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# $^{13}$C n.m.r. and g.p.c.–low-angle laser light scattering measurements on polyacrylonitrile prepared by urea clathrate polymerization in the solid state for the optimization of tacticity

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The molecular weight and molecular weight distribution of isotactic polyacrylonitrile (PAN) prepared by urea clathrate polymerization in the solid state were studied by the g.p.c.–low-angle laser light scattering (l.a.l.l.s.) method. The experimental details of this method for PAN are described. Measurements were carried out on three different kinds of urea clathrate PAN, and the results were compared with those of free-radical PAN (i.e. prepared using the aqueous redox slurry system). The characteristics of the urea clathrate PAN were (1) an asymmetrical shape in the g.p.c.–l.a.l.l.s. curve and (2) a remarkable contribution of the lower-molecular-weight component to the high stereoregularity (>80%) of the sample. An experimental prediction for the solid-state synthesis of a perfectly stereoregular PAN sample (isotacticity of 100%) has been derived from a combination of the g.p.c.–l.a.l.l.s. and $^{13}$C n.m.r. results.

**(Keywords: polyacrylonitrile; urea clathrate polymerization; isotatic configuration)**

## INTRODUCTION

Information on the molecular weight and molecular weight distribution of a given polymer can be obtained by measuring solution properties[1]. Gel-permeation chromatography (g.p.c.) and related techniques are particularly useful for this purpose[2,3]. Recently, the low-angle laser light scattering (l.a.l.l.s.) detector has become widely used by connecting it with the g.p.c. apparatus, i.e. the g.p.c.–l.a.l.l.s. method[4,5]. With this method, no elaborate procedures, such as a Zimm plot of the two parameters concentration ($c$) and scattering angle ($\theta$), is necessary. Obstacles of external impurity can be excluded by use of a line filter, which enables the signal from an external impurity to be recorded as a spike noise. Above all, absolute values of the molecular weight and molecular weight disrtribution of the sample can be obtained. This method has become widely used in many polymer systems, but its application to stereoregular polyacrylonitrile (PAN) has never been reported.

In this article, g.p.c.–l.a.l.l.s. measurements for PAN prepared using urea clathrate were carried out, and an experimental prediction for the preparation of the perfectly stereoregular sample (isotacticity of 100%) is described.

## EXPERIMENTAL

### *Samples*

Stereoregular PAN was obtained by urea clathrate polymerization at low temperatures[6], and free-radical PAN was obtained by aqueous redox slurry polymerization[7]. The sample preparation conditions are given in *Table 1*.

### *$^{13}$C n.m.r. measurements*

A JEOL JNM GX-270 n.m.r. spectrometer was used under similar conditions to those described in ref. 6. Analysis of the n.m.r. spectra was carried out according to the manner given in refs 8 and 9. Typical n.m.r. spectra are shown in *Figure 1*.

### *G.p.c.–l.a.l.l.s. measurements*

A conventional type of g.p.c. instrument (Waters, Model 201 D) equipped with feeding pump (Model 510), injector (Model U6K) and differential refractometer (Model 410), was directly coupled with a l.a.l.l.s. instrument (Chromatix Co. Ltd, Model KMX-6) containing a flow cell (10 $\mu$l), and a fluoro-pore line filter (0.1 $\mu$m). Two columns (Shodex KF-80M; Showa Denko Co. Ltd) were used in the g.p.c. apparatus, and in the l.a.l.l.s. instrument the scattering angle was 6–7° and the

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**Table 1** Characterization of samples

| Code | Type | Temp. (°C) | Viscosity $[\eta]^a$ (dl g$^{-1}$) | N.m.r. results (%)$^b$ mm | mr | rr |
|---|---|---|---|---|---|---|
| R-1 | Radical redox$^c$ | 40 | 2.27 | 28 | 49 | 23 |
| R-2 | Radical redox$^c$ | 40 | 1.60 | 28 | 49 | 23 |
| R-3 | Radical redox$^c$ | 40 | 2.26 | 28 | 49 | 23 |
| R-4 | Radical redox$^c$ | 40 | 3.29 | 28 | 49 | 23 |
| C-1 | Canal in source$^d$ | −78 | 4.96 | 48 | 36 | 16 |
| C-2 | Canal in source | −78 | 2.67 | 65 | 25 | 10 |
| C-3 | Canal post$^e$ | −78 | 2.52 | 83 | 14 | 3 |
| C-4 | Canal in source$^f$ | −78 | 1.81 | 65 | 26 | 9 |
| C-6 | Canal in source$^f$ | −78 | 2.45 | 56 | 30 | 14 |

[a] In *N,N*-dimethylformamide
[b] Intensity was calculated based on methine (CH) carbon peak
[c] Aqueous redox slurry system ammonium persulfate/$NaHSO_3$), at 40°C (see Figure 6 in ref. 7)
[d] Irradiation in source-polymerization (polymerization occurs in the canal under gamma-irradiation)
[e] Irradiation post polymerization (polymerization occurs during storage after gamma-irradiation)
[f] Samples were prepared in an open system (in air)

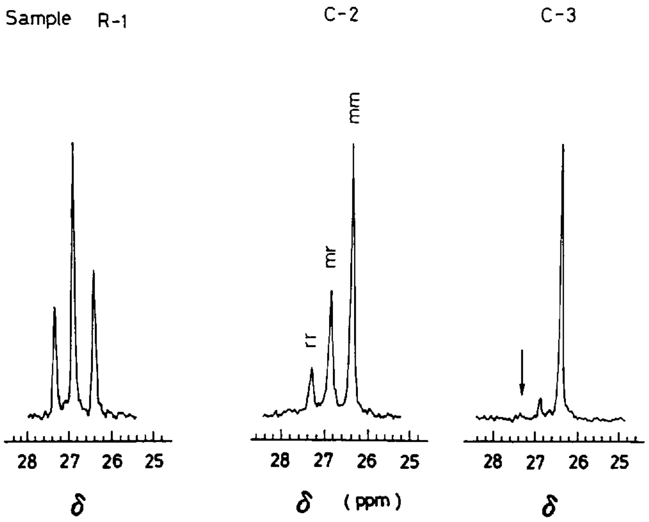

**Figure 1** $^{13}C$ n.m.r. spectra at 67.5 MHz of different kinds of PAN. Only methine (CH) carbon regions are presented. The notation given in refs 8 and 9 was used. An arrow indicates the position of the (rr) peak. It is apparent that urea clathrate PAN is highly isotactic in its configuration. With regard to the stereoregularity of PAN, there is a considerable confusion even for the normal free-radically prepared sample (see refs 11 and 12). See *Table 1* for sample codes

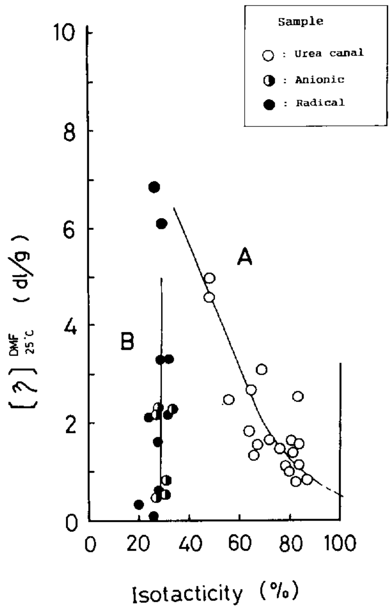

**Figure 2** Stereoregularity–viscosity relationship in PAN. (A) Urea clathrate PAN[6,10]; (B) free-radical and anionic PAN[7,12]

field stop was at 0.2 mm. The system was operated at room temperature (23°C).

All the solutions were prepared at high temperature (above 140°C) by use of *N,N*-dimethylformamide (DMF) as a solvent, since isotactic PAN was totally insoluble in DMF at room temperature (see ref. 10). A trace amount of LiCl (0.05 mol%) was added to avoid the anomalous solution behaviour of PAN[13,14].

## RESULTS AND DISCUSSION

### *Tacticity–molecular weight relationship in PAN*

We previously carried out a detailed study on urea clathrate polymerization of acrylonitrile (AN)[6]. The stereoregularity and molecular weight of those samples were determined by $^{13}C$ n.m.r. spectra and viscosity measurements. These results are summarized in *Figure 2* and experimental data are given in *Table 1*. *Figure 2* shows that in urea clathrate-polymerized PAN, the stereoregularity increased when the molecular weight decreased (curve A). In contrast, in free-radical and anionic PAN, the stereoregularity was low and almost constant (curve B), even though the molecular weight varied widely according to the chain-transfer reaction during polymerization. In an aqueous redox slurry system, particularly, the molecular weight is determined by a rapid chain transfer mechanism to an activator[15,16]. From *Figure 2*, it is apparent that the extrapolated value of curve A gives a critical point, which is the viscosity of the perfectly stereoregular PAN (isotacticity of 100%).

Its value was 0.5 (the molecular weight calculated by the Cleland–Stockmeyer equation[17] was $M_v = 26\,000$). It must be noted that the viscosity value is an averaged value for a solution and more detailed information such as molecular weight distribution must be obtained by g.p.c. measurements.

### *G.p.c.–l.a.l.l.s. measurements of isotactic PAN solution*

The experimental data for stereoregular PAN are shown in *Figures 3* and *4*. Fractionated components are continuously detected by both l.a.l.l.s. and refractive index (r.i.) detectors (*Figure 3*). Since there is a time lag between the detector responses, a correction is carried out by a computer program[18,19]. It must be noted that the g.p.c.–l.a.l.l.s. curve contains about 50 fractions (*Figure 4*), and that the molecular weight of each fraction is obtained directly by a calibration curve prepared beforehand.

### *Molecular characteristics of isotactic PAN by the g.p.c.–l.a.l.l.s. method*

*Figure 5* shows experimental data obtained by the g.p.c.–l.a.l.l.s. method. One can easily determine $M_n$, $M_w$ and $M_z$, together with molecular weight distribution, $M_w/M_n$. The results are summarized in *Table 2*.

From *Figure 5*, it is apparent that when the

**Table 2** Molecular characteristics of several PAN samples obtained by g.p.c.–l.a.l.l.s. method

| Sample | Isotacticity (%) | $M_n$ | $M_w$ ($\times 10^4$) | $M_z$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| R-1 | 28 | 7.3 | 11.7 | 43.4 | 2.42 |
| C-1 | 48 | 13.9 | 52.3 | 114.6 | 3.76 |
| C-2 | 65 | 11.0 | 24.1 | 41.7 | 2.19 |
| C-3 | 83 | 7.8 | 19.7 | 31.6 | 2.53 |

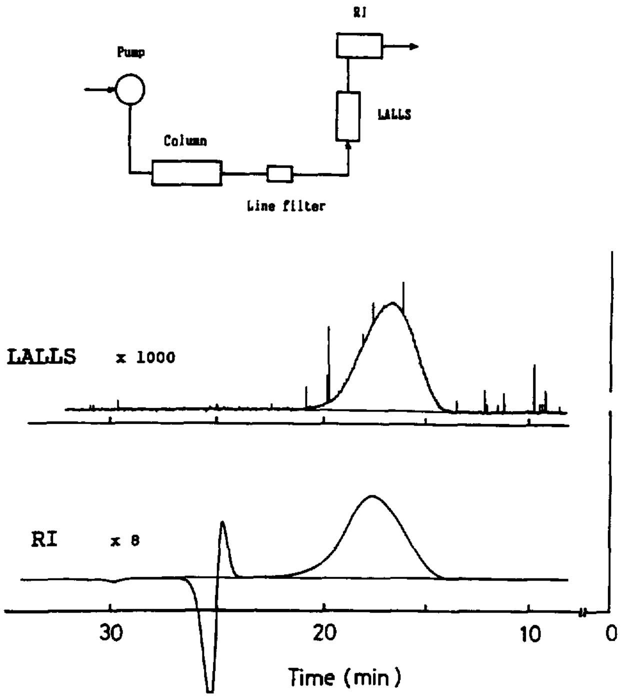

**Figure 3** Diagram of g.p.c. system and responses from l.a.l.l.s. and r.i. detectors. The sample used was urea clathrate PAN (C-3)

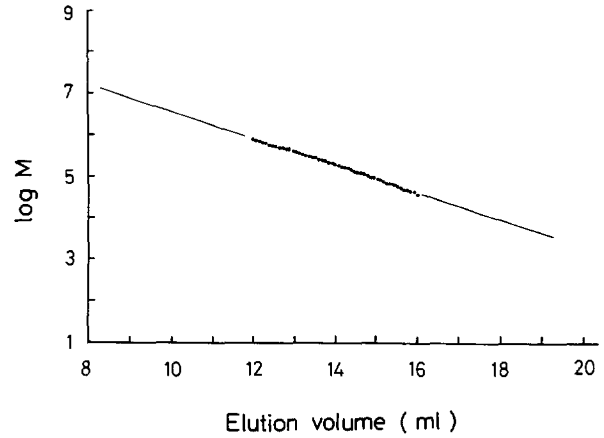

**Figure 4** Calibration curve of g.p.c.–l.a.l.l.s. measurements. Good linearity indicates reasonable selection of column packing agent. Fifty data points were recorded. It should be noted that a projection of 50 data points on the y-axis forms a curve (abscissa) in *Figure 5*

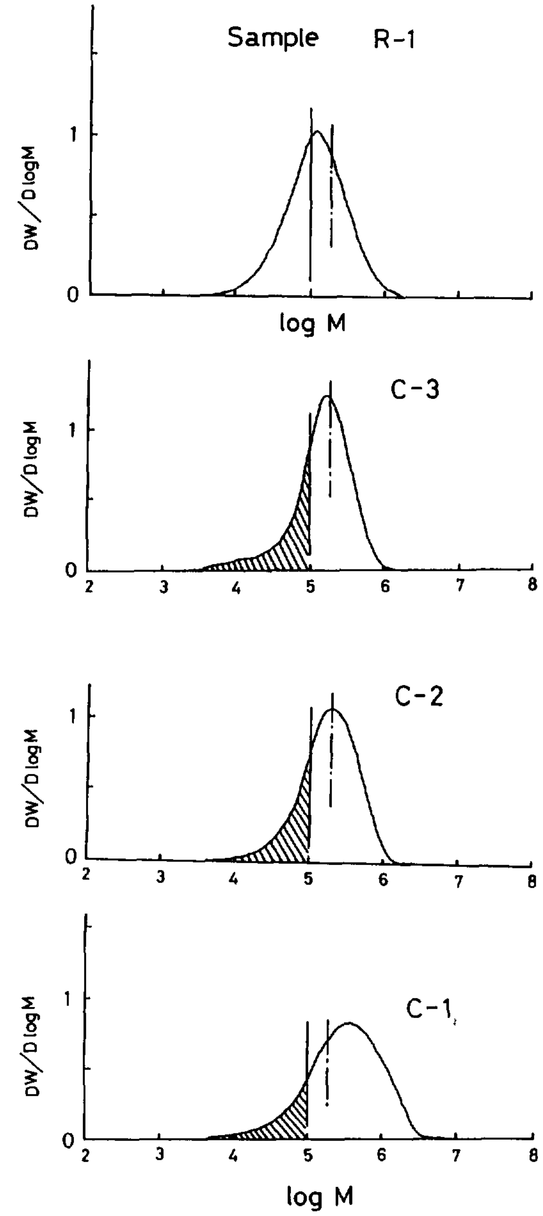

**Figure 5** Variation of g.p.c. curves for different kinds of PAN. Each subline was drawn through the peak position of the sample (C-2). The lower-molecular-weight component ($< 10^5$) is represented by shading

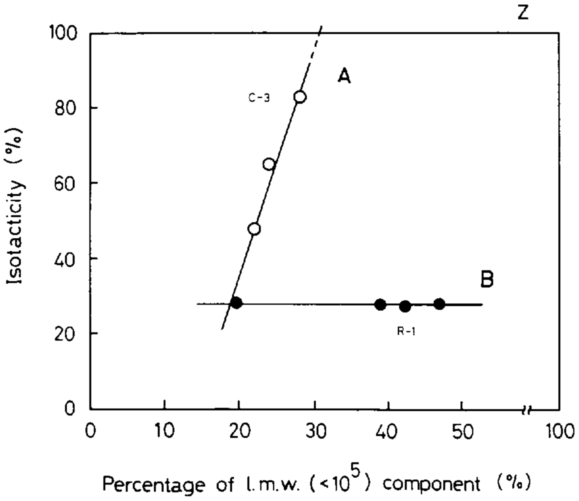

**Figure 6** Isotacticity of PAN as a function of the percentage of lower-molecular-weight ($<10^5$) component. Line A: Urea clathrate PAN; line B: Free-radical PAN

stereoregularity of PAN is increased, the average molecular weight is smaller and the molecular weight distribution is narrower. Further, the following observations can be made. (1) Atactic PAN showed an almost ideal symmetrical shape in the g.p.c. curve, whereas (2) urea canal PAN showed an asymmetric one. (3) The extent of this asymmetry was enhanced when the stereoregularity of the sample was increased. (4) This asymmetry is particularly evident in the lower-molecular-weight component.

In order to evaluate the effect of the lower-molecular-weight component, the percentage of the lower-molecular-weight-component ($M < 10^5$) was plotted against the stereoregularity (*Figure 6*). It is clear that the stereoregularity of urea clathrate PAN depends markedly on the fraction of the low-molecular-weight component, while in the aqueous redox slurry system the stereoregularity is low and almost constant over a wide range of molecular weight. In *Figure 6*, the junction between line A and line Z gives a critical point, which is very important in this case. Thus, when the content of low-molecular-weight component ($M < 10^5$) exceeds 31%, a perfectly stereoregular sample (isotacticity of 100%) will be obtained. Although no such conditions have been found experimentally, the use of chain transfer agents in urea clathrate polymerization may be effective in this case.

## CONCLUSIONS

1. The g.p.c.–l.a.l.l.s. measurements were carried out for three different kinds of isotactic PAN. The results were compared with those of atactic PAN prepared in an aqueous redox slurry system.
2. The characteristics of the g.p.c.–l.a.l.l.s. curves of isotactic PAN were extracted and discussed. The asymmetric features, and the significant contribution of the lower-molecular-weight component to high stereoregularity, were clarified.
3. From the analyses of the g.p.c.–l.a.l.l.s. curves and $^{13}C$ n.m.r. results, an experimental prediction for the solid-state synthesis of a perfectly stereoregular PAN sample was presented (~100% isotacticity).

## ACKNOWLEDGEMENT

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