

The Changes of Polymer Crystals due to Irradiation with Electrons Accelerated at Various Voltages*

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Damages of organic polymer crystals (specimens) due to the electron bombardment were studied with a 300 kV microscope. All of the measurements were carried out with the specimen thicknesses permitting only single inelastic collision of the incident electron to make the results simple to interpret. The dose necessary to change the diffraction spots of polymer single crystals into halo rings is constant when the velocity of incident electrons is fixed, and is independent of the dose rate applied. The necessary dose decreases with the increase of the accelerating voltage of incident electrons in the range of 75-300 kV. It is thus proved that the damage to the specimen is inversely proportional to the energy (eV) of the incident electron. This result suggests that the rate of the secondary reactions is not linearly proportional to the primary events (inelastic cross-section). Cooling of the specimen does not serve to prevent it from irradiation defects. The decay process of polymer crystals irradiated with electrons is discussed.

INTRODUCTION

Before the development of radiation chemistry, the damage of specimens due to the electron irradiation was considered by many electron microscopists as the result of drastic temperature rise which occurred in the specimens. The phenomena of rapid fading or blurring of electron diffraction spots into halos were interpreted as the result of the melting or thermal decomposition of the specimen by heat¹⁾ due to the electron bombardment. When the specimens are organic substances and the irradiation intensities (i.e. incident beam currents) are high, these interpretations would be correct to some extent. To prevent the "melting" or "carbonizing (charring)" of organic specimens, several cooling devices were proposed and used in practice²⁾.

The radiation chemistry offered us the knowledge about the actual changes of the organic materials induced by ionizing radiations^{3,4)}, and the energy spectra of electrons scattered inelastically were measured by means of the velocity analysers⁵⁾. The spectra of energy loss of electrons passing through organic polymer membranes revealed the fact that the ionization of carbon atoms was the dominant effect in the inelastic collisions of fast electrons with organic molecules. The ionization of carbon atoms is succeeded by the secondary chemical reactions, such as crosslinking between neighboring molecular chains, scission of chains, production of double bonds between carbon atoms, radical formation etc.

Any quantitative measurement on the temperature rise of specimen has not yet been carried out. However, the semi-quantitative studies on the sublimation of

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trinitrocresol and several other organic crystals by Hall⁶⁾ and melting of bismuth film by Sakaoku⁷⁾ showed the actual temperature rise of their specimens were not so high as were expected from the theory, in which all the absorbed energy was assumed to change into heat. This means that the theoretical values were overestimated. It is clear that the probability of inelastic collision of incident electrons with carbon atoms and also that of subsequent ionization of carbon atoms are not dependent upon the temperature of the specimens. Only the rates of secondary processes depend on the temperature of specimens. If the specimens are organic polymer solids and are kept at the temperatures below their softening points, we can assume that the rate of secondary reaction is linearly proportional to that of primary process. This condition will be satisfied when the dose rate of irradiation is not too high and the overall reaction is stationary. In other words, by measuring the secondary effects we can estimate the numbers of primary processes produced by the electron irradiation on organic specimen.

It is a well established fact that the effective inelastic cross sections are reduced with the increasing velocity of electrons⁸⁾. Taking the relativistic correction into account, this effect for carbon atoms will be traced up to several hundreds kV. From these viewpoints, we have pursued the effects of electron irradiation on the organic specimens under the electron microscopes, comparing the rate of damage to the specimen by the electrons at various accelerating voltages in the range of 75-300 kV. We found that a high voltage electron microscope was superior to the conventional one for the observation of organic specimens highly sensitive to the decomposition by the electron irradiation. These organic specimens can be observed with the least deterioration in its molecular textures by this powerful instrument.

EXPERIMENTAL PROCEDURES

A 300 kV electron microscope⁹⁾ was employed which was constructed by us with the cooperation of Shimadzu Seisakusho Ltd. Among the various merits of this instrument the most distinctive one is the fact that it permits us to change the accelerating voltage from 75 to 300 kV continuously with an easy operation. Otherwise it is difficult to perform the comparative measurements. It was proved that the contamination of the specimen, i.e. deposit of decomposed oil vapor was very small at high accelerating voltage. This effect makes it possible to conduct prolonged measurements (more than a quarter of an hour) without being disturbed by the growth of effective thickness of the specimen.

The degree of damages or defects introduced to the specimens can be detected by several means. Among them the best measure of the changes occurring in the molecular texture of the specimen is to be the tracing of the transformation of its diffraction pattern into a definite diffuseness, when the substance is crystalline. The disappearance of the moiré patterns can also be utilized for this purpose. We adopted single crystals of organic polymers as the specimens on which degradations by electron irradiation were to be inspected. All of these polymer single crystals are very thin platelets with the thickness of less than 200 Å. Some of them are composed of the spirally grown lamellae of crystals.

For this experiment the crystals thinner than Von Borries's "Bremsdicke"¹⁰⁾ were

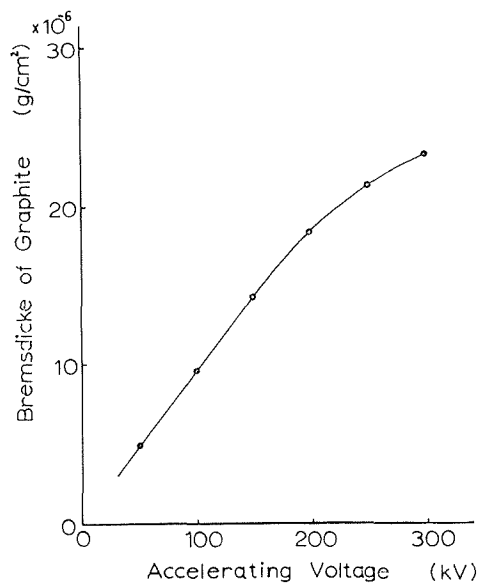


Fig. 1. "Bremsdicke" calculated for carbon (graphite).

selected by the preliminary observation with the 300 kV microscope. In such crystals we can deal with the single inelastic collision only as the primary act of the electron irradiation. The lamellae of crystal have no continuity between their flat surfaces though they are grown spirally, and the irradiation defects in any lamella have no effect on the adjacent one. Since the probability of inelastic collisions is linearly proportional to the thickness of the specimen in this range, the damage to the unit lamella is to be equivalent regardless of the number of superposition of lamellae. Then it is expected that quite similar change or blurring in diffraction patterns of the specimen will be observed at the same dose of irradiation, as far as the total thickness of the spirally grown lamellae is smaller than the "Bremsdicke". Owing to this simple effect it is unnecessary to measure the thickness of the specimen one by one.

In respect to the secondary reactions derived from the primary acts of inelastic collisions, most of the organic polymers are classified in two groups. One is the "cross-linking" type and the other is the "scission" type. Typical example of the former group is polystyrene in which crosslinking between molecular chains is predominant in the early stage of deterioration due to the irradiation. For the latter group fractures of the polymer chains take place preferentially as observed with polymethylmetacrylate^{3,14}. In an evacuated electron microscope column the fragments of degraded chains sublime readily even at temperatures lower than their evaporating points. Accordingly, when the polymer specimens are one of the "scission" group, their diffraction patterns are not blurred but fade out by reducing the diffraction intensity. In order to make the measurements simpler we used polymers of the "crosslinking" type as the objects, such as linear polyethylene, polyethylene oxide of high molecular weight and nylon 6. These were precipitated from their dilute solutions to form single crystals. The only one sample adopted from the "scission" group was polyoxymethylene. The methods for

Table 1.

Polymer	Polyethylene	Polyethylene oxide	Polyoxymethylene	6 Nylon
Solvent	Xylene	Butylcellosolve	Cyclohexanol	Glycerine
Crystallization technique	Gradually cooled in a double sealed thermos, 1°C/hr.	Gradually cooled in a double sealed thermos, 2°C/hr.	Gradually cooled in a double sealed thermos, 2°C/hr.	Cooled to room temperature in a glass bottle

preparing these single crystals are tabulated in Table 1.

After 1957 it has been established that these polymers are crystallized in the form of platelets of homogeneous thickness by folding their molecular chains regularly¹¹⁾. In contrast to some authors who maintain that "amorphous regions" exist on both surfaces of platelets¹²⁾, we have a firm conviction of the absence of such amorphous portions. By the use of a high voltage electron microscope we were able to obtain the electron diffraction patterns of original molecular arrangements of the specimen undisturbed by the irradiation.

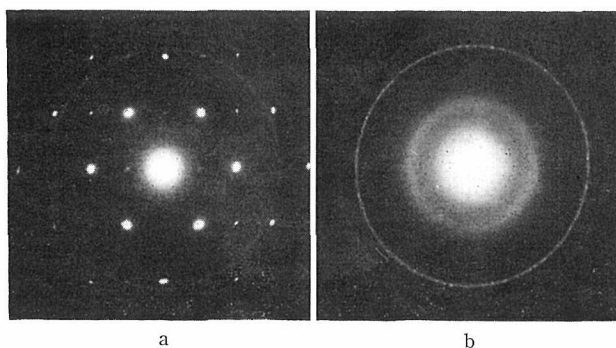


Fig. 2. Electron diffraction patterns of a polyethylene single crystal mounted on an evaporated Al film.

Fig. 2. shows a pair of electron diffraction patterns of a polyethylene single crystal mounted on an aluminum evaporated film. Fig. 2-a was taken immediately after the specimen was exposed to the electron beam and 2-b after a prolonged exposure to the beam. In 2-b all the crystalline structure is lost but an "amorphous" halo remains. It is noticeable in 2-a that no trace of such a halo ring is detected. This proves that the amount of amorphous regions in the polyethylene single crystal, even if exist, is negligibly small before the irradiation. Another evidence obtained by Kobayashi for this matter is the well defined epitaxial growth of these polymer single crystals on the cleavage surfaces of alkali halides or muscovite crystals¹³⁾. In other words our starting materials have no distinct "amorphous region", although they are not as "perfect" as inorganic single crystals. The blurring of spots and their smearing into halo rings are brought about by the defects, such as crosslinkings between molecular arrays or double bond formation along chains, introduced in the crystal lattices by the electron irradiation. Nevertheless we call those rings "amorphous" halos for convenience even though they are of different origin from conventional ones.

Besides the polymer single crystals the drawn polymer films were subjected to the same kind of electron diffraction study. The polymer films were prepared by spreading the hot solutions of polymers on hot water surfaces. After the evaporation of the solvents, the resultant very thin films were stretched with two needles. The thickness of these drawn films was estimated to be less than 1000 Å.

The optical system of the electron microscope was set to be used for the micro-diffraction of the selected area, and a number of serial photographic records were made on the decay process of diffraction patterns of polymer single crystals. The durations of exposures and their intervals were varied in wide range with the dose rate (beam current density on the unit area of the specimen) and with the accelerating voltage of electrons. The exposure time for photographing had to be increased with the accelerating voltage of electrons. The sensitivity of photographic emulsions for 200 kV electrons is about one half of that for 100 kV electrons.

Total dosage of electron irradiation was the sum of each photographic exposure time and the time of interval. The first exposures are carried out always just after a clear diffraction pattern or an electron microscopic image of an adequate single crystal has been detected on the fluorescent screen. The time consumed in switching the optical system from microscopy to diffraction work is included in the total dose for the first exposure at higher dose rate or lower accelerating voltage, since the change is very fast under these conditions. For 50 kV electrons, any polymer specimen could hardly "survive" without losing its original crystalline structure after the first exposure for micro-diffraction.

The spread of the incident electron beam is kept at several microns on the plane of the specimen to prevent the other crystals mounted on the same grid from any pre-irradiation to them. The precaution was paid to avoid the generation of the excess heat by direct bombardment to the metal grid itself. If the high voltage electrons were wholly stopped by metal, the heat generated is enormous.

The dose rate or electron beam intensity applied to the specimen was measured with a microammeter or a $\mu\mu$ ammeter connected to a Faraday's cage inserted just before the intermediate lens or between the projector lens and the fluorescent screen. Our 300 kV microscope has a slight hysteresis in lens power and the error due to this hysteresis amounts up to 5 % when the magnification is estimated from the lens current. This brings about 10 % error at maximum in evaluating the beam intensity per unit area of specimen.

In the present experiment a very simple and sure scale was employed for the determination of irradiation effect. That is an "end point" method. Examining the serial records (up to one dozen in one series) of selected area diffraction patterns, it is easy to determine the total dose by which the patterns have changed completely into halo rings. That means the single crystals of polymers have turned into so-called amorphous state by crosslinking. Beyond this point there is no distinct change in the diffraction patterns. This end point is never overlooked even when the diffraction angles are so small at higher accelerating voltages. The dose is given in the unit of Amp. min./cm taking into account the inaccuracy of intensity measurements and the change during the photographic record.

RESULTS AND DISCUSSION

Distorsion of Crystal Lattices

Fig. 3-a, b and c are the electron diffraction patterns of the same polyethylene single crystal. Fig. 3-a was taken just after 300 kV electron beam had been applied to the

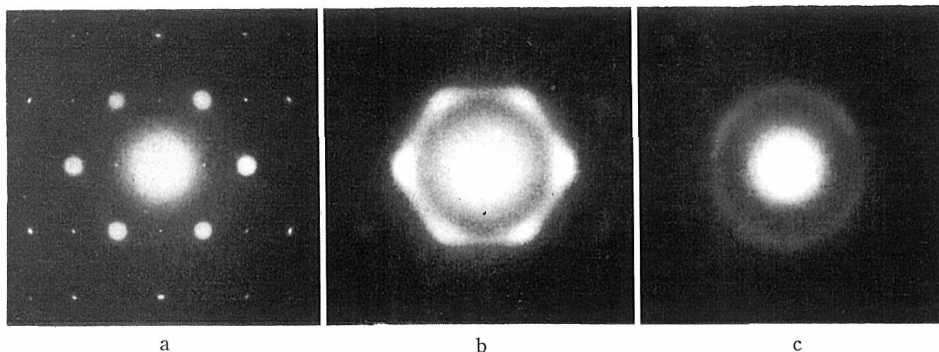


Fig. 3. Electron diffraction patterns of polyethylene single crystal mounted on carbon film. In (b) the second and third order spots blurred.

specimen. Many higher order spots are detectable in the photograph besides the faint spots of (100) and (010) reflections which are prohibited to appear, as they belong to the extinction interferences. The weak halo ring observed is due to the carbon membrane supporting the specimen. Continuing the irradiation, the pattern changed with blurring and fading of the spots from higher order ones, as shown in Fig. 3-b. The remaining strong reflection from (200) and (110) gradually moved inward, that means the spacings of these planes increased. The shift of (200) is larger than that of (110) and these spots blur to make small arcs which joined together finally in a halo ring as shown in Fig. 3-c. The spot of (020) also blurs but the shift is too small to be measured precisely.

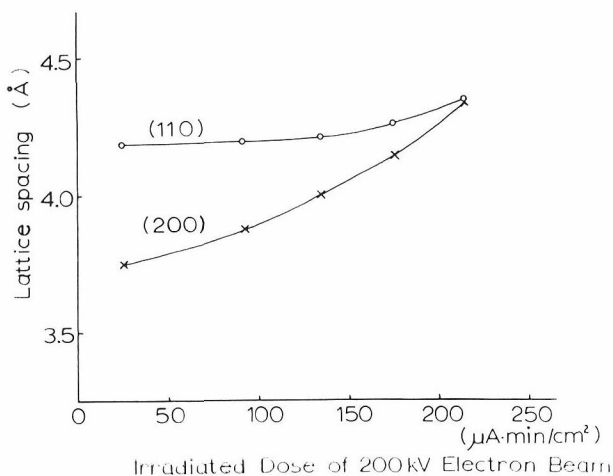


Fig. 4. Expansion of lattice spacings of polyethylene crystal by irradiation.

The changes of the spacings by the irradiation of 200 kV electrons are plotted in Fig. 4. This measurement was carried out with the polyethylene single crystals mounted on aluminum thin film utilizing the diffraction rings of aluminum as the reference (cp. Fig. 2.). The left half of this curve is in good agreement with the result reported by Fischer¹⁴⁾ which was worked out by a 100 kV electron microscope and hence the dose was much smaller than ours.

The trend of the preferable expansion of the spacings in the a-axis direction of crystal during the irradiation with electrons is similar to that of thermal expansion¹⁵⁾, and the diffraction pattern of the specimen melted by heating gives a halo ring. The transformation of a polymer crystal during irradiation appears to be promoted only by the temperature rise in the specimen. If so, the change must be reversible. As to the irradiated specimen the change is quite irreversible. Provided that the polymer crystals are melted by strong irradiation, they ought to recrystallize after an interruption of irradiation for some minutes. This is not the case.

The main secondary reaction induced by ionization of the carbon atoms is the crosslinking between adjacent molecular chains. In the crystals of folded molecules both inter- and intra-molecular crosslinking will occur.

Recent observations by many researchers¹¹⁾ referred to the strange behavior of polymer single crystals at the temperatures a little below their melting points. The thin crystals increase their thickness, which is the fold length of the molecular chains, by heat treatment. The translational motion of folded chains along the neighboring chains is the origin of this phenomenon and it results in the growth of crystal thickness and it forms many holes in the specimen as compensation. Fig. 5-a illustrates this phenomenon. The unirradiated single crystals melt at their melting points and by cooling they recrystallize in polycrystalline form as shown in Fig. 5-b.

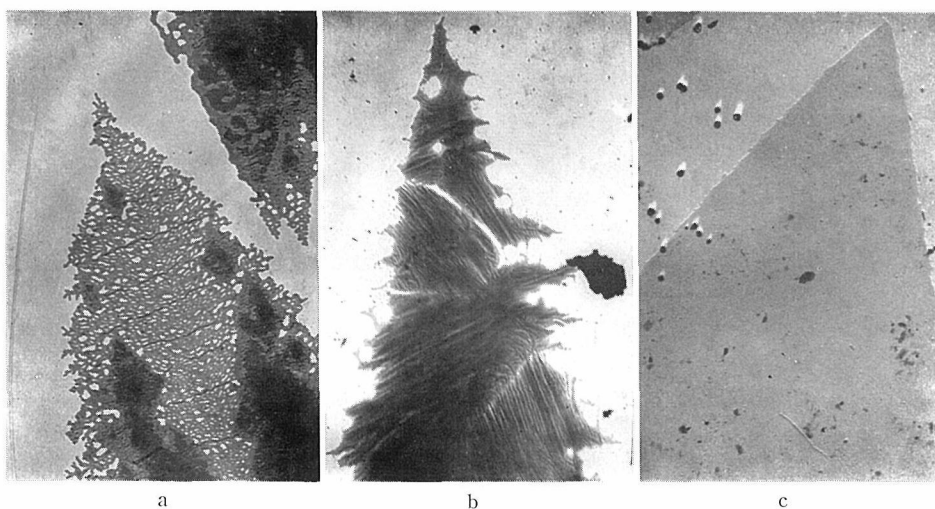


Fig. 5. Effects of heat treatments on polyethylene single crystals. (a) annealed at 120°C. (b) melted at 135°C and recrystallized before the electron microscopic observation. (c) irradiated and then annealed at 160°C in vacuum.

The introduction of numerous crosslinkings between adjacent chains will hinder such a thermal motion of the chains. Fig. 5-c is the image of crystals intensely irradiated with the electron beam prior to the heat treatment, retaining its original size and shape even after the annealing at the temperature higher than the melting point. These photographs render a direct proof for the existence of intra-molecular crosslinking in the folded chains. The inter-molecular crosslinkings were proved already to exist by the insolubility (or the gelation) of irradiated polymers in the solvent.

In spite of the expansion of crystal lattice along its *a*-axis, the same polyethylene single crystal, doubly shadowed with metal before and after a long exposure to electron beam, showed no detectable change in shape and size under a high magnification electron microscope. On the other hand, the change of size during heating is clearly revealed by the double shadowing technique. From these facts it is obvious that the expansion of crystal lattice in the irradiated specimen is different from that due to thermal expansion.

As the theory concerning the broadening of diffraction spots indicates, the half breadth of the higher order interference is proportional to $1/\cos \theta$ when the crystallite size and the thermal vibrations of molecular segments are the main factors of the broadening, or it is proportional to $1/\tan \theta$ when the regularity of lattice spacing is distorted, where θ is Bragg angle of the spot in question.

In the electron diffraction of polymer crystals $\tan \theta$ is assumed to be equal to θ since θ is very small. On the diffraction patterns of moderately irradiated polyethylene

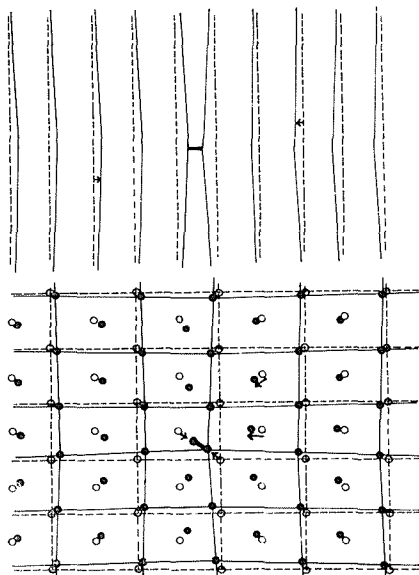


Fig. 6. Distorted crystal lattices of polyethylene with a crosslink between molecular chains. Side view along *b*-axis (above) and projection on *a*-*b* plane (below). Dotted lines represent original (undistorted) lattices.

crystals, the degree of blurring of spots is strongly proportional to the order of reflections¹⁴⁾, i.e. to the angle of θ . Therefore, it is concluded that distortion of lattice spacings should be induced by the irradiation.

The force necessary to shift the molecular chain is very anisotropic in the directions perpendicular to chain axis (c-axis of the crystal), and that along b-axis is 2.5 times stronger than that along a-axis. This estimation was based on the intermolecular interaction with diverging force of Lennard-Jones type. Therefore, any crosslink between molecular chains in polyethylene crystals will result in the local expansion of the crystal lattices along a-axis and subsequently produce the distortions of lattices surrounding the crosslinked portion. The schema of this deformation of crystal lattices is illustrated in Fig. 6.

From this illustration it is easy to understand that the regularities along the chains, the repeating period in c-axis, are not so severely distorted as are the lateral periodicities. This was proved by the observation of the changes of diffraction patterns of stretched thin films of polyethylene during electron irradiations. Fig. 7. is one of the serial

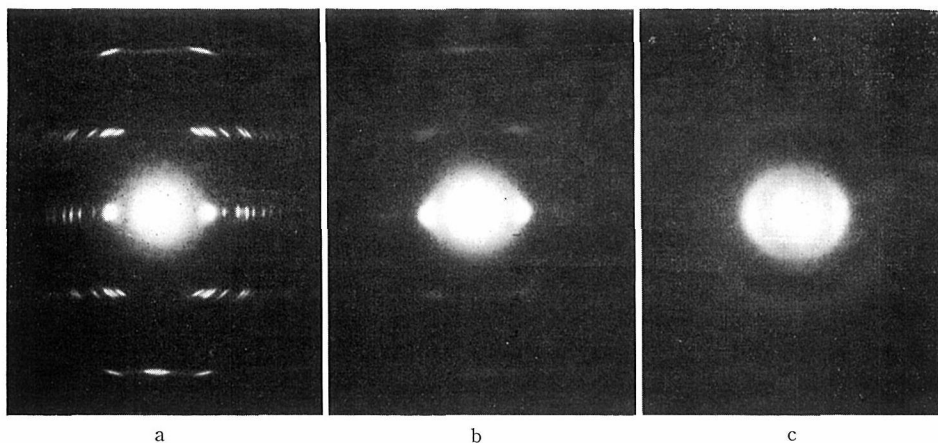


Fig. 7. Electron diffraction patterns of stretched thin film of polyethylene at three different doses of irradiation.

records of them. The (002) reflection and layer lines, although smearing in streaks, are resistant against the irradiation, while the equatorial spots fade rapidly.

Effect of Dose Rate

Prior to evaluating the effects of the increase of accelerating voltages to the irradiation defect of polymer crystals, the effects of the dose rate and the total dose of irradiation to the specimen were studied. The results of these two series of experiments are plotted in Figs. 8-a and b. Though the measured values are scattered, it is confirmed that the total dose necessary to transform the electron diffraction patterns of polyethylene crystals from distinct spots to amorphous halo is nearly constant.

The temperature rise of the specimen exposed to the electron beam during the experiment is difficult to measure directly. However, in the range of the dose rate

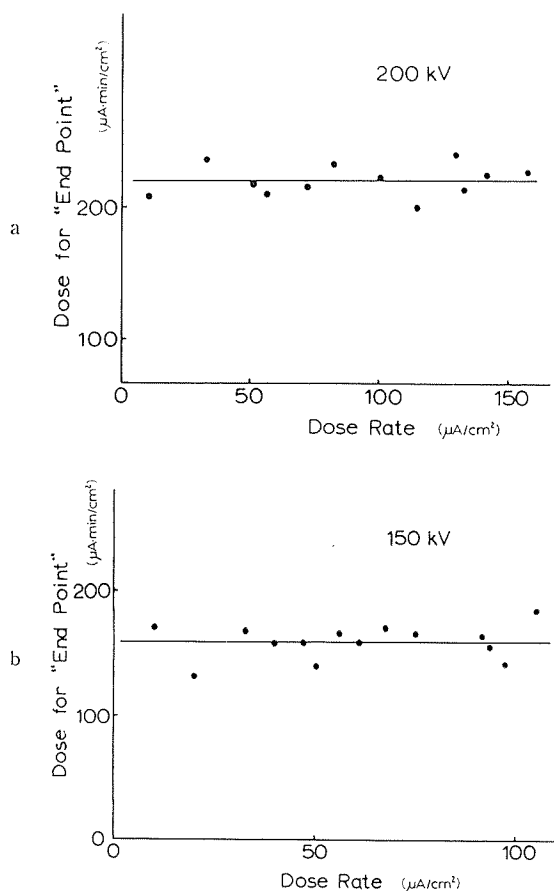


Fig. 8. The relation of dose rate to the total dose for the "end point" where polyethylene crystals change into amorphous structure.

applied to this experiment, the calculated value of the temperature rise did not exceed 50°C higher than room temperature (20°C).

Since this estimation is based on the assumption that the whole energy transferred from inelastically scattered electron to the specimen changes into heat, the calculated value is somewhat overestimated as mentioned in the introduction of this paper. The actual temperature rise has to be less than this calculated value, and the temperature of the polyethylene crystals is to be kept lower than its softening point. Therefore, the translational motion of the molecular chains are so restricted that the radicals produced by the primary events of the inelastic collisions are hard to move from its original position on the long molecular chains. Then the number of secondary processes, crosslinkings between adjacent chains in this case, is to be linearly proportional to the number of primary events.

The number of primary events does not depend on the dose rate of incident electron but the total number of inelastic collisions. Hence, the latter is known to be proportional to the total number of incident electrons (that is the dose), where the

probability of collision is expressed as inelastic cross section, provided that the mass thickness of the specimen is smaller than the "Bremsdicke". This leads to an important conclusion that the damage to the polymer crystals by the electron irradiation is proportional to the inelastic cross-section as well as the dose, when the mass thickness of the specimen is in the range of single inelastic scattering for the incident electron. Since the inelastic cross-section is inversely proportional to the square of β , ratio of electron velocity to that of light, the dose resulting the same effect to the specimen has to be nearly proportional to the accelerating voltage of the incident electrons, when the increment of the relativistic effect is small. The results of the same experiments shown in Figs. 8-a and -b substantiates this conclusion. The ratio of the dose necessary to destroy the crystallinity of the polyethylene is approximately equal to the ratio of accelerating voltages within the error of the dosimetry (less than 10 %).

The average dose of electrons necessary to transform the polyethylene crystals into amorphous structure is $220 \mu\text{A} \cdot \text{min}/\text{cm}^2$ at any dose rate of 200 kV electrons as shown in Fig. 8-a. Since these experiments have been carried out with very thin lamellar crystals where the inelastic collision of incident electron with carbon atoms should be single, the number of inelastic collisions per molecule chain can be known by a simple computation as follows:

The "Bremsdicke" $d\rho$ of carbon for 200 kV electron is estimated to be $18.24 \times 10^{-6} \text{ g}/\text{cm}^2$ as shown in Fig. 1. Within this mass thickness of polyethylene, 1.44×10 carbon atoms with the spacing of $1.267 \text{ \AA}$ arrange along c-axis of the crystal. C-axis, the chain axis, is parallel to the incident electron beam. The practical unit of dose $1 \mu\text{A} \cdot \text{min}/\text{cm}^2$ means 3.7452×10^{14} electrons irradiating a unit area of the specimen during one minute. Taking the structure of polyethylene crystal in account, containing two molecule chains per unit cell, the total number of incident electrons per molecule chain at the dose of $220 \mu\text{A} \cdot \text{min}/\text{cm}^2$ is 150. Dividing this value by the number of carbon atoms, 1.44×10^3 , the number of inelastic collision of electron per carbon atom is estimated to be 1/9.6.

Hence one inelastic collision of electron per 10 carbon atoms is sufficient to destroy the all traces of crystallinity of polyethylene. It should be noticed here that this value holds as a constant for wide range of the dose rate as well as the accelerating voltage of the incident electrons.

Effect of Temperature

On the contrary to our results, Belavtseva¹⁶⁾ and Fisher have suggested that at high dose rate the total dose necessary to produce the same effect upon the organic specimen was small. Fisher and Orth¹⁷⁾ observed such effect in the line broadening of the Debye-Scherrer rings of stacked polyethylene single crystals. The difference in results can be attributed to the temperature effect on the secondary reaction which was implicit in their experiments. With the mass thickness of the specimen the heat produced by electron bombardment increases. The temperature of the specimen is determined by the equilibrium between the input of energy from incident electrons and the output as the radiation and conduction of heat to the environment of the specimen. When the dose rate is high, the heat is accumulated, raising the temperature of

the specimen and as the consequence the secondary reaction is accelerated. Therefore the dependence of the specimen damage on the dose rate appears to be indirect.

Another series of experiments was prepared by us for the examination of the temperature effects upon the structure changes due to irradiation. The specimens for this object were very thin polyethylene single crystals and the dose rates were kept very low. These conditions were chosen to minimize the temperature rise by the electron bombardment only. Using a cooling and a heating device the temperatures of specimens were changed in the range from liquid nitrogen temperature up to 100°C. The results of this serial experiment are demonstrated in Fig. 9.

Above the softening point of this material, i.e. at 80°C. and 100°C., the acceleration of the secondary reaction seems to be very distinct. However, below room temperature down to -160°C., there is no noticeable variation in the rate of the decay process of the crystallinity. This result will be responsible for the evaluation of the cooling and heating specimen holders in the study of organic materials.

In this experiment the dose necessary to transform crystals into amorphous structure remained nearly constant in the range from room temperature down to -160°C, while the early experiments of the irradiation effects to polyethylene reported by Black¹⁸⁾ and by Charlesby and Davison¹⁹⁾ showed a remarkable increase of G value for crosslinking with temperature in this range; the G value at room temperature was 2.5 times higher than that at -120°C. This discrepancy is due to the difference of the measuring techniques as well as the dose applied. In the present experiment, the effect was measured while the specimen being irradiated at the temperatures concerned. In the early experiments referred above, the measurements of crosslinking density (by solubility or by swelling) were carried out at the temperatures different from those for irradiations.

It is obvious that the inelastic cross section has no temperature dependence, and therefore the rate of the primary events of inelastic collision, ionization and excitation, do not vary with the temperature in this range. This was also proved by Charlesby and Davison¹⁹⁾ who showed that G value for the evolution of hydrogen measured simultaneously with that for crosslinking was constant in this range of temperature. This result is considered to be an evidence justifying the result of our experiment on the temperature effect.

Our results show that the rate of secondary reactions cannot be decreased by cooling, while the elevation of temperature enhances the secondary reaction to such a great extent that the temperature coefficient of these chemical reaction cannot answer for. The extraordinary high rate of the crystallinity decay at the temperature higher than the softening point has to be attributed to the relaxation of the inner strains induced into the crystal by the electron irradiation, since the translational motion of the chain is not so large at these temperatures. This presumption is justified by the fact that the moderately irradiated polyethylene film loses its crystallinity mostly by a heat treatment after irradiation.

As for the cooling effect on the irradiation damage to organic substances, Honjo and Watanabe used a cooling device in an electron microscopic study of cellulosic membranes, and they obtained sharply defined electron diffraction patterns of this material. In their paper²⁾ they stated that the crystalline structure of cellulose had not been damaged

even under strong irradiation during the observation with high magnification. However, their experiment was rather qualitative, and the dose rate to the specimen was not measured.

It has been established by our experiment that the cooling device of the specimen is not useful to prevent the specimen from the damage due to the electron bombardment in electron microscopy, although the device would be useful for other purposes.

Effect of Accelerating Voltage of Incident Electrons

After the preliminary experiments mentioned above, the experiment was carried out to reveal the effect of accelerating voltages of the electron on the irradiation damage to the polymer crystals. Fig. 10 is an example of the serial records of the decaying process of the irradiated crystals. Comparing the total dose for the every end point where the diffraction spots transform into halo rings, the correlation with the accelerating voltages of electrons becomes clear (Fig. 11). The accelerating voltages are inversely proportional to the effective cross-section for the inelastic collisions of electrons. This means that the total inelastic collisions leading to the same effect on the specimen are constant at every accelerating voltage of the incident electron. The scattering of the measured values has to be due to experimental errors, especially caused by the inaccuracy in the determination of dose rates.

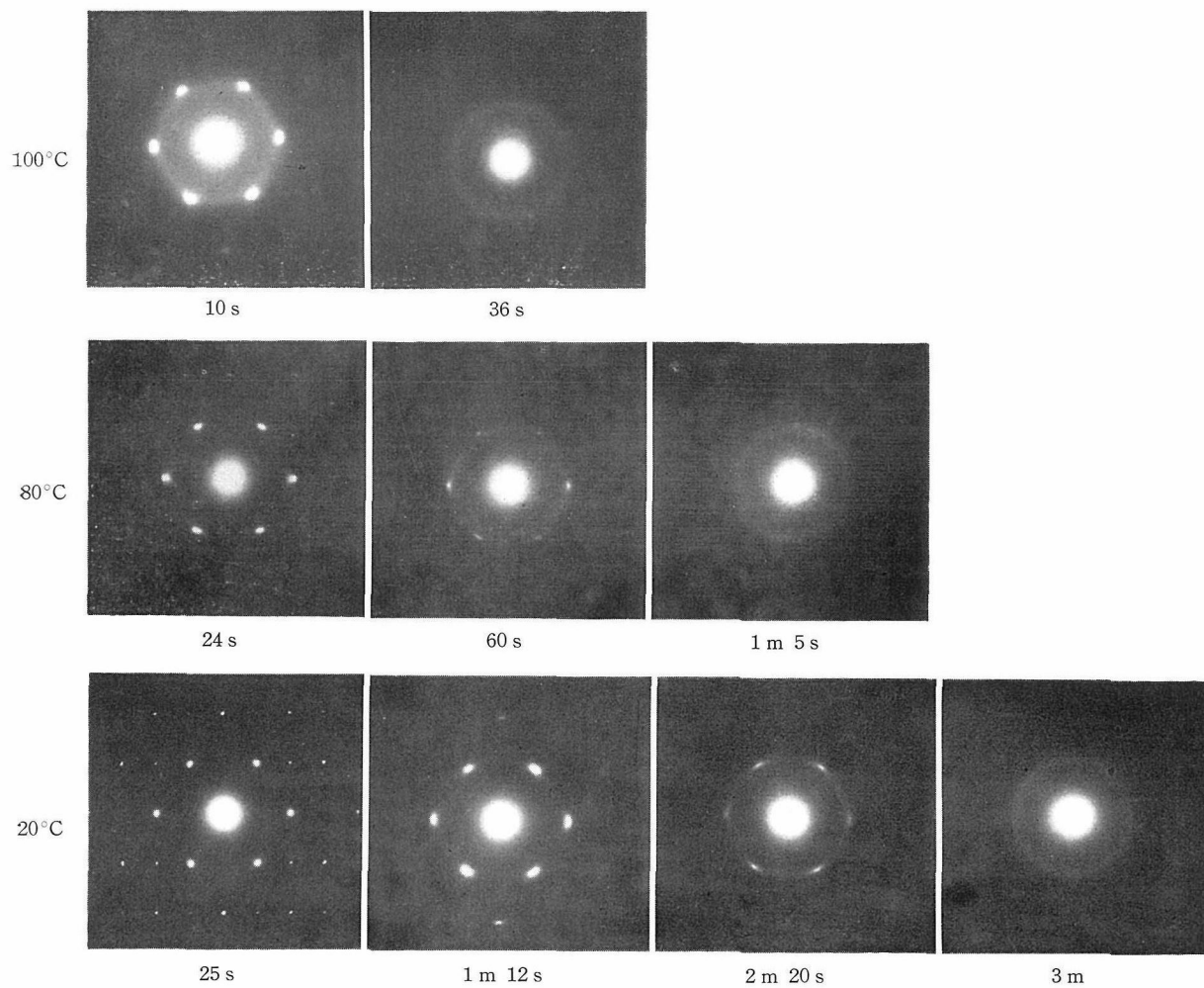
The resistivity of the crystal decay seems to be related to its melting point, since nylon 6 has the highest resistivity. The nature of the resistivity is not yet clarified²⁰⁾. There are many complexities, for example, the single crystals of polyvinyl alcohol have less resistivity to the electron irradiation than that of polyamide crystals. Both materials have similar melting points and hydrogen bondings between their molecular chains.

The extremely low resistivity of polyethylene oxide crystals is supposedly due to its low melting point (66°C). A slight temperature rise by the irradiation causes a rapid decay of crystalline structure of polyethylene oxide just as polyethylene crystals behave at 80°C.

For polyoxymethylene the observed values are widely scattered because of the difficulty in the determination of the end points. Polyoxymethylene which belongs to the "scission" type loses its crystalline texture by the sublimation of disintegrated fragments.

Some other measures can be employed for the comparison of destructive power of electrons of different energies. One of them is the time of decay of the second or third order reflexions. Polyethylene single crystals require about 50 % of the total dose for halo ring formation until the second order spots disappear. Dose for the disappearance of the third order spots is about one half of that for the second order spots. The moiré patterns, if observed, disappear in the same range of the dose where the second order spots diminish. Unfortunately the accuracy of these measurements is not high enough to carry out further quantitative electron microscopy.

Through these experiments, reduction of the cross-section for inelastic scattering with the increase of accelerating voltages is positively proved. It is therefore shown that the application of the high accelerating voltage of electron is more efficient for the reduction of damage to the specimen than the cooling of the specimen.



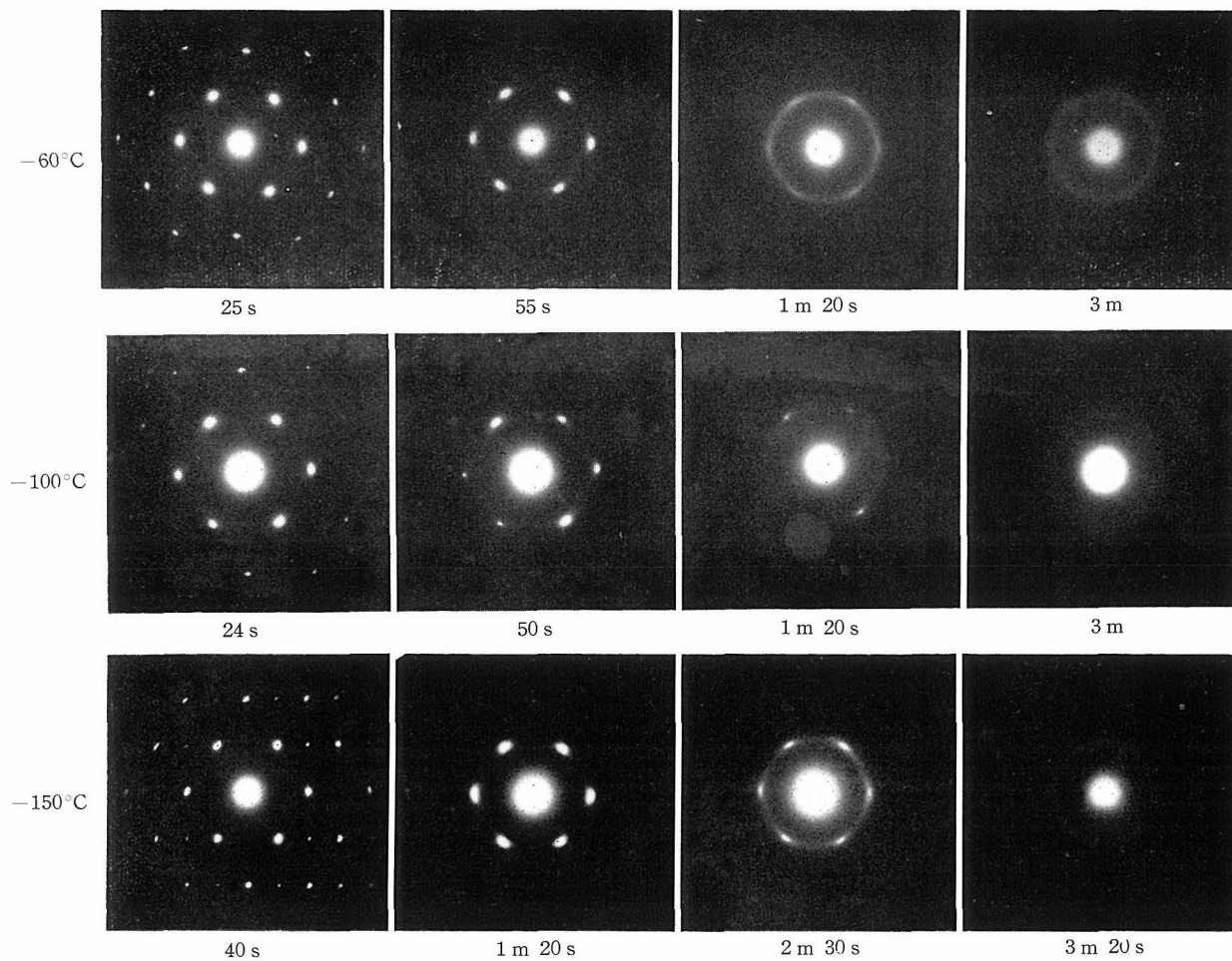
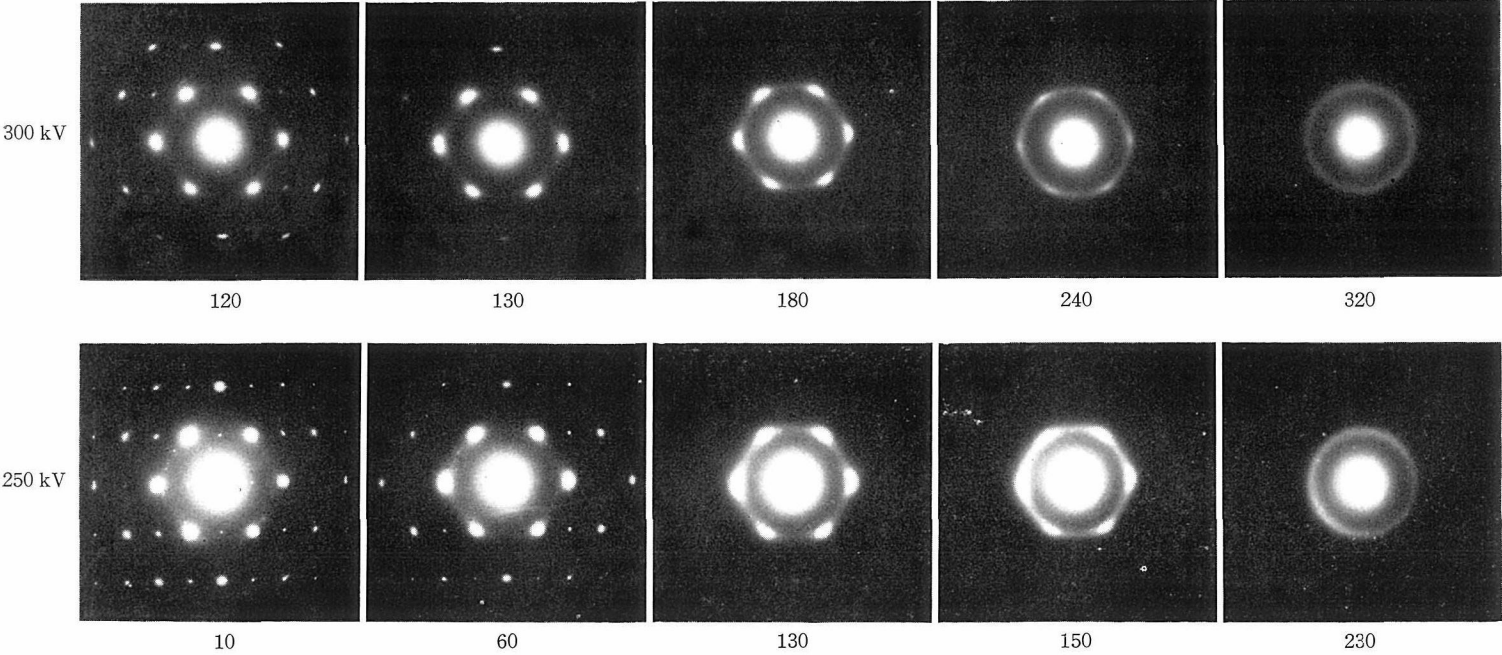


Fig. 9. The effect of specimen temperatures upon the decay of polyethylene single crystals by electron irradiation. The total doses for the end points are nearly the same (3 min. at the same dose rate) from room temperatur down to -150°C .



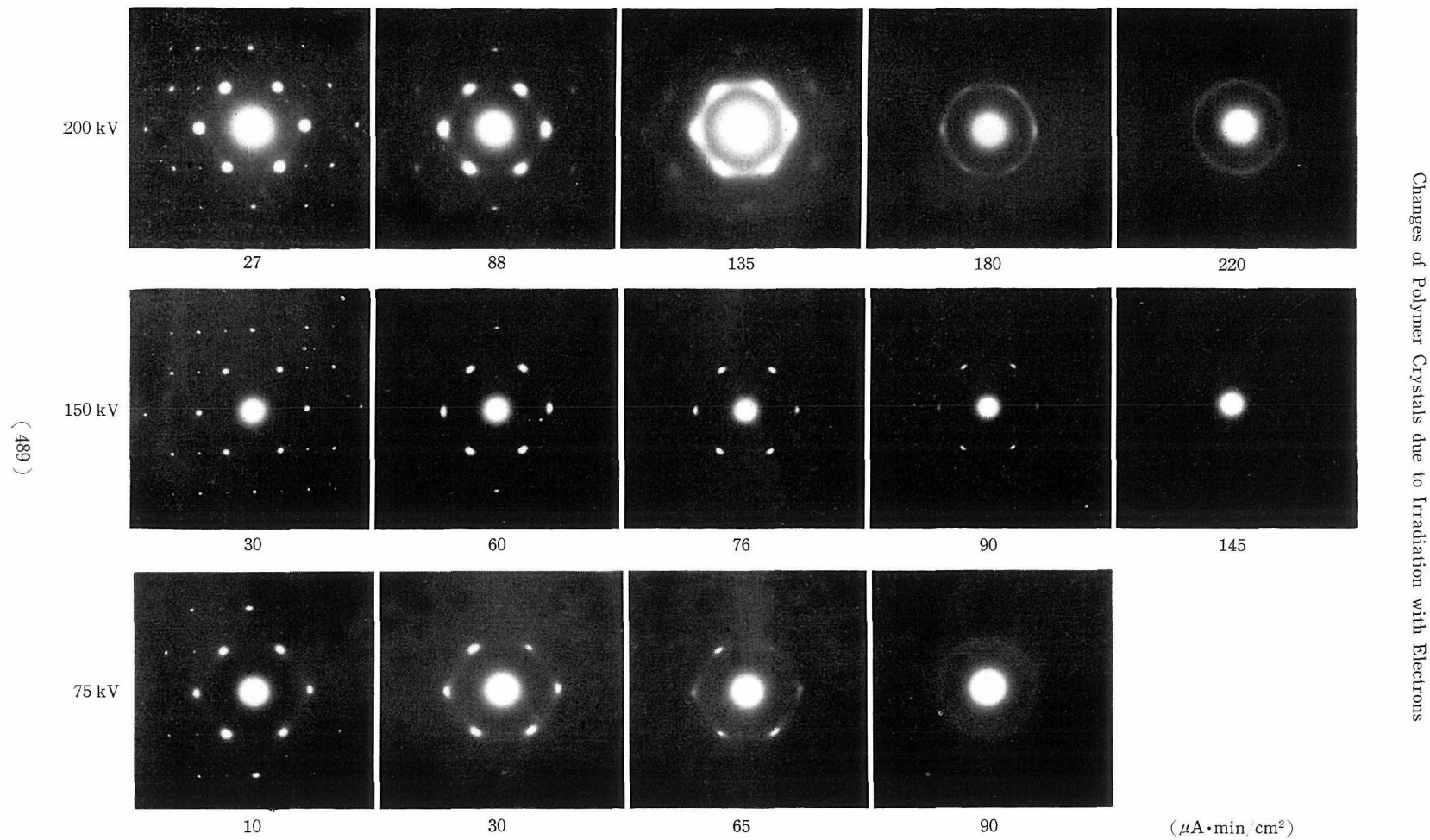


Fig. 10. Serial records of decay of polyethylene crystals irradiated with electrons at various accelerating voltages. The end point is shown at the right end of each series.

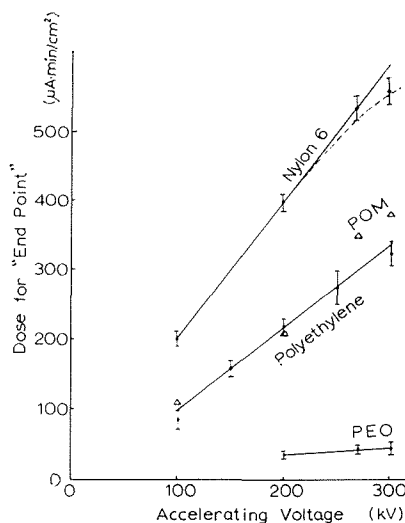


Fig. 11. Total doses necessary to make polymer crystals amorphous vs. accelerating voltages of incident electrons. POM (Δ) and PEO are poly (oxymethylene) and poly (ethylene oxide) respectively.

So far the nature of damages to the polymer crystals induced by the electron irradiation has been clarified in the range of single scattering where most of the electron microscopic works are carried out. It has to be emphasized that, in the radiation chemistry of polymer solids, no work has been conducted in the range of single scattering.

From the results mentioned above it is likely that the cross-sections for inelastic collision decrease linearly with the accelerating voltage up to 300 kV. According to the relativistic theory the reduction rate of the cross-section should decrease at the accelerating voltages over 200 kV. Fig. 11 shows that the plots for nylon 6 deviate a little from linearity over 200 kV as indicated with dotted line. This tendency coincides with that of the theoretical mass thickness "Bremsdicke" which is the reciprocal of the inelastic cross-section with relativistic correction as shown in Fig. 1. The decrease due to the relativistic correction in the range of 200–300 kV is not determined clearly because of the experimental error in our dosimetry. The inelastic cross-section for 80–100 kV electrons is reduced to one half by increasing accelerating voltage to 200 kV, as shown in this study. However, it is estimated, taking the relativistic effect into account, that up to 1000 kV is required to reduce the cross-section for 200 kV to one half.

Supposing the dose-eV relations to be linear as shown in Fig. 11 and the inelastic cross-section to be proportional to $1/\beta^2$, it will be helpful to consider that the dose is proportional to β^4 , because β^4 increases almost linearly with accelerating voltage up to 500 kV. If the proportionality to β^4 is established, we have to assume the number of secondary reactions (cross-linkings) to be proportional to the square of the probability of primary events (inelastic collisions). Such a process has never referred in the radiation chemistry to the crosslinking of irradiated polymers. To confirm this

important relationship it is necessary to carry out similar measurements at 500 kV and 1000 kV.

Effect of Specimen Thickness

An electron traversing the specimen of thickness beyond the "Bremsdicke" is suffered from more than one inelastic collision. When the specimen is thicker than several tens microns, even 300 kV electrons scatter multiply. Due to the decrease of the velocity of electrons by multiple inelastic collisions with the atoms in the specimen and the increase of the number of secondary emitted electrons, the radiation damage to the polymer crystals varies with the depth of penetration of incident electrons.

Though the details of our experiments on this matter will be described in separate papers, we quote an example from these experiments for the comparison with the results obtained at the range of single inelastic collision.

One dozen strips, cut out of an inflation film (0.065 mm thick) of polyethylene, were piled and placed in the camera chamber of the 300 kV electron microscope. Using the projector lens we irradiated evenly the pile with electrons accelerated at various voltages. The dose rate was kept very low to prevent temperature rise of the thick specimen (total thickness was 0.78 mm).

After the irradiation, the damage to the crystalline structure in each strip was measured with an X-ray diffractometer.

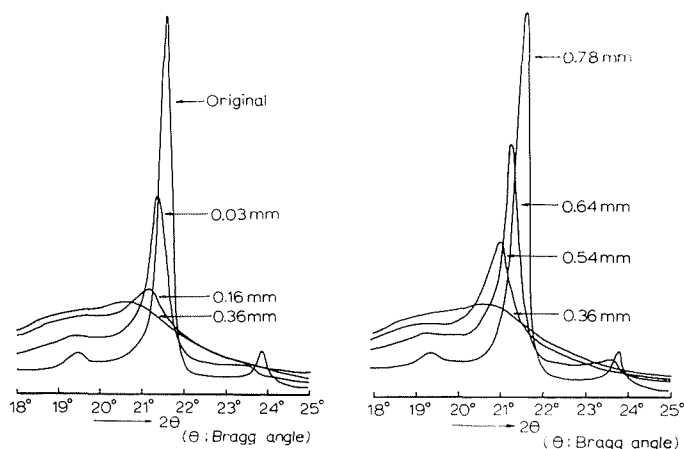


Fig. 12. Intensity curves of X-ray diffractions of irradiated polyethylene films. The depth of penetration 0.03 mm and 0.64 mm represents the first and tenth layer respectively.

When the incident electrons are accelerated at 300 kV, the decay of crystalline structure is most severe in 6th strip, that is, at the depth of 0.36 mm as indicated in Fig. 12. Even with very small dose ($22.5 \mu\text{A} \cdot \text{min./cm}^2$) of the incident electrons the crystalline structure is destroyed perfectly at this depth of penetration. Comparing with the dose producing the same effect to the single crystals of polyethylene ($320 \mu\text{A} \cdot \text{min./cm}^2$ at 300 kV), this value is only 1/15. To make the first layer of the pile (0.03 mm in the mean depth of penetration) amorphous, it needs a dose of $75 \mu\text{A} \cdot \text{min./cm}^2$.

The depth of specimen where the radiation effect is maximum increases with the accelerating voltage of the incident electrons and the dose necessary to produce same effect also increases with the accelerating voltage. For the 100 kV electrons only the first layer is effected while the 300 kV electrons give effect to the eleventh layer of piled strips of polyethylene. The range (R) or the maximum depth of penetration measured by this method or like is in a good agreement with the value calculated from the empirical formula given by Glendenin and Coryell²¹⁾ as follows:

$$R = 4.07 E^{1.38} \times 10^{-1} \text{ g/cm}^2$$

$$(0.15 \text{ MeV} < E < 0.8 \text{ MeV})$$

Accelerating voltage (kV)	200	250	300
Observed range (mm)	0.42	0.63	0.77
Calculated range R (mm)	0.46	0.62	0.76

And the depth of penetration for the maximum effect is always one half of this range.

The damage of polymer crystal due to the electron irradiation is enhanced very rapidly with the depth of penetration from the thickness for single inelastic collision to that for multiple one. Therefore the energy absorbed by the specimen varies with the depth of penetration of the irradiating electrons. According to Trump, Wright and Clarke²²⁾, the stopping power for the electrons has its maximum at a fixed depth of the specimen, and the absorbed energy at this depth is 1.7 times larger than that at the depth close to the surface of the specimen. Our results obtained for the specimen thinner than 1μ show that the factor is 15 which is about 9 times larger than the value obtained by them. Our measurements carried out within the mass thickness for the single inelastic collision are to contribute to the evaluation of the real G value of the radiation effect on the crystalline polymer solid.

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