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Solid-State Polymerization of Acrylonitrile Induced by High-Energy Protons

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Summary

Studies on energy effect in the field of radiation-induced polymerization are quite rare as far as the author knows (1). In previous investigations (2) it was pointed out by us that the energy of radiation is also very important for radiation-induced polymerizations, particularly in solid-state polymerizations.

To examine the effect of energy on the solid-state polymerization of acrylonitrile, some experiments were carried out by bombardment of high energy protons using a synchrotron and a synchrocyclotron.

EXPERIMENTAL

Acrylonitrile was dehydrated and purified by distillation. The monomer was introduced into an aluminum ampule, and the ampule was mechanically shielded under vacuum.

Irradiation was carried out with high-energy protons from a synchrotron Saturne at Saclay, and a synchrocyclotron at CERN. The energy of the accelerated protons was 3000 MeV for the synchrotron and 600 MeV for the synchrocyclotron.

After irradiation, the samples were kept at liquid-nitrogen temperature for 20–30 hr. Then, by introducing methanol into the ampule, postpolymerization was inhibited.

Viscosities of the polymers were measured in dimethylform-

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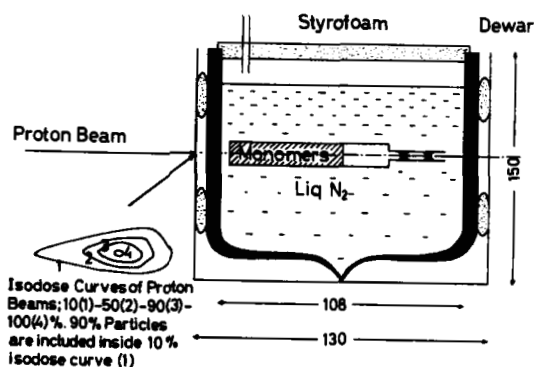


FIG. 1. Irradiation vessel for 3000-MeV protons from a synchrotron.

amide at $35 \pm 0.1^\circ\text{C}$. Infrared spectra of polymers were also measured.

The irradiation vessel for 3000-MeV protons is shown in Fig. 1. The beam of protons was extracted from the synchrotron. The pulse length of the proton beam was 0.3 sec and the repetition rate of the machine was 720 pulses/hr. The beam intensity was 5×10^{10} protons/pulse.

The irradiation device for the 600-MeV protons is shown in Fig. 2. The level of liquid nitrogen in the vessel was controlled automatically. The diameter of the proton beam was 50 mm, and the position was adjusted by observing the luminescence from a Cd

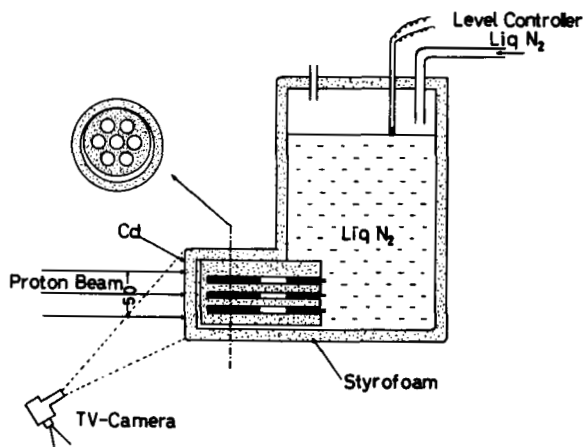


FIG. 2. Irradiation vessel for 600-MeV protons from a synchrocyclotron.

plate placed in the front of samples. A television camera was used for the adjustment. The proton beam has a mean energy of 597 ± 1 MeV. Its pulse length was about 200 μ sec. The repetition rate of the synchrocyclotron was 54 cps.

To compare the polymerization induced by high-energy protons with those by other radiations, γ ray- and electron-induced polymerizations were also carried out.

ESTIMATION OF DOSE RATE

The velocity of high-energy particles can be calculated easily. The velocity is $0.774C$ (V_{600}) for 600-MeV protons, and $0.971C$ (V_{3000}) for 3000-MeV protons (C is the velocity of light).

The linear energy transfer (LET) of the particles can be also easily calculated, from Bethe's equation:

$$-\frac{dE}{dx} = \frac{4\pi e^4 Z_1^2}{mv^2} N_0 Z_2 \ln \left[\frac{2mv^2}{I(1-\beta^2)} - \beta^2 \right] \quad \beta = \frac{v}{C}$$

where E is the energy of the moving atom, v its velocity, $Z_1 e$ its charge, N_0 the density of atoms in the medium, m the mass of an electron, I the mean excitation potential of the electrons in the stopping material, and Z_2 their effective atomic number.

For the solid acrylonitrile, the LET is estimated to be 0.0261 eV/Å for 600-MeV protons, 0.0193 eV/Å for 3000-MeV protons. These are the same order as the LET of γ rays from ^{60}Co .

For example, the energy deposition rate to the solid monomer by the proton beam, 1.2×10^{10} protons/cm²-sec, corresponds to 1.97×10^6 rad/hr for the 600-MeV protons.

For the 3000-MeV proton beam, the intensity distribution was estimated from an autoradiograph, as shown in Fig. 1.

The dose rate was estimated to be $4.5 \pm 1.5 \times 10^5$ rad/hr for a beam of 5×10^{10} protons/pulse. It was very difficult to get an exact dose rate by this method.

For 600-MeV protons from the synchrocyclotron, the beam intensity was determined by activation methods. One of the methods was the measurement of activity of ^{18}F which was produced by a nuclear reaction of $^{27}\text{Al}(p, 5p5n)^{18}\text{F}$. A small aluminum circular plate 9 mm in diameter, 0.05 mm thick, and 0.0076 g in weight was placed in the front of the ampule, as shown in Fig. 3, for the measurement of ^{18}F .

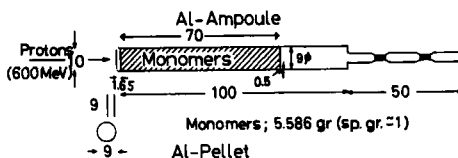


FIG. 3. Schema of Al ampoule and explanation for dosimetry.

Similarly, the activity of ^{24}Na produced by other nuclear reactions of $^{27}\text{Al}(p, 3pn)^{24}\text{Na}$ was measured. An aluminum plate 9 mm in diameter, 1 mm thick, and weighing 0.179 g was used as the target.

Irradiation with high-energy neutrons and protons produced by the nuclear reactions may be important in these systems. Therefore, these contributions were estimated, assuming that the monomers are irradiated by all protons and neutrons produced by nuclear reactions of $^{27}\text{Al}(p, 5p5n)^{18}\text{F}$ and $^{27}\text{Al}(p, 3pn)^{24}\text{Na}$. The total thickness of aluminum placed in the front of the monomers was 1.65 mm.

The number of nuclei N reacted with incident protons can be estimated by the relation

$$N = I_0(1 - e^{-\sigma nx})$$

where I_0 is the intensity of incident protons (particles/cm²), σ the cross section of the nuclear reaction (cm²), x the thickness of the aluminum (cm), and n the number of atoms per cm³.

For the reaction of $^{27}\text{Al}(p, 5p5n)^{18}\text{F}$, σ is 18×10^{-27} , x is 0.165, and n is $6.02 \times 10^{23} \times (2.70/27)$.

For $I_0 = 2 \times 10^{13}$ protons, N was obtained to be 3.63×10^9 , and this corresponds to the number of ^{18}F . In this nuclear reaction, five neutrons and five protons are produced from one Al atom. About 500 MeV is shared by these particles from the incident 600-MeV proton, and so the produced protons and neutrons have a kinetic energy of 50 MeV for each particle. The LET of the particles is about 0.2 eV/Å in solid acrylonitrile.

Now, the deposition of energy to the solid monomers by the initial protons, and that by the secondary produced protons and neutrons, can be compared; the deposited energy is 0.0261 (eV/Å) $\times 2 \times 10^{13} \times 5 \times 10^8$ (Å) for incident protons and 0.2 (eV/Å) $\times 3.63 \times 10^{10} \times 2.5 \times 10^8$ (Å) for the secondary produced neutrons and protons. The thickness of solid monomer was 5 cm and the range in solid acrylonitrile is 2.5 cm for 50-MeV protons.

TABLE I

Energy Deposition by Nuclear Reactions of Al, C, and N ($I_0 = 2 \times 10^{13}$ protons)

Nuclear reaction	Cross section, ^a 10 ⁻²⁷ cm ²	No. of fissions	Average LET of secondary particles, eV/Å	Number of recoil particles	Absorbed energy, 10 ¹⁸ /eV
²⁷ Al(<i>p</i> , 3 <i>p</i> 3 <i>n</i>) ²² Na	18.0	4.40 × 10 ⁹	0.20	6	2.20
²⁷ Al(<i>p</i> , °) ¹³ N	1.0	0.24 × 10 ⁹	0.23	15	0.144
²⁷ Al(<i>p</i> , °) ¹¹ C	3.2	0.72 × 10 ⁹	0.26	17	0.432
²⁷ Al(<i>p</i> , °) ⁷ Be	3.2	0.72 × 10 ⁹	0.30	21	0.432
²⁷ Al(<i>p</i> , °) ⁶ He	1.0	0.24 × 10 ⁹	0.33	22	0.144
²⁷ Al(<i>p</i> , 3 <i>p</i> <i>n</i>) ²⁴ Na	11.0	2.60 × 10 ⁹	0.086	4	0.624
²⁷ Al(<i>p</i> , 5 <i>p</i> 5 <i>n</i>) ¹⁸ F	7.0	1.7 × 10 ⁹	0.12	10	0.857
					4.83
¹² C(<i>p</i> , 3 <i>p</i> 3 <i>n</i>) ⁷ Be	{ 12 (340 MeV) 11 (3000 MeV)	5.74 × 10 ¹⁰	0.12	6	14.5
¹² C(<i>p</i> , <i>p</i> <i>n</i>) ¹¹ C	{ 26 (600 MeV) 22 (3000 MeV)	12.4 × 10 ¹⁰	0.063	2	5.47
¹² C(<i>p</i> , °) ³ T	{ 7.5 (1000 MeV) 7.0 (3000 MeV)	2.4 × 10 ¹⁰	0.12	10	10.1
¹² C(<i>p</i> , °) ⁸ Li	7 (340 MeV)	33.2 × 10 ¹⁰	0.10	5	58.1
					88.2
¹⁴ N(<i>p</i> , °) ³ T	{ 21 (450 MeV) 28 (2200 MeV)	3.3 × 10 ¹⁰	0.20	12	27.9
¹⁴ N(<i>p</i> , <i>p</i> <i>n</i>) ¹³ N	{ 6 (400 MeV) 3 (3000 MeV)	0.96 × 10 ¹⁰	0.063	2	0.423
¹⁴ N(<i>p</i> , °) ⁸ Li	55 (340 MeV)	8.76 × 10 ¹⁰	0.14	7	30.0
					58.3

^a From Ref. 3.° Fission elements were assumed to be a type of *xp yn*.

It is obvious from these calculations that the energy absorption by secondary produced protons and neutrons is only about 1% of the absorbed dose by incident protons.

In the nuclear reaction of ²⁷Al(*p*, 3*p**n*)²⁴Na, the number of produced ²⁴Na is 2.2 × 10⁹ for incident protons of 2 × 10¹³, and the produced protons and neutrons have 150 MeV kinetic energy. The energy deposition is smaller than the case of ²⁷Al(*p*, 5*p*5*n*)¹⁸F.

Energy deposition from the aluminum wall of the ampule to the solid monomers can be estimated, assuming that a one half the re-

coiled particles emitted from the Al wall go to the inside of the ampule and that one half the energy is absorbed effectively by the monomers.

Since the dimensions of the ampule are shown in Fig. 3 and the specific gravity of monomers in the solid state is approximately 1, the energies deposited from secondary induced recoil particles can be estimated. The result of the calculations are given in Table 1.

The energy deposition to solid monomers by recoil particles from the nuclear reactions of Al, C, and N with high-energy protons can be obtained from the calculations. If the number of incident 600-MeV protons, I_0 , is 2×10^{13} and the weight of the monomers is 5.5869 g (7 ml at 20°C), the deposited energies are as follows:

4.83×10^{18} eV	from nuclear reaction of Al
88.17×10^{18} eV	from nuclear reaction of C
58.32×10^{18} eV	from nuclear reaction of N
365×10^{18} eV	from incident protons

The energy deposition by the secondary induced radiation is 1.70×10^{20} eV, and then 47% of the direct energy absorption by incident high-energy protons must be added as the absorbed dose given by the secondary induced radiation:

$$(1.70/3.65) \times 100 = 47(\%)$$

RESULTS

The relation between conversion and irradiation time is shown in Fig. 4 for irradiation with 3000-MeV protons. The data are consid-

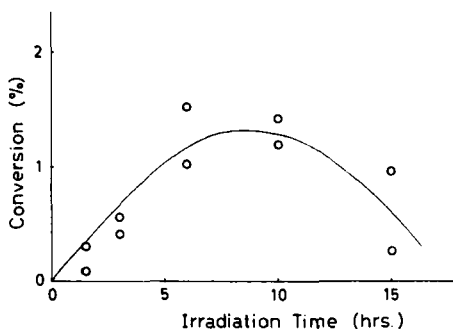


FIG. 4. Relation between conversion and irradiation time. Polymerization was carried out by 3000-MeV protons at -196°C . Dose rate was about 4.5×10^6 rad/hr.

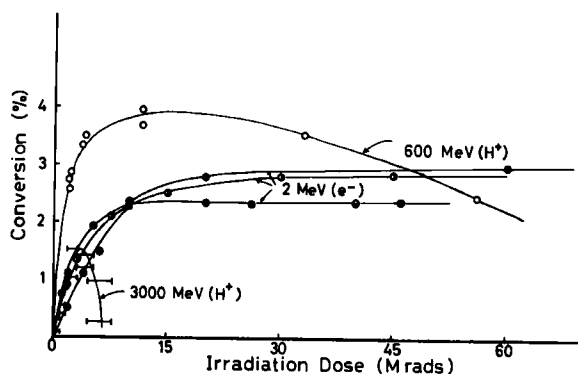


FIG. 5. The relations between conversion and irradiation dose in solid-state polymerizations induced by 600- and 3000-MeV protons, and 2-MeV electrons at -196°C : \circ , protons (600 MeV), $0.3\text{--}6 \times 10^2$ rad/sec; \bullet , electrons (2 MeV), 2×10^5 rad/sec; \ominus , electrons (2 MeV), 3×10^5 rad/sec; \oplus , electrons (2 MeV), 4×10^5 rad/sec.

erably scattered, because the dose rate could not be determined exactly, as mentioned before.

It is very curious that the conversion has a maximum at a dose of 3 Mrad, and by further irradiation the yield decreases rapidly with the irradiation dose. This may be due to the depolymerization or degradation of polymers produced in the monomer matrix by irradiation with the initial high-energy protons, and with secondary produced high-energy neutrons and protons.

The relation between conversion and irradiation dose is shown in Fig. 5 for irradiation with 600-MeV protons. It is obvious from the figure that the conversion increases rapidly with the irradiation dose in the initial stage of polymerization, and then the conversion yield decreases gradually.

The polymerization induced by the high-energy protons (600 MeV) was compared with those induced by other radiations. As is shown in Figs. 5 and 6, the initial rate of polymerization induced by the high-energy protons is most rapid among various kinds of radiations. Also, the saturation yield is much higher in the proton-induced polymerization than the other cases. As is well known, the rate of polymerization of acrylonitrile in the solid state depends profoundly on the crystal structure and the crystalline state of monomers (4). For example, the rate is faster in a quenched crystal than in an annealed monomer for irradiation by accelerated electrons, as shown in Fig. 5 (5).

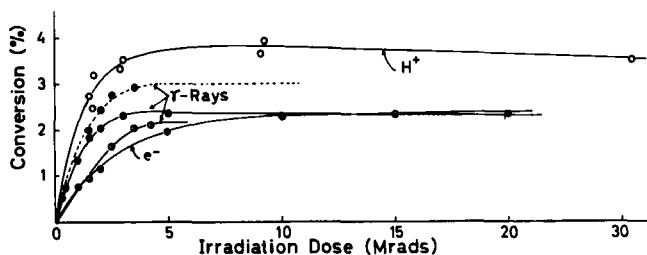


FIG. 6. Comparison of the high-energy proton-induced polymerization with polymerizations induced by γ rays and accelerated electrons at -196°C : \circ , protons (600 MeV), $0.1\text{--}2 \times 10^6$ rad/hr; \bullet , γ rays from ^{60}Co , 5×10^4 rad/hr; \ominus , γ rays from ^{60}Co , 6.5×10^4 rad/hr; \bullet , γ rays from ^{60}Co , 5×10^4 rad/hr; \otimes , electrons from a van de Graaff accelerator (2 MeV), $3\text{--}7 \times 10^8$ rad/hr. The first three are for rapidly cooled monomers, the fourth for annealed monomers, and the fifth for rapidly cooled monomers.

It was observed that the conversion decreases gradually at higher irradiation doses in polymerization with 600-MeV protons, as in the case of 3000-MeV protons.

Such a phenomenon has never been observed in the polymerization of acrylonitrile initiated with X rays, γ rays, and high-energy electrons. This may be also due to the depolymerization or degradation of polymers formed in the monomer matrix by bombardment of high-energy protons and neutrons. Such a phenomenon is more distinguished in 3000-MeV protons than 600-MeV protons.

The results of viscosity measurements are shown in Fig. 7. The results were compared with those of γ ray- and electron-induced polymerizations. The figure indicates that the molecular weight of polymers obtained by the proton-induced polymerization decreases most rapidly with the irradiation dose in comparison with others.

Infrared spectra of polymers obtained by proton bombardment and by radiation in a pile (6) are shown in Fig. 8. The spectra of polymers obtained by irradiation in a pile for 5 min were similar to those of polymers obtained by γ ray- and electron-induced polymerizations. As reported before, in polymers obtained by reactor radiations from monomers including boron, relatively strong absorptions at 2210 cm^{-1} , 1610 cm^{-1} , and 971 cm^{-1} were observed. The absorption at 2210 cm^{-1} was only observed in the polymerization induced by reactor radiations. The absorption at 970 cm^{-1} is characteristic of pile irradiation and high-energy electrons above

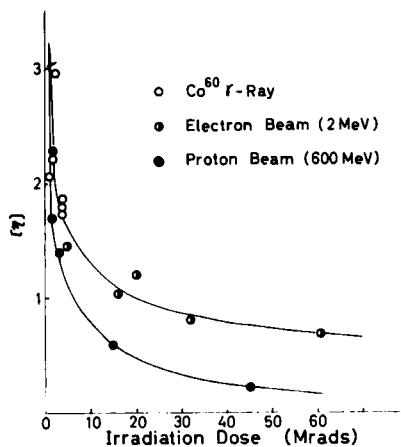


FIG. 7. Relations between the intrinsic viscosities of polymers and the irradiation dose.

15 MeV (*I*). While absorption at 880 cm^{-1} is characteristic of high-energy proton-induced polymerization, it has never been observed in other cases.

The spectrum of polymer obtained by proton bombardment in the region $600\text{--}900\text{ cm}^{-1}$ is shown in Fig. 9. As is obvious from the figure, two absorptions appear at 880 cm^{-1} and 667 cm^{-1} in the polymer obtained by proton irradiation. The absorption at 667 cm^{-1} has also never been observed in the polymers obtained by other radiations. This is due to the structure of *cis*-vinylene.

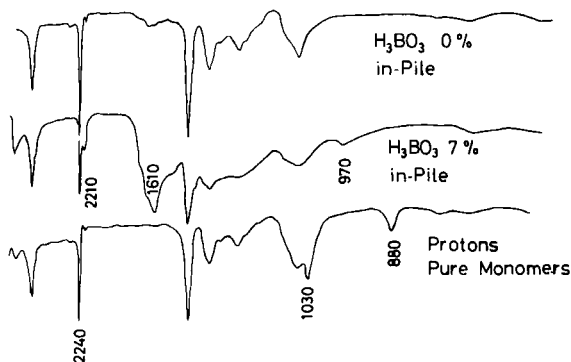


FIG. 8. Infrared spectra of polymers obtained by reactor radiations and high-energy protons.

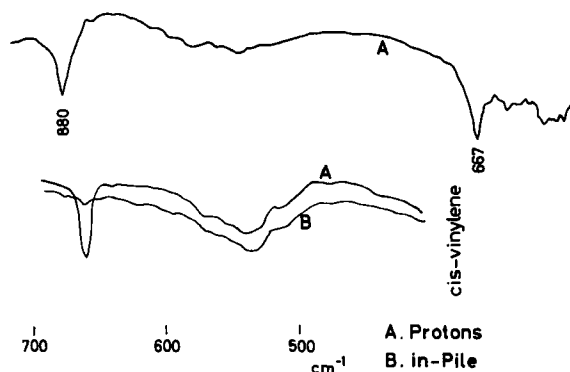


FIG. 9. Infrared spectrum of polyacrylonitrile obtained from the high-energy proton-induced polymerization in the region $500\text{--}900\text{ cm}^{-1}$. In pile irradiation the monomer, including 1% H_3BO_3 , was irradiated for 10 min at liquid-nitrogen temperatures.

The spectrum in the KBr prism region of the polymer was also compared with that of polymers obtained by reactor radiations. The results are shown in Fig. 8.

It is well known that the polymerization of acrylonitrile is profoundly affected by the quality of monomer crystals (2). It is very interesting that the initial rate of polymerization is much faster in high-energy-proton-induced polymerizations than in those induced by γ rays, accelerated electron beams, or X rays under the same conditions as far as the crystalline states are concerned (Fig. 5). This might be due to the energy effect, since there is a possibility that solid-state polymerization at low temperature is affected by secondary produced internal radiations. Cerenkov radiation can be produced only by high-energy radiation above the threshold energy (7). Assuming that the reflex index of the solid monomer be 1.4 (1.393 in the liquid at 20°C) and the density 1.0 (l) at -196°C , the threshold value was calculated to be 402 MeV for the proton beam. The solid monomers were always irradiated by protons with high energies, above the threshold value, in our experiments.

The energy loss per unit path by Cerenkov radiation for a fast proton ($\beta \sim 1$) is of the order of several keV per cm; this corresponds to about 0.1% of the energy loss by ionization for a relativistic particle. The LET of Cerenkov radiation is rather small in comparison with that of the incident radiation. But the internal radiation, which has a broad energy spectrum in the visible and

ultraviolet regions, seems to play an important role in polymerization. It has been reported recently that several photobleaching phenomena are very important in radiation chemical processes in glassy solids at low temperature (8). The effective absorption dose by the visible or ultraviolet rays is rather small in that case, but the effect may sometimes be drastic. We can easily expect some effects of internal radiation in solid systems.

The other important factor may be multiionization by high-energy particles. Although the cross section of the multiionization is relatively small, the effect can be reached in a long range.

The molecular weight dependency of polymers on the irradiation dose was most distinguished in the proton-induced polymerization, as shown in Fig. 8. This may not be due to the effect of radiation intensity, probably due to an energy effect. The intensities of various radiations for the experiments indicated in the figure are given in Table 2.

It is well known that the energy which is transferred to an atom struck by high-energy particles is given by

$$T_m = [4M_1M_2/(M_1 + M_2)^2]E$$

where T_m is a maximum energy which is transferred in a head-on collision. M_1 and M_2 are the masses of accelerated particle and target element, respectively, and E is the energy of the particle.

For the bombardment of the 600-MeV protons, the T_m value is easily calculated, i.e., $T_m^H = 600$ MeV, $T_m^C = 170$ MeV, and $T_m^N = 150$

TABLE 2
Dose Rates of Various Radiations

Radiations	Dose rate, rad/hr
γ Rays from ^{60}Co	10^4 – 10^5
Electrons from a van de Graaff (1–2 MeV) 50–100 A	4 – 8×10^8
Protons from a synchrotron (3000 MeV, 0.2 pps) 10^9 protons/cm ² -sec as the mean value; protons/cm ² -sec in a pulse	4.5×10^5 2×10^{10}
Protons from a synchrocyclotron (600 MeV, 54 pps) 10^9 – 10^{10} protons/cm ² -sec, as the mean value; 10^{12} protons/cm ² -sec in a pulse	1.5 – 4.5×10^6

MeV. An average number of displaced atoms per secondary knock-on, $\bar{\nu}$, is calculated by

$$\bar{\nu} = \frac{1}{2} \left(\frac{T_m}{T_m - E_d} \right) \left(1 + \ln \frac{T_m}{2E_d} \right)$$

E_d is a certain threshold from which the atom is never displaced at lower energies. Taking $E_d = 25$ eV, the equation gives $\bar{\nu} = 8.1$ for the solid acrylonitrile by using the weight-average atomic weight of the components as a first approximation.

For 3000-MeV protons, the average number of displaced atoms per secondary knock-on, $\bar{\nu}$, is obtained as 9.0.

On the other hand, if the relation

$$\bar{\nu} = M_H \bar{\nu}_H + M_C \bar{\nu}_C + M_N \bar{\nu}_N$$

is used to calculate the number of displaced atoms, where M is the fraction of component atoms, $\bar{\nu}$ is estimated to be 8.3.

The number of displacement atoms was estimated to be about 4×10^{13} atoms/g for Mrad irradiation of incident protons, as a maximum value. Recoil particles are produced by nuclear reaction of component atoms with incident protons, and one recoil particle is obtained by five incident protons. Therefore, the number of displacements should be corrected by a factor of an additional 20%. This value is rather small in comparison with the pile irradiation (6). The number of displacement atoms in the reactor is $3\text{--}15 \times 10^{15}$ atoms/g/Mrad.

As is obvious from the calculation, the rapid decrease of the molecular weight with irradiation dose may be difficult to explain by only the displacement of atoms.

The number of defects produced by incident high-energy protons and by the secondary produced neutrons and protons is quite small in comparison with the number of reacted monomers. But the decrease of polymerization degree is considerably large in the polymerization induced by high-energy protons. This strongly suggests that the production of small amounts of defects may be very effective for the depolymerization or degradation of polymers, indicating the existence of a long-range energy transfer in the system.

The absorption at 880 cm^{-1} is due to the C—H out-plane deformation of $\text{CR}_1\text{R}_2=\text{CH}_2$, and the absorption at 667 cm^{-1} is due to

the C—H deformation of $\text{CHR}_1=\text{CHR}_2$ (*cis*). These have been only observed in the polymers obtained by the high-energy protons.

The experimental results were compared with the polymerizations induced by various radiations. These are summarized in Table 3.

These phenomena may not have a direct effect on the solid-state polymerization. But this is very interesting from the point of chemical reaction. The formations of *cis*-vinylene and vinylidene are very characteristic of high-energy proton-induced polymerization, as obvious from the table.

The phenomena may be the irradiation effect on the polymers produced. If the polymer structure is a planar zigzag, an isomerization is necessary to form the *cis*-vinylene structure. It is very curious and puzzling that the chemical isomerization and transforma-

TABLE 3
Structures of Polyacrylonitrile Obtained by Various Radiations^a

	Far ultra- violet	γ Ray	Electrons,		Protons, 600–3000 MeV	Reactor, $\gamma + n$	Reactor, $\gamma + n +$ Li/He
			below 15 MeV	above 15 MeV			
	—	—	—	—	—	0	0
	0	—	—	—	—	0	0
	—	—	—	—	0	—	—
	—	—	—	0	—	0	0
<i>trans</i>							
	—	—	—	—	0	—	—
<i>cis</i>							

^a —, absence; 0, presence.

tion may be a very selective reaction to the energy of radiation and may be induced only by high-energy protons.

It is also interesting to note that since the anomalous formation of vinylidene and *cis*-vinylene structures should take place during irradiation with high-energy protons at -196°C , the formation strongly indicates that the polymerization occurs at -196°C during polymerization.

The energy effect on the solid-state polymerization of acrylonitrile seems to suggest that a collective excitation process may be involved in polymerization at liquid-nitrogen temperatures.

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Zusammenfassung

Um den Einfluss der Energie auf die im Festzustand verlaufende Polymerisation von Acrylnitril zu untersuchen, wurden Versuche mit Protonen hoher Energie in einem Synchrotron und einem Synchrocyclotron durchgeführt.

Résumé

Dans le but d'examiner l'effet d'énergie sur la polymérisation à l'état solide d'acrylonitrile, on a fait des essais utilisant le bombardement des protons possédant une énergie élevée, à l'aide d'un synchrotron et d'un synchrocyclotron.

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