</sub> paraffin

Table I. The transition temperatures,  $T_t$  (°K) and heats of transition,  $\Delta H_t$  (kcal/mol.) of paraffins from the monoclinic form to the orthorhombic form, and the number of molecules transformed by a crosslink,  $N$ .

paraffin	$T_t$	$\Delta H_t$	$N$
$n$ -C <sub>36</sub> H <sub>74</sub> *	345.1	2.1	16.6
$n$ -C <sub>40</sub> H <sub>82</sub>	347.8	3.1	11.3
$n$ -C <sub>44</sub> H <sub>90</sub>	351.6	4.4	7.9

\* reference (12)

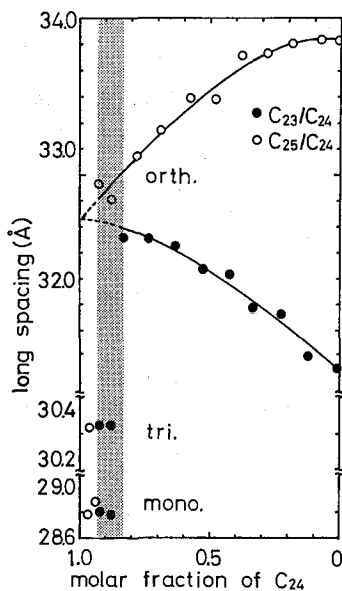


Fig. 5. The long periods of mixed crystals of  $n$ -C<sub>23</sub> and  $n$ -C<sub>24</sub> (●) and of  $n$ -C<sub>24</sub> and  $n$ -C<sub>25</sub> (○) as functions of molar fraction of  $n$ -C<sub>24</sub>. The dotted region shows the co-existence of two forms.

invariably crystallizes in the triclinic form. If a small amount of another component,  $n$ -C<sub>23</sub> or  $n$ -C<sub>25</sub>, is added, monoclinic crystals are also formed. When the content of this component is more than 10% in molar fraction, only orthorhombic crystals are precipitated. The long period monotonically decreases with further addition of the component of  $n$ -C<sub>23</sub> and increases in the case of  $n$ -C<sub>25</sub>. It is assured that each mixture of paraffin molecules co-crystallized to form mixed crystals, because in the lower composition of impurity two long periods corresponding to the stable phase of the respective pure paraffin are not observed separately and because in the higher part the long period changes continuously with the composition of the mixture. The similar phase transition is also observed on the crystallization of the binary mixtures of  $n$ -C<sub>27</sub> and  $n$ -C<sub>28</sub>, of  $n$ -C<sub>35</sub> and  $n$ -C<sub>36</sub> and of  $n$ -C<sub>40</sub> and  $n$ -C<sub>44</sub>. However, the phase diagram is not so well defined as in the case of  $n$ -C<sub>24</sub>, because pure even-numbered paraffins such as  $n$ -C<sub>36</sub>,  $n$ -C<sub>40</sub> and  $n$ -C<sub>44</sub> crystallize in a different form, monoclinic or orthorhombic form, with a slight change of the crystallization condition (temperature etc.).

## DISCUSSION

It is clear from above results that the phase transition of normal paraffins takes place due to electron irradiation. The shorter the molecular length, the more sharply the phase transforms. The mobility of molecules in crystals is reflected in the ease of the phase transformation. Since this transition also occurs thermally, the secondary effect of an electron exposure, that is, the temperature rise of specimen, may not be neglected as a factor to induce this transition.  $n$ -C<sub>24</sub> and  $n$ -C<sub>28</sub>, whose melting temperatures are 323.8 and 334.4 °K respectively, still remain to be a crystalline state at the irradiation dose where the phase

change of  $n\text{-C}_{36}$  ( $T_f=345.1^\circ\text{K}$ ) is completed, and the orthorhombic form which is never observed as a stable state in the normal condition appears. These observations show that the phase transition is not thermally induced as the side-effect of irradiation.

The scission of molecular chains and the formation of cross-links are caused by electron irradiation.<sup>13)</sup> The phase transition is surely associated with this change of chemical structure of molecules. These molecular irregularities work as lattice defects and thus the lattice around these defects is distorted and stressed. As the oblique orientation of molecular chains transfers to the normal orientation in  $n\text{-C}_{36}$ , the strain of thus distorted lattice may be relaxed by the shearing displacement of molecular chains in the direction parallel to their axes. In the transition of the triclinic form to the orthorhombic, shearing must accompany the rotation of molecular chains around their axes. This is easily seen by comparing the side-by-side packing of molecules of Fig. 2(c) with that of Fig. 2(a). Thus, molecular displacement and rotation (a phase transition to a high energy phase) accommodate the radiation-induced stress. The orthorhombic form is often observed in the electron diffraction of even-numbered paraffins with the shorter chain length.<sup>14)</sup> This may not be an as-grown stable phase but the resulting one due to transition by electron irradiation.

The chain length differs by the length of one carbon atom (1.27 Å) between  $n\text{-C}_{23}$  and  $n\text{-C}_{24}$  and between  $n\text{-C}_{24}$  and  $n\text{-C}_{25}$ . The result of Fig. 5 shows that this small difference in chain length has a large effect on the crystal form of mixed crystal, when these impurity components are incorporated into the host lattice of  $n\text{-C}_{24}$ . The crystal structures of mixed crystal are not yet made clear<sup>15)</sup> and therefore the effect and behavior of end groups of impurity components within matrix crystals are not fully understood. It is convinced, however, that these chain end groups should play a important role as lattice imperfections, especially point defects. This phase transition is speculated as follows: once a impurity molecule deposits on the growth front of a platelet, matrix molecules depositing one after another are not arranged in a stable configuration in the vicinity of the impurity because of the misfit of chain ends in the host lattice. Thus, the mixed crystal is stressed. When the content of impurity component becomes high over a certain limit, the mixed crystal transforms into a high energy phase to relieve the imposed stresses. From Fig. 5, the content of impurity component where the crystal form changes is estimated at about 10% in molar fraction. As reported to be a few percent,<sup>16)</sup> this critical content may depend on the molecular length of matrix crystals and the kind of impurity. Roughly speaking, the phase transition occurs when the impurity content reaches not less than 10%. In other words, the form of mixed crystals alters when ten matrix molecules contain one impurity molecule on an average. In terms of the relaxation of stresses around lattice imperfections, the phase transition of radiation-damaged crystals is interpreted in the same way as in the case of mixed crystals. It is concluded that the crystal form of paraffins changes when one lattice imperfection or defect is introduced into the volume occupied by ten host molecules.

It is not made clear what kind of lattice defects are introduced by electron radiation damage, and now we assume that the cross-link are formed (as shown in Fig. 6).<sup>17)</sup> Guiu and Shadrake have calculated the strain field produced by the cross-link by applying the theory of elasticity to this model and estimated the excess strain energy due to this defect at  $(2.54 \pm 0.07) \times 10^{-19}$  Joule/cross-link.<sup>18)</sup> In their calculation, the crystal lattice is



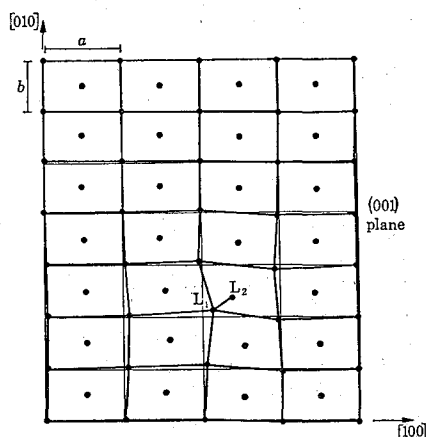


Fig. 6. The proposed model of lattice distortion of (001) plane due to a cross-link. The link  $L_1$ - $L_2$  is a cross-link. Dots denote the position of chain molecules. Here,  $a$  and  $b$  show the dimension of the unit cell in the  $\mathbf{a}$  and  $\mathbf{b}$  axes, respectively.

assumed to be extended infinitely and therefore it is not always correct to apply this model to the distorted paraffin crystals which are bounded and discontinuous at the plane (identical to (001) plane) consisting of chain ends. This difference will be neglected as a first approximation and the phase transition is assumed to be originated on this excess strain energy. In other words, the new phase accommodate this excess energy. This assumption is equivalent to the proposition that this strain energy is stored as the thermal energy in the specimen. The enthalpy change  $\Delta Q$  to induce the phase transition is expressed as

$$\Delta Q = \int_T^{T_t} \Delta C_p dT + \Delta H_t, \quad (1)$$

where  $T_t$  and  $T$  denote the transition and reference temperatures,  $\Delta C_p$  the difference of specific heat between two phases (cal/°K·mol) and  $\Delta H_t$  the heat of transition (cal/mol). Since the difference of specific heats between two forms is believed to be small, the first term of the right-hand side of Eq. (1) is not taken into account. The thermal effect on specimens arising from electron exposures (for example, the thermal energy liberated by the formation of cross-links) is also neglected, because it can not be evaluated in any way. Under this assumption, the number of molecules which undergo the phase transition on the energy corresponding to one cross-link is given in Table I on the basis of Eq. (1). From this table, it is seen that the number of molecules transformed by a cross-link ranges from 8 to 16. The phase transition occurs when a cross-link is introduced in every domain consisting of ten molecules. Cross-links possibly behave as lattice defects or imperfections, and their effect on the lattice around them may differ from that of impurities in mixed crystals. However, the contents of structural irregularities enough to produce the phase transition agree well between mixed and damaged crystal, approximately one lattice imperfection per domain composed of ten molecules. This content of defect is also independent of their chain length and the type of defect and is achieved at an electron exposure of  $1.5 \times 10^{-3}$  C/cm<sup>2</sup> at 500 kV.

ACKNOWLEDGMENT

The authors are indebted to Dr. Naomichi Baba for his help of measuring by gas chromatography and Mr. Masakazu Suzuki for his assist in DSC measurement.

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