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## Solid-State Polymerization of Acrylonitrile Induced by Li/He Recoil Particles at Low Temperature

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# Solid-State Polymerization of Acrylonitrile Induced by Li/He Recoil Particles at Low Temperature

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## SUMMARY

Solid-state polymerization of acrylonitrile induced by reactor radiation, including recoil particles from a nuclear reaction of $^{10}B$ (n, $\alpha$) $^{7}Li$, was carried out at low temperature. It was observed from the experiments that the effect of the recoil particles on polymerization is significant. The effect is characterized by cross-linking of polymers produced, and formation of trans-vinylene and C=C bonds conjugated with a bond C$\equiv$N group in the polymerization during irradiation.

## INTRODUCTION

In a previous paper [1], the solid-state polymerization of acrylonitrile at low temperature induced by reactor radiations was reported. The contribution of thermal neutrons to polymerization was not so important. In this paper solid-state polymerization induced by recoil particles (Li/He) from a nuclear reaction of $^{10}B$ (n, $\alpha$) $^{7}Li$ is reported.

The polymerization of various vinyl monomers in the liquid state induced by the Li/He recoil particles has been reported by Henglein et al. [2]. But solid-state polymerization induced by the recoil particles has not been studied.

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## EXPERIMENTAL

Acrylonitrile monomers and methanol were dried and distillated. Boric acid was used as a source of B. The solubility of the boric acid in the monomer is very small at an ordinary temperature. Therefore, the boric acid was dissolved into mixtures of acrylonitrile and methanol. The alcohol solution of the monomer (5.5 ml monomer + 1.5 ml methanol) was always employed. The concentration of boric acid to the monomer was 0, 1, 2, 4, and 7 wt.%.

The monomer solution containing boric acid was introduced into an aluminum ampoule. The ampoule was prepared as described in a previous paper [1]. Irradiation was carried out in a cryogenic vessel installed in a Mélusine reactor [3]. The intensities of flux of thermal and fast neutrons were determined by nuclear reactions of Ni and Co with neutrons. The measurements were carried out in five different positions inside the container of ampoules. The results are given in Table 1 for 80 min of irradiation.

Table 1.   Measurements of Flux Intensities of Neutrons

| Position | Flux of fast neutrons ($> 1MeV$), $10^{15}$ n/cm$^2$ | Flux of thermal neutrons (2200 m/sec), $10^{15}$ n/cm$^2$ |
|:---:|:---:|:---:|
| 1 | 10.2 | 35 |
| 2 | 8.25 | 35 |
| 3 | 8.10 | 35 |
| 4 | 9.55 | 35 |
| 5 | 11.0 | 35 |

The flux of fast neutrons can be taken to be $2.0 \times 10^{12}$ n/cm$^2$/sec and the flux of thermal neutrons $7.3 \times 10^{12}$ n/cm$^2$/sec. The intensity of $\gamma$ rays was $9.7 \times 10^7$ rads/hr. To know the effect of $\gamma$ rays only, some experiments on the solid-state polymerizations of monomers containing boric acid induced by $\gamma$ rays from $^{60}$Co were carried out. Because, in solid-state polymerization, the effect of additives on the crystal and crystalline structure of monomers is very important.

The contents of isotopic $^{10}$B is 18.83% for the total boron quantity in $H_3BO_3$. In the monomer solution including 1 wt.% $H_3BO_3$ for the monomer, $15.4 \times 10^{18}$ $^{10}$B atoms are included in 1 ml of the solution.

## ESTIMATION OF DOSE RATE

The energy deposition to the solid acrylonitrile by fast neutrons $(2.0 \times 10^{12}$ n/cm$^2$/sec) was calculated to be $2.38 \times 10^7$ rads/hr. The energy-deposition rates in the solid monomers by the nuclear reactions $^{14}$N (n, p) $^{14}$C and $^1$H (n, $\gamma$) $^2$D were estimated to be $4.8 \times 10^6$ rads/hr and $3.0 \times 10^5$ rads/hr, respectively. The rates with the nuclear reaction $^{10}$B (n, $\alpha$) $^7$Li was $1.15 \times 10^7$ rads/h for the solid monomer containing 1% $H_3BO_3$. The total dose rates were calculated and are shown in Table 2.

## RESULTS

The relations between polymerization yield and irradiation time are shown in Fig. 1 and 2 in the case of $\gamma$ irradiation. As is obvious from the figures, the rate of polymerization decreases by adding boric acid and methanol, and the effect of the boron concentration on the polymerization is very small.
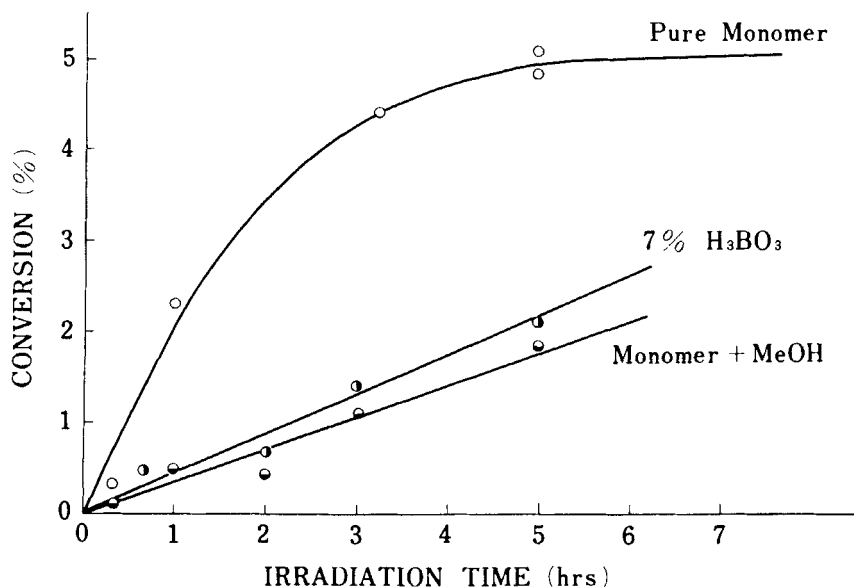


**Fig. 1.** $\gamma$ ray-induced solid-state polymerization of acrylonitrile in the presence of methanol and boric acid (21. 4 vol.% methanol added). Dose rate: $9.53 \times 10^5$ rads/hr.

**Table 2.** Energy Deposition in Monomers (rads/hr $\times 10^{-7}$)

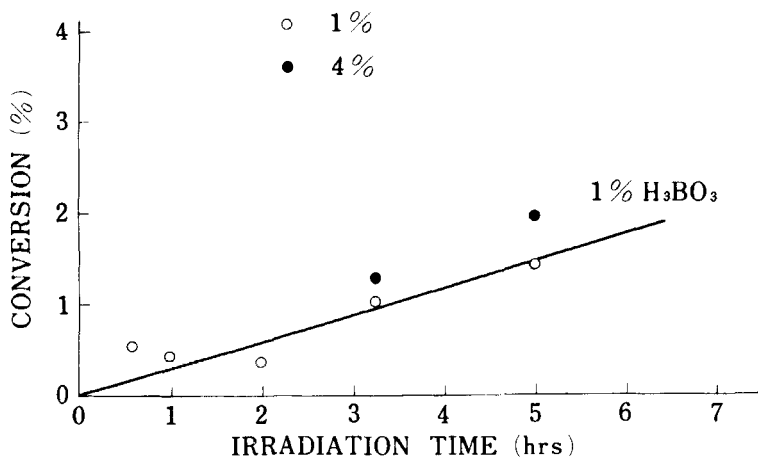| | $\gamma$ ray | Fast neutrons | Thermal neutrons | | | Total |
|---|---|---|---|---|---|---|
| | | | $^{14}N\,(n,p)$ | $^{14}C\,\,^{1}H\,(n,\gamma)\,\,^{2}D$ | $^{10}B\,(n,\alpha)\,^{7}Li$ | |
| $C_2H_3CN + CH_3OH$ | 9.1 | 2.38 | 0.48 | 0.03 | 0 | 12.0 |
| $C_2H_3CH + CH_3OH$ $+ 1\% \ H_3BO_3$ | 9.1 | 2.38 | 0.48 | 0.03 | 1.15 | 13.2 |
| $C_2H_3CH + 2\% \ H_3BO_3$ | 9.1 | 2.38 | 0.48 | 0.03 | 2.30 | 14.3 |

**Fig. 2.** $\gamma$ ray-induced solid-state polymerization of acrylonitrile. Dose rate: $9.53 \times 10^5$ rads/hr.

The relations between polymerization yield and irradiation time in the reactor experiments are shown in Fig. 3, 4, and 5. In the initial stage of polymerization, there is a great difference between the pure monomers and a mixture of the monomers and methanol, as observed in the $\gamma$ ray irradiation. This may be due mainly to the change of crystalline state caused by the addition of methanol.
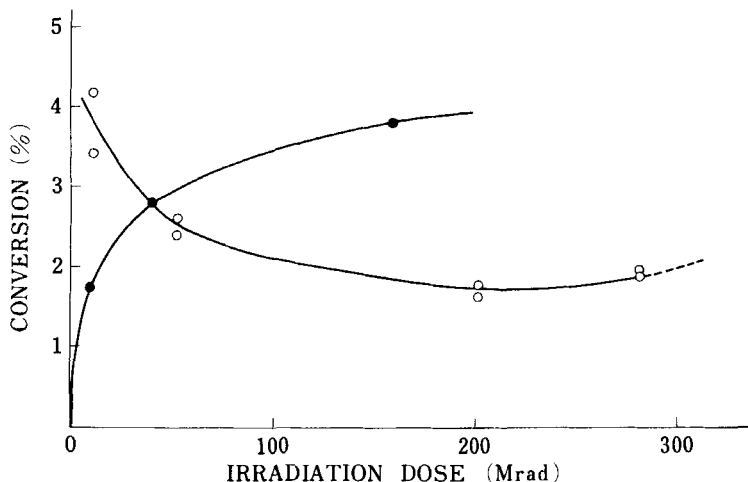
**Fig. 3.** Relations between conversion and irradiation dose in polymerizations induced by reactor radiations. $\bigcirc$, pure monomer; $\bullet$, monomer in presence of methanol.

From Figs. 4 and 5 it is obvious that the polymerization yield in the presence of boron decreases gradually with the irradiation dose after the initial stage, and then the conversion increases quite rapidly. This acceleration phenomenon has not been observed in our experiments with monomers without boron.

In the $\gamma$-ray-induced polymerization, the effect of boron concentration on the polymerization was examined. The results are shown in Fig. 6. The effect is not so distinguished as far as the polymerization yield is concerned.
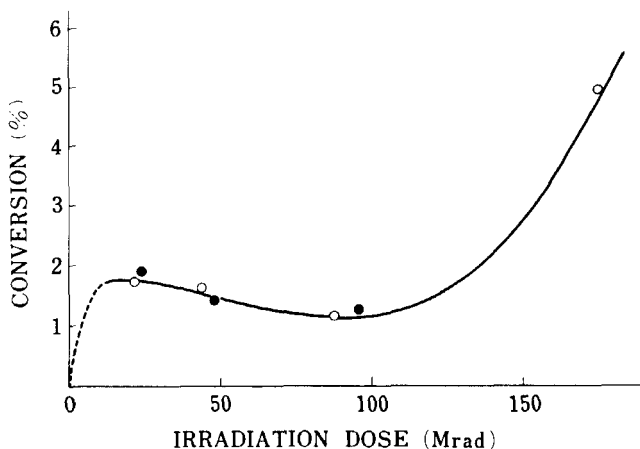
**Fig. 4.** Polymerization induced by He/Li recoil particles. Relations between conversion and irradiation dose. $\bigcirc$, 1% $H_3BO_3$; $\bullet$, 2% $H_3BO_3$.

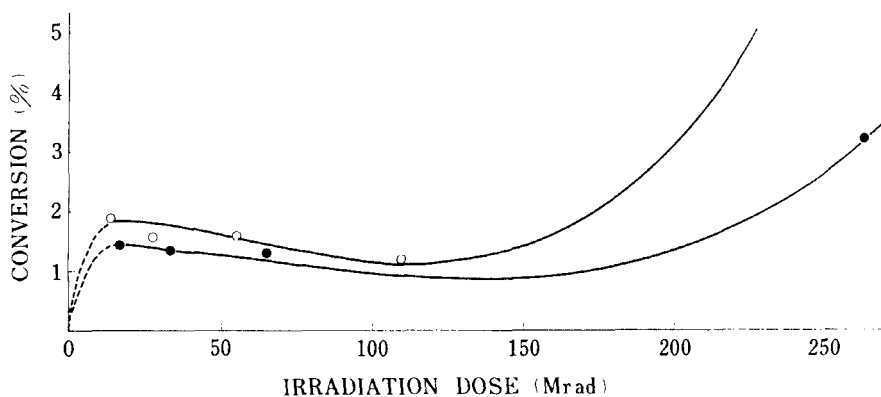**Fig. 5.** Polymerization induced by He/Li recoil particles. Relations between conversion and irradiation dose. $\bigcirc$, 4% $H_3BO_3$; $\bullet$, 7% $H_3BO_3$.
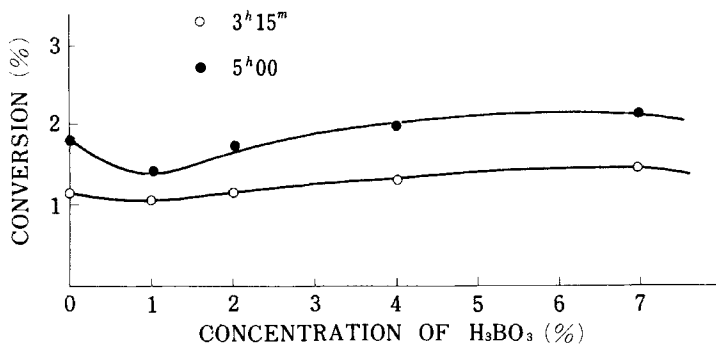
**Fig. 6.** Effect of boron concentration on the $\gamma$-ray-induced solid-state polymerization of acrylonitrile. The relations between the conversion and the concentration. Dose rate: $9.53 \times 10^5$ rads/hr.

The relations between conversion and concentration of boron in the solid system are shown in Figs. 7 and 8 for Li/He recoil-induced polymerization. It is obvious from the figures that the conversion increases with boron concentration in a region of low concentrations, while the conversion decreases in a region of higher concentrations.
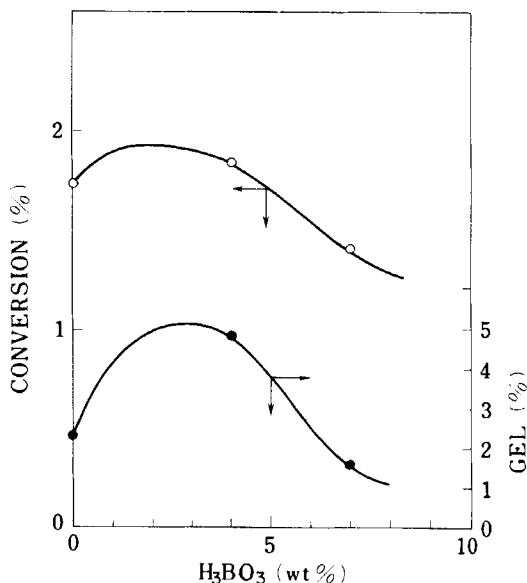


**Fig. 7.** Effect of boron concentration on the Li/He recoil-particle-induced solid-state polymerization of acrylonitrile. Irradiation time: 5 min. ○, Conversion; ●, gel contents.

The polymers obtained in the presence of boron were partially
not soluble in dimethylformamide, unlike the polymers obtained from
pure monomers. The gel contents of the polymers are also shown in
Figs. 7 and 8. The concentration dependences of the gel contents
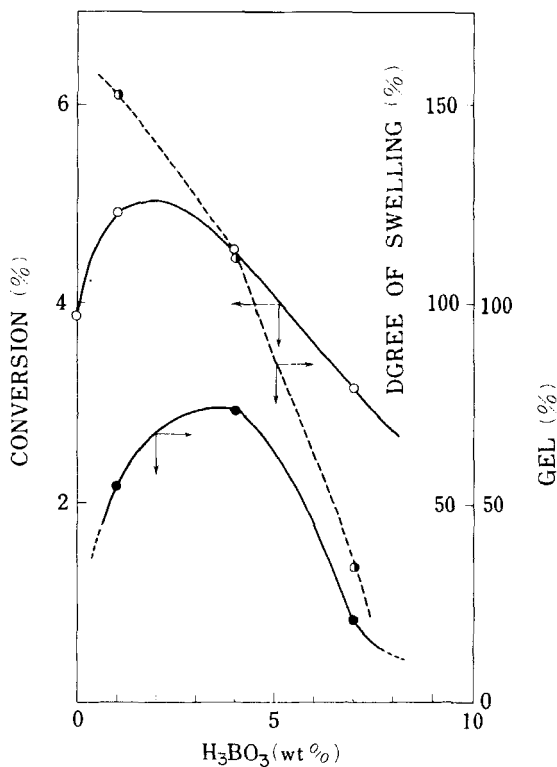were very similar to those of conversion.



**Fig. 8.** Effect of boron concentration on the Li/He recoil-particle-
induced solid-state polymerization of acrylonitrile. Irradiation time:
80 min. $\bigcirc$, Conversion; $\bullet$, gel contents; $\circleddash$, swelling degree.

For polymerization performed during 80 min of irradiation, the
swelling degree of polymers is plotted against the boron concentra-
tion, as shown in Fig. 8. The degree of swelling decreases rapidly
with boron concentration.
Infrared spectra of polymers obtained from the polymerization
of mixtures of monomer and methanol are shown in Fig. 9. Absorp-
tions at 1610 and 2210 $cm^{-1}$ were observed, and the intensity in-
creases with the irradiation time. This is due to the irradiation with
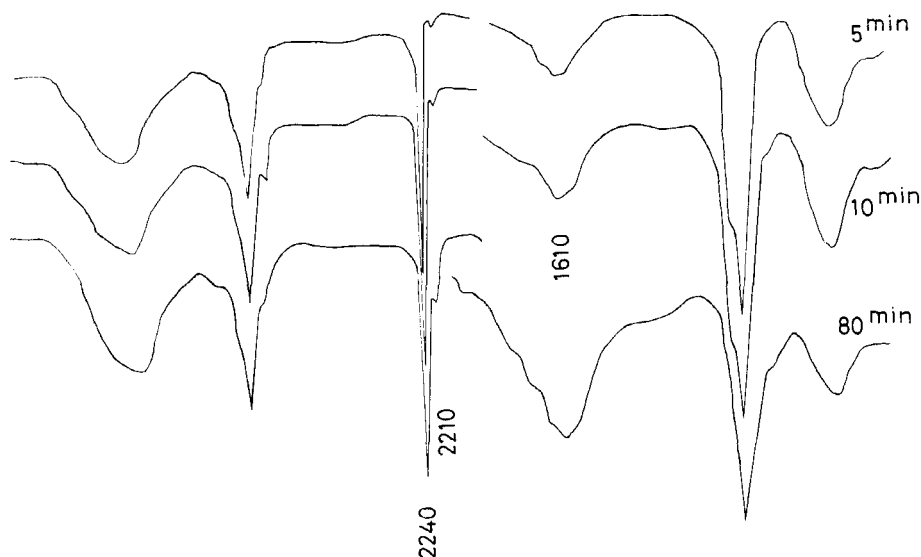fast neutrons.

**Fig. 9.** Infrared spectra of polymers obtained from a mixture of acrylonitrile and methanol. Irradiation time: 5, 10, and 80 min.

An infrared spectrum of polymer obtained from monomers containing boron was compared with one from pure monomers. A large difference between the two spectra was not found.

Electron spin resonance spectra of polymers, obtained in various conditions, have been measured, using a K-band spectrometer. It was observed in the measurements that appreciable amounts of conjugated double bonds exist in the polymers, and that the quantity of the double bonds and the half-width of the signal of electron spin resonance depend on the boron concentration.

## DISCUSSION

As reported in a previous paper [1], polymers obtained in the polymerization of pure monomers induced by reactor radiation were always soluble in dimethylformamide, whereas polymers obtained by Li/He recoil particles and other associated radiations were partially not soluble, as shown above. The gel content and the swelling degree depend on the boron concentration and the irradiation time. This is clearly due to the irradiation effects induced by Li/He recoil particles.

In solid monomers containing 1% $H_3BO_3$, the number of [10]B atoms is $15.4 \times 10^{18}$ per gram, and the number of monomers 3.93

$\times 10^{22}$ per gram. As the flux of thermal neutron is $\phi = 7.3 \times 10^{12}$ n/cm$^2$/sec, the number of fissions of boron atom is calculated to be $7.3 \times 10^{10}$ per gram per second. Therefore, one can expect that one fission takes place for each $1.8 \times 10^{10}$ monomers for 5 min of irradiation.

The recoil $^4$He particle has an energy of 1.47 MeV, and the range in solid acrylonitrile is estimated to be $3.28 \times 10^{-4}$ cm. Therefore, the mean linear energy transfer is 45 eV/Å.

Assuming that the radius of the melting region along the track of the particle is 10 Å, and that the monomer crystals in a cylindrical region within a radius of 100 Å from the center of the track can be deformed by the track formation, the volume of zone affected by the recoil He$^4$ particles can be easily calculated. For 5 min of irradiation with 1% $H_3BO_3$ concentration, 2.3% volume of the monomer system can be influenced by the recoil $^4$He particles.

When the volume of the deformed region becomes large enough and the value arrives at a threshold value, an enhanced deformation of the crystal matrix may be expected. For a long period of irradiation, many active centers are accumulated in the system at low temperature. The acceleration of polymerization in a later stage may be explained by such reasons.

The formation of gel is due to the branching or cross-linking of polymers. Such a phenomenon has never been observed in polymerizations induced by other radiations. It seems that the polymerization takes place partially in a locally melted region produced by Li/He recoil particles.

The decreases in both gel contents and swelling degree in a region of higher concentrations of boron may be due to degradation of the network polymers into small fragments by Li/He recoil particles. The formation of trans-vinylene and conjugated $C \equiv N$ groups may be due to the irradiation effect of fast neutrons on the polymers.

Although the electron spin resonance spectra of polymers obtained from pure monomers or the mixture with methanol are very narrow, in the range 7 to 11 g, the spectra of polymers obtained by the Li/He recoil-induced polymerization are relatively broad. This indicated that the length of conjugated double bonds is not very long, probably due to the irregularity of polymers. Since the polymerization is considered to proceed in a locally melted region, the stereo-regulation may not be possible.

## CONCLUSION

Solid-state polymerization of acrylonitrile induced by Li/He recoil particles at low temperature was carried out by using a cryo-

genic device in a reactor. The solid monomers containing methanol and boric acid were irradiated at − 196°C.

1. In the initial stage of the polymerization, the conversion was lower in the presence of boric acid than with pure monomers, while in the later stage of polymerization, the conversion increases very rapidly with irradiation time, and the yield of polymerization was much higher than with pure monomers. It may be due partially to the accumulation of a great amount of active centers, partially to the degradation of crystal structure by Li/He recoil particles and also by bombardment of fast neutrons. The change of thermal conductivity due to the polymer formation may also play an important role for the acceleration phenomena.

2. A decrease in yield in the region of high concentration of $H_3BO_3$ was observed and is probably due to the degradation of monomer crystals and the polymer produced. In the case of $\gamma$ ray-induced polymerization, the yield increases slowly with concentration.

3. The polymers obtained were not soluble in dimethylformamide, unlike the polymers obtained from polymerization of pure monomers. This is due to the branching and cross-linking of polymers. It seems that the polymerization takes place in a small hot zone produced by Li/He recoil particles. The formation of branching and cross-linking polymers has never been observed in solid-state polymerization of acrylonitrile with other radiations under irradiation.

4. The degree of swelling of the polymers decreases with boron concentration. This indicates that the cross-linking density increases with concentration. In spite of the increase of the degree of cross-linking, the gel quantity decreases with increasing the concentration. These facts indicate that the cross-linking polymers were degradated into small fragments by Li/He recoil particles.

5. The formation of conjugated $C \equiv N$ bond and trans-vinylene structure was observed, as in the case of the polymerization of pure monomers. This may be due to the recoil effects of fast neutrons.

6. Appreciably great amounts of free radicals have been observed in the polymers obtained.

## REFERENCES

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