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ORIGINAL CONTRIBUTION

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# Tacticity, molecular weight, and molecular-weight-distribution relationships in stereoregular polyacrylonitrile prepared by electron beam irradiation canal polymerization

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The effectiveness of other irradiation sources has been reported, such as X-rays [5] and UV radiation [6].

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**Abstract** The preparation and characterization of stereoregular isotactic polyacrylonitrile (PAN) by electron beam (EB) irradiation on a urea canal complex are described. The EB method has several advantages over the ordinary $\gamma$-ray irradiation method: a very short polymerization time is needed (within a few seconds) and EB irradiation is carried out intermittently, and so all the polymer properties can be studied as a function of the EB irradiation dose. The structure–properties relationships of PAN, such as intrinsic viscosity versus the number-average molecular weight and the viscosity versus the isotacticity range were clarified. Significant information for the optimization of the tacticity of PAN was extracted.

**Key words** Isotactic polyacrylonitrile · Canal polymerization · Electron beam irradiation · Structure–properties relationships

## Introduction

Stereoregular polyacrylonitrile (PAN) can be prepared by the solid-state polymerization (urea clathrate complex) of acrylonitrile (AN) at low temperatures [1, 2]. In this synthesis, either strong $\gamma$-ray irradiation or electron beam (EB) irradiation is generally used. Comprehensive studies of PAN with the former have been carried out [3, 4], but no research has been made with the latter.

There is a distinct difference between the $\gamma$-ray irradiation and the EB irradiation methods:

1. The latter is stronger than the former, but the penetration depth is quite different. The depth into pure water is about 90 cm in the former and about only 1 cm in the latter; therefore, the thickness of the sample layer is important.
2. In the EB irradiation method, a very short polymerization time is needed. This is in contrast to the $\gamma$-ray irradiation method, where the sample is continuously irradiated (0.5–2 h) with $\gamma$-rays.
3. Since the total EB irradiation dose is given as the product of the unit intensity (10 kGy) multiplied by time, one can study the polymer properties as a function of the irradiation dose.

In this article, the EB irradiation canal polymerization of AN is described in relation to the characterization of the resulting polymer. Particularly, stereoregular PAN can used as a specialty polymer, such as a starting material for high-quality PAN-based carbon fiber and the EB procedure is widely used in many industrial areas, such as EB curing of rubberlike materials.

## Experimental

### Sample preparation

AN and urea were prepared as described previously [7, 8]. A schematic representation of the preparation process is given in Fig. 1. After the formation of a canal complex, the reactants were transferred to a cooled thin polyethylene envelope. The weight of the complex was about 10 g, and the sample size was 5 × 7 cm with a thickness of less than 5 mm. The sample was exposed to the EB shower emitted from a Cockcraft–Wardon type of EB accelerator (Dynamitron, Radiation Dynamics; 2 MeV, 10 mA). The total irradiation dose is given by Eq. (1).

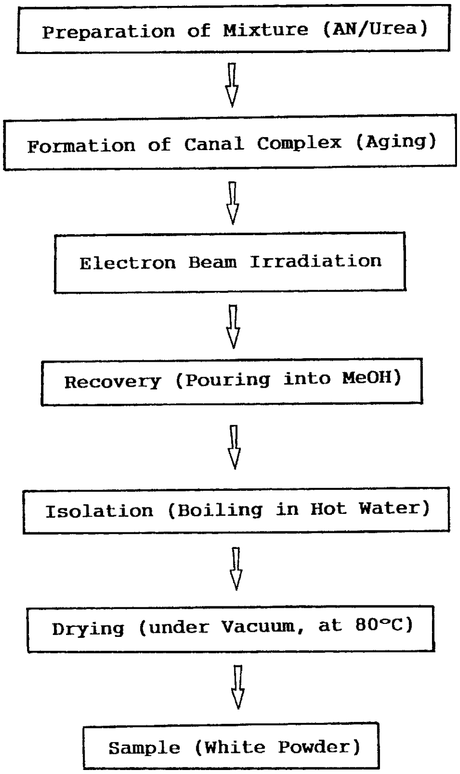

**Fig. 1** Representation of the sample preparation process

$$\text{Total irradiation dose} = \text{unit dose (10 kGy)} \times \text{the irradiation time} \tag{1}$$

Besides this equipment, a small-area-beam type of EB accelerator (Curetron, Nisshin High-Voltage Co.; 300 KeV, 100 mA) was also used. To remove a trace amount of urea, the sample was boiled in hot water, methanol extraction was carried out, and the sample was dried in a vacuum at 80 °C. The characterization of the sample is given in Table 1.

### $^{13}$C NMR measurements

A Jeol, JNM GX-400 spectrometer was used under similar conditions to those in Ref. [9]. NMR pulse conditions were as follows: PW1 6.0 $\mu$s (45° pulse); PD 2.000 s (pulse repetition time), and point 13 K (data point).

### Viscosity measurements

A Ubbelohde type of capillary viscometer was used under the following conditions:

1. Solvent, *N*,*N*-dimethylformamide (DMF); concentration, 0.1 g/dl; temperature, 25 °C
2. Concentrated $HNO_3$ (70%); concentration, 0.1 g/dl; temperature, 0 °C.

### Gel permeation chromatography measurements

A Waters gel permeation chromatography (GPC) instrument (ALC/GPC 150-C type, Waters Co.) with a differential refractom-

**Table 1** Characterization of polyacrylonitrile samples. The viscosity was measured in N,N-dimethylformamide at 25 °C

| Irradiation conditions | | A/U[a] | Yield (%) | Viscosity (dl/g) | NMR results Triad tacticity (%) | | | |
|---|---|---|---|---|---|---|---|---|
| Type | kGy | | | | mm | mr | rr | $4IS/H^2$ |
| EB1[b] | 10 | 1/2 | 20 | 1.56 | 67 | 25 | 8 | 3.43 |
| EB2 | 20 | 1/2 | 39 | 1.51 | 63 | 27 | 10 | 3.46 |
| EB3 | 30 | 1/2 | 47 | 1.42 | 61 | 30 | 9 | 2.44 |
| EB4 | 50 | 1/2 | 57 | 2.58 | 50 | 37 | 13 | 1.90 |
| EB5 | 10 | 1/3 | 16 | 1.38 | 66 | 26 | 7 | 2.73 |
| EB6 | 20 | 1/3 | 48 | 1.62 | 61 | 29 | 10 | 2.90 |
| EB7 | 30 | 1/3 | 61 | 1.72 | 57 | 33 | 11 | 2.30 |
| EB8 | 50 | 1/3 | 63 | 1.56 | 55 | 31 | 14 | 3.20 |
| EB13 | 10 | 1/7 | 13 | 0.80 | 68 | 25 | 7 | 3.05 |
| EB14 | 20 | 1/7 | 68 | 1.36 | 65 | 27 | 8 | 2.85 |
| EB15 | 30 | 1/7 | 69 | 1.35 | 61 | 30 | 10 | 2.71 |
| EB16 | 50 | 1/7 | 76 | 1.14 | 59 | 29 | 12 | 3.37 |
| GR1[c] | 0.5 | 1/3 | 72 | 4.18 | 61 | 29 | 10 | 2.90 |
| GR2 | 2 | 1/3 | 56 | 3.01 | 65 | 26 | 9 | 3.25 |
| GR3 | 3 | 1/3 | 68 | 3.13 | 58 | 30 | 12 | 3.09 |
| GR4 | 5 | 1/3 | 72 | 3.37 | 53 | 36 | 11 | 1.80 |
| GR5 | 1 | 1/1 | 70 | 4.50 | 50 | 34 | 16 | 2.77 |

[a] Molar ratio of acrylonitrile to urea
[b] EB: electron beam
[c] GR: $\gamma$-ray

eter was used. Two columns (Shodex AD80M/S) were connected in series and operated at 70 °C. The flow rate was 1.0 ml/min. A small amount of LiBr (0.01 mol%) was added to the DMF solvent to prevent anomalous viscosity behavior [10, 11].

## Results and discussion

### The effect of EB irradiation conditions on the yield and tacticity of PAN

The yield was plotted against the total irradiation dose (Fig. 2). The yield was low at the initial irradiation stage and then rapidly increased and became saturated. The final level was about 55–75% depending on the molar ratio of AN/urea.

The effect of the irradiation dose on the stereoregularity of PAN is shown in Fig. 3. In the initial irradiation stage the stereoregularity was relatively high; however, at a later stage the regularity decreased. The stereoregularity was isotactic as shown in Fig. 4, although there was considerable confusion in the stereoregularity of PAN [14–17]. The gradual decrease in stereoregularity with the repeated EB irradiations is interesting. Since the yield increased with the increase in the total irradiation dose (Fig. 2), the apparent decrease in stereoregularity would be caused by the formation of a new and less stereoregular component.

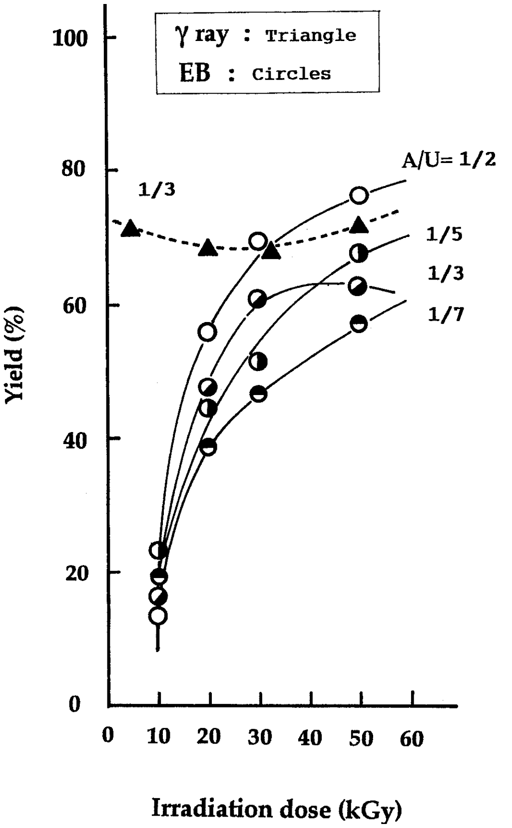

**Fig. 2** Yield as a function of electron beam (*EB*) irradiation dose. The dependence of the yield on the EB irradiation dose is presented in comparison with that of $\gamma$-ray irradiation. The yield was calculated from the weight of recovered polymer

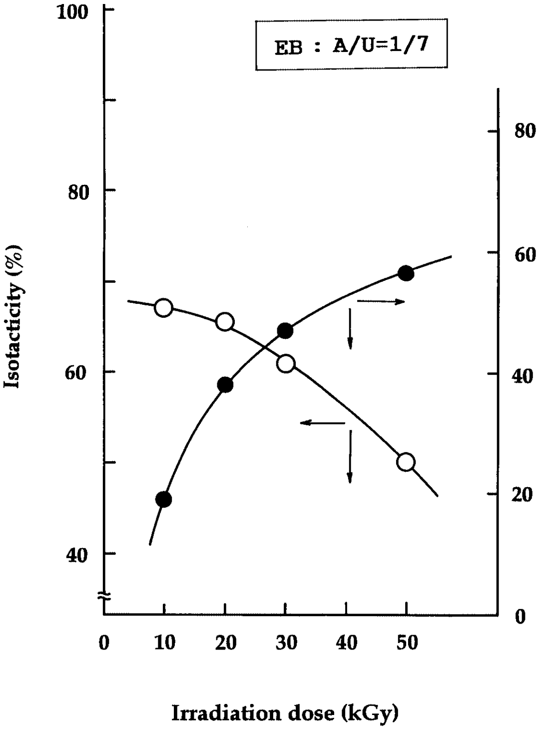

**Fig. 3** Stereoregularity as a function of EB irradiation dose. The isotacticity was determined based on the $^{13}$C NMR spectra

### EB canal polymerization mechanism of AN

When the viscosity was plotted against the yield, Fig. 5 was obtained. A clear maximum appeared. The following explanation is possible: the results can be regarded as the overlapping of a rising curve and a decreasing curve, which suggests the simultaneous occurrence of polymerization of AN and a chain-scission reaction of the resulting polymer. The rising curve is no problem, since the yield increased continuously (Fig. 2). The decreasing curve may be a matter of dispute, since it is questionable that the PAN molecular chain is chain-ruptured by repeated EB irradiation.

In order to check this possibility, chain-scission experiments were carried out by use of the small-area type of EB accelerator: isotactic PAN was mixed with fine urea and the mixture was subjected to EB irradiation. The results are summarized in Fig. 6. EB irradiation surely caused chain scission, as evidenced by the decrease in the viscosity.

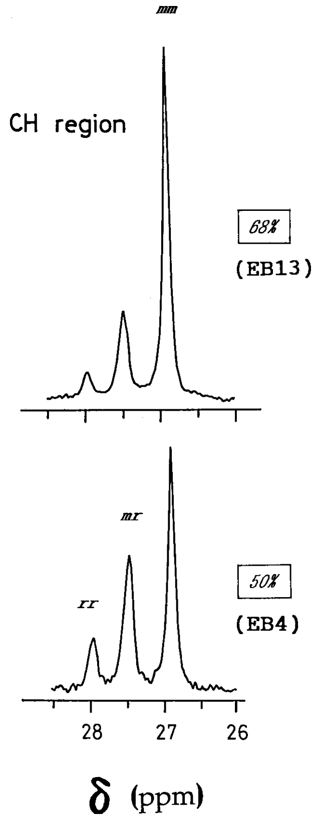

**Fig. 4** Typical $^{13}C$ NMR spectra of EB canal polyacrylonitrile (*PAN*). Only the methine carbon region is presented. The notation in Refs. [12, 13] was used. The isotacticity (%) was calculated from the percentage of the peak area of (mm) placement

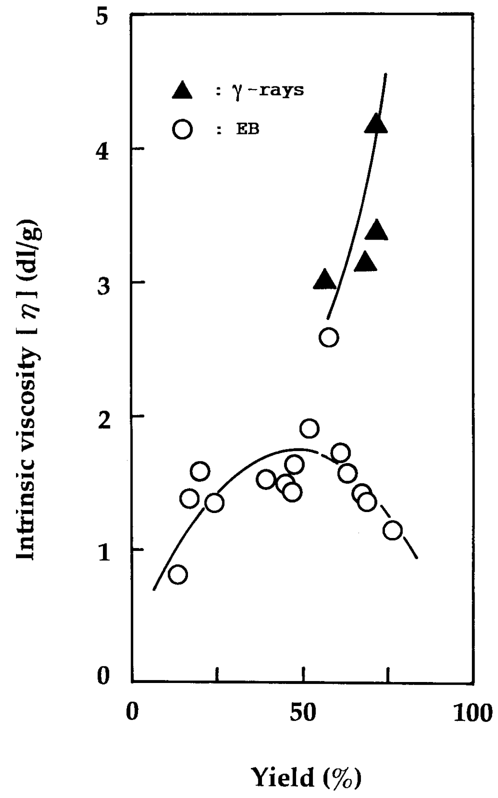

**Fig. 5** Relationship between the viscosity and yield. The appearance of the maximum in the EB canal PAN must be noted

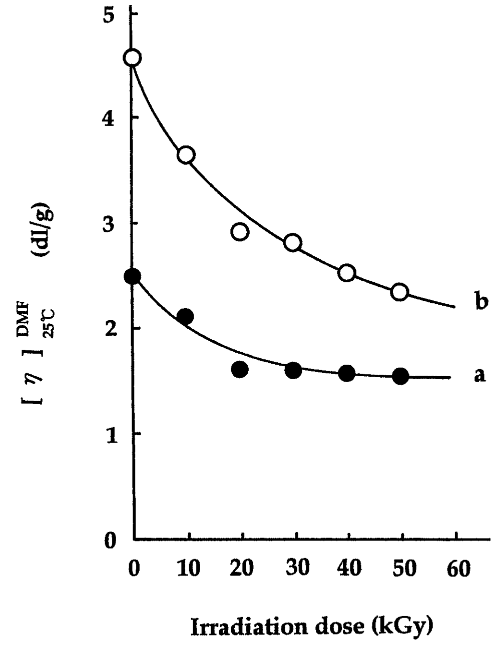

**Fig. 6** Chain-scission experiments by EB irradiation. Two different samples were used for comparison. These were prepared by γ-ray irradiation postpolymerization (*a*) and insource polymerization (*b*) methods [4]

## Molecular weight and stereoregularity of EB canal PAN

The molecular-weight range of PAN obtained here together with the ranges obtained previously (γ-ray and UV irradiation methods) [4, 6] are shown in Fig. 7. The EB method ensured that the molecular weight of the polymer was in the lower to middle range. This is due to the previously mentioned chain rupture by repeated EB irradiation in an open system. From this figure, it is apparent that the lowest range is obtained by UV irradiation, the middle one by EB irradiation, and the highest one by γ-ray irradiation. Ultra-high-molecular-weight PAN ($M > 10^6$) with extremely high isotacticity could not be obtained within this experimental range.

When the NMR data were plotted against isotacticity, Fig. 8 was obtained. The data from γ-ray irradiation (postpolymerization) under the optimum conditions found empirically [4] are also plotted in this figure. It is apparent that both results lie on two different lines with different slopes. The highest isotacticity (above 80%) was attained by γ-ray irradiation (postpolymerization) under the optimum conditions, whereas the

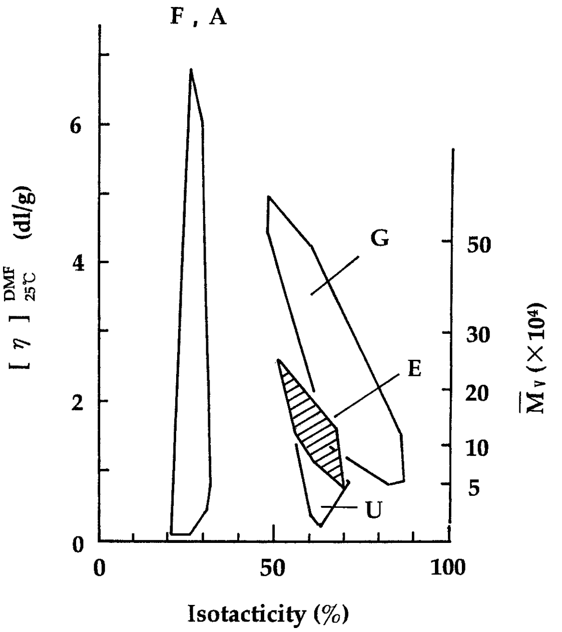

**Fig. 7** Relationship between intrinsic viscosity and isotacticity of PAN. The molecular-weight range of EB canal PAN (*E*) is represented by the hatched area. *F*, *A*, *G*, and *U* indicate free radical, anionic, $\gamma$-ray irradiation, and ultraviolet irradiation. The data, except the EB canal PAN, were taken from Ref. [6]

middle-range tacticity was obtained by EB irradiation canal polymerization. The $\gamma$-ray irradiated samples prepared here showed similar results to the latter, both of which are characterized as an insource method in terms of irradiation chemistry [4]. Although the extent of stereoregularly is not so high, the easy operation by using the EB apparatus would be helpful for the clarification of the structure and properties of this polymer.

## Molecular-weight distribution by GPC measurements

The molecular weight ($M_n$, $M_w$, $M_z$) and the molecular-weight distribution ($M_n/M_w$) were studied by GPC. Typical GPC curves of the resulting PAN samples are shown in Fig. 9. When the molar ratio of AN to urea (A/U) was small (A/U = 1/7), the GPC curve was little affected, whereas when the molar ratio is large (A/U = 1/2), the GPC curve was strongly affected by the increase in EB irradiation. In the latter case, particularly, the peak became broader in a higher-molecular-weight region and the formation of a higher-molecular-weight component was evident.

These results can be understood in terms of the perfectness of the canal complex. There exist at least two different canal complexation states with regard to the perfectness of the complex (an ideal perfect canal and a less ordered imperfect canal). The weak EB irradiation

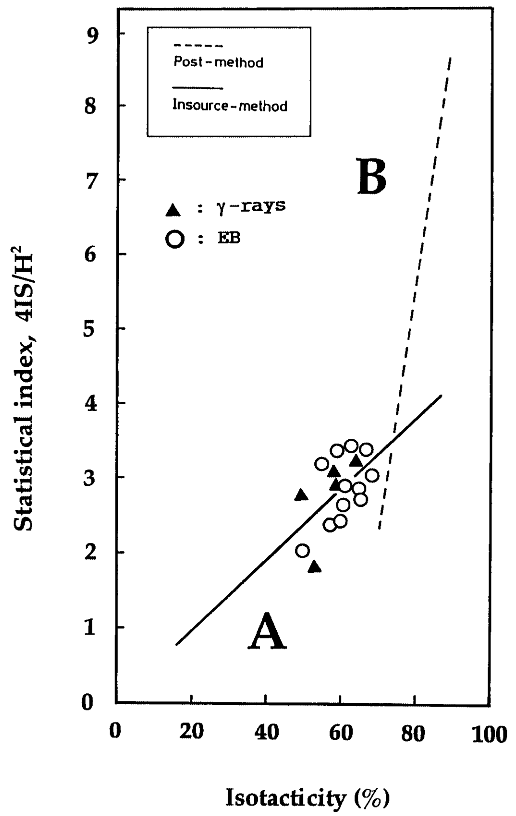

**Fig. 8** Relationship between statistical index ($4IS/H^2$) and stereoregularity of PAN. The experimental data on *lines A* and *B* are given in Ref. [4]. It is worthwhile noting that *line B* was derived from the samples prepared by $\gamma$-ray irradiation postpolymerization under the optimum conditions

causes polymerization in the former, while strong irradiation does so in the latter. In the case of the larger molar ratio of AN to urea (A/U > 1/3), particularly, low isotactic components are formed abundantly by strong EB irradiation (repeated EB irradiation). This explanation agrees well with the experimental results presented earlier. The existence of two different complex states has also been pointed out by Yamazaki et al. [5].

From these results, the information concerning the optimization of the tacticity of PAN by solid-state synthesis can be extracted: if highly stereoregular PAN is required, weak EB irradiation is recommended (small amount of products), while if a less stereoregular sample is needed, strong EB irradiation should be used (large amount of products).

## Viscosity–molecular weight relationship in EB canal PAN

The relationship between the intrinsic viscosity and the number-average molecular weight ($M_n$) is shown in Fig. 10. The results obtained here were plotted on the

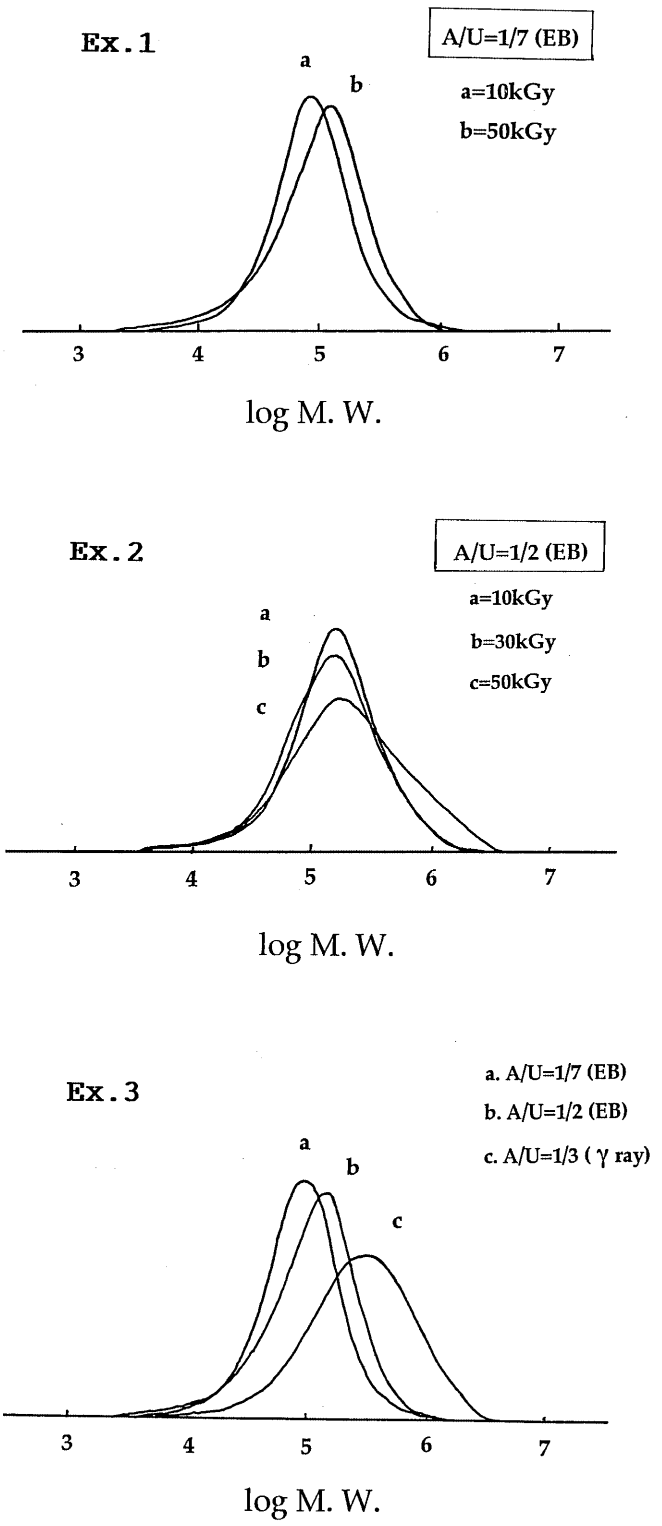

**Fig. 9** Typical gel permeation chromatography (*GPC*) curves of EB canal PAN (*Ex.1*, *Ex. 2*) in comparison with $\gamma$-ray irradiated canal PAN (*Ex. 3*). *Ex. 1* Peak shifted to a higher-molecular-weight side without a change in the half-width value. *Ex. 2* The formation of the higher-molecular-weight component was enhanced at higher EB intensity. *Ex. 3* $\gamma$-ray irradiated PAN ensured a very broad GPC curve

previously reported experimental data for $\gamma$-ray irradiated canal PAN [8]. Both results agree well, although the slope is slightly different from that of the previous one (0.94 → 0.81). This linear relationship can be expressed in the following quantitative form.

$$\eta_{\mathrm{sp}}/C = 1.48 \times 10^{-4} M_{\mathrm{n}}^{0.81} \ . \qquad (2)$$

From Eq. (2), one can easily obtain the value of $M_{\mathrm{n}}$ of a given EB canal PAN sample. An arrow in Fig. 10 indicates the experimental data deviating from an ideal linear relationship. That is, when the total EB irradiation dose was increased (above 30 kGy), the extent of the deviation was larger. This is due mainly to partial oxidative cross-linking, as estimated by the insolubility of the resulting polymer at higher irradiation doses. Of course, it may be necessary to consider the possibility of chain-branching, but its effect cannot be evaluated quantitatively here. It is possible to consider that at least linear polymers are obtained in the initial stage, where only pure polymerization in the one-dimensional crystal lattice of urea is permitted and deteriorate secondary reaction is avoided.

## Conclusion

1. The heterogeneous characteristics of EB canal polymerization of AN in the solid state have been described. The system is very simple and the polymer-

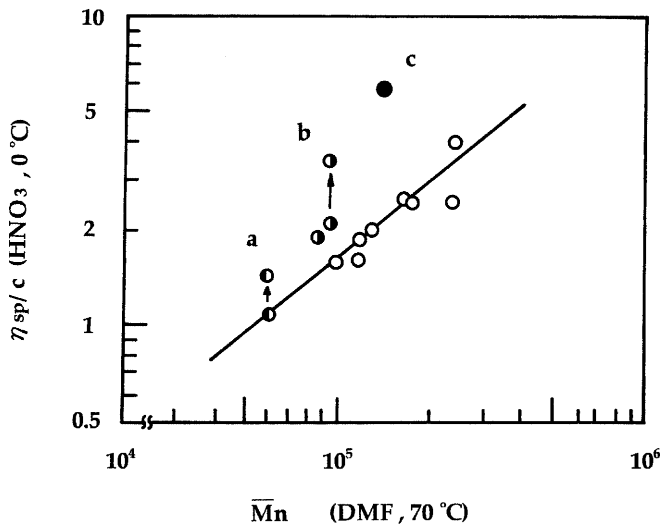

**Fig. 10** Viscosity versus number-average molecular weight relationship in EB canal PAN. *a*: ($A/U = 1/7$), 1M → 5M; *b*: ($A/U = 1/2$), 1M → 5M; *c*: $\gamma$-ray irradiated

ization time is quite short. PAN samples were prepared as a function of irradiation dose.

2. The extent of stereoregularity was between 70 and 50% (mm fraction). An isotactic-rich sample was obtained in the initial irradiation stage, whereas a less rich one was obtained in the later stage.

3. At least two different states of canal complex were suggested (an ideal perfect canal and a less ordered imperfect canal). Weak irradiation permits polymerization in the former, whereas strong irradiation does so in the latter.

4. The significance of the molar ratio of AN to urea was clarified. The higher the molar ratio, the broader the molecular-weight distribution. The results can be connected with the existence of the previously mentioned two different AN complexing states.

5. Structure–properties relationships, such as the intrinsic viscosity versus the number-average molecular weight and the molecular weight versus the isotacticity range of EB canal PAN were obtained.

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