

## Molecular Aggregation in Poly(vinyl Chloride). A Novel Analytical Technique

AHMED H. ABDEL-ALIM and A. E. HAMIELEC, *Department of  
Chemical Engineering, McMaster University, Hamilton, Ontario, Canada*

### Synopsis

A novel experimental technique based on gel permeation chromatography (GPC) has been developed for the measurement of molecular aggregation in poly(vinyl chloride) (PVC). PVC having a range of syndiotacticity was synthesized using polymerization temperatures of 30–70°C. Tacticity and molecular aggregation of these PVC samples were measured by NMR and GPC, respectively. The temperature dependence of molecular aggregation was found to be much greater than that of tacticity. This GPC technique is inherently more sensitive than NMR in the temperature range normally employed for commercial production of PVC. It should find extensive use in the control of PVC reactors and in PVC processing.

### INTRODUCTION

The phenomenon of molecular aggregation in dilute solutions of PVC is well known. The presence of these aggregates leads to difficulties in measurements using dilute PVC solutions. For example, a downward curvature was noticed<sup>1-4</sup> in the plot of  $KC/R_\theta$  versus  $\sin^2(\theta/2)$  for light-scattering measurements. It was suggested that this nonideality was due to microgel particles with a diameter of about 2500 Å and an apparent molecular weight of the order of  $10^8$ . Hengstenberg,<sup>5</sup> using other measuring techniques, concluded that these aggregates are made up of associated molecules with a diameter 140–180 Å and with an apparent molecular weight of 11–25 times that of the single molecule.

These aggregates can be made to disintegrate into single molecules at elevated temperatures.<sup>5-7</sup> Various heat treatments have been employed. Crugnola and Danusso<sup>8</sup> showed that PVC produced at very low temperatures (–40°C) produced aggregates which did not disintegrate with heat treatment at 150°C for 2 hr. On the other hand, PVC produced at 30–50°C and having a much lower syndiotacticity was found to readily disintegrate with the same heat treatment.

In the present study, GPC is used to measure the total mass of these PVC aggregates or crystallites as a function of the temperature of polymerization and of the free-radical initiator used. GPC separates molecules according to their hydrodynamic volume in solution. It is therefore

admirably suited for the separation of these aggregates from the single PVC polymer molecules. In fact, these aggregates give rise to a second apparently high molecular weight peak. The areas under the two peaks may be measured and the weight fraction of aggregates determined. At room temperature, the rate of dissolution of these aggregates is very slow in tetrahydrofuran (THF is our GPC solvent). This permits a GPC measurement at room temperature over several hours, without significant dissolution taking place. Heat treatment of the solution of PVC in THF greatly increases the disintegration and dissolution of the aggregates. At 90°C, disintegration is complete in 10 min. After heat treatment, a GPC analysis at room temperature shows only a peak for single PVC molecules.

If the weight fraction of these aggregates can be related to tacticity or to crystallinity, this new analytical technique could be used to measure these quantities.

In the present study, we have correlated GPC measurements of weight fraction aggregates with syndiotacticity measured by NMR.

## EXPERIMENTAL

### Polymerization Procedure

Bulk polymerization of vinyl chloride was carried out in glass ampoules 10 mm O.D. and 8 mm I.D.; this size gave negligible temperature rise during polymerization. Polymerization temperatures were 30°, 37°, 40°, 45°, 50°, and 70°C controlled to  $\pm 0.1^\circ\text{C}$ . The following initiators were used: AIBN, IPP, dicyclohexyl peroxydicarbonate (A), di(*sec*-butyl) peroxydicarbonate (B), and di(2-ethylhexyl) peroxydicarbonate (C).

### GPC Measurements

A Waters GPC Model 200 was used, under the following conditions: solvent, THF (25°C); polymer concentration, 0.2 wt %; flow rate, 3 ml/min; and nine columns in series of the following specifications: Bioglass, 2500/1500 Å; CPG 10, 2000/1250 Å; CPG 10, 2000/1250 Å; CPG 10, 2000 Å; CPG 10, 700 Å; Styragel, 10<sup>4</sup> Å; Styragel, 800 Å; Styragel, 350/100 Å; and Styragel, 350/100 Å. This column combination gave very good resolution, and correction for axial dispersion was negligible.

### NMR Measurements

Measurements were made by the Ontario Research Foundation using 220-MHz NMR, solutions of PVC in *o*-dichlorobenzene (15 mg/ml), 2% HMDS as internal reference, and at a temperature of 120°C. Areas of peaks were measured by actual count and by the triangular method; both agree within 2% on the average.

## RESULTS AND DISCUSSIONS

### Effect of Polymerization Temperature

It has been known<sup>9</sup> that the amount of aggregates in PVC increases as the polymerization temperature decreases. Our GPC analyses also show this. In Figure 1 are shown GPC responses for six samples prepared at the same conversion and initiator (AIBN) concentration, 33% and 0.27 mole-%, respectively, but at different temperatures. The GPC chromatograms show that the second peak at the high molecular weight end gradually decreases in size with increase in polymerization temperature; at high temperatures, e.g., 70°C, the chromatogram is essentially unimodal where the apparent high molecular weight peak is almost absent. The arrows shown on the baseline in Figure 1 give an indication of the molecular weight.

### Heat Treatment

It was reported<sup>5-7</sup> that heating dilute solutions of PVC dissolves the aggregates. Lyngaae-Jorgensen<sup>10</sup> noticed the disappearance of the second peak when the sample was reinjected in the GPC after heating at 120°C for 3 hr. However, in the present work, it was noticed that heating the solutions at 90°C for 10 min was generally adequate. Figure 2a shows the effect of heating on a sample prepared at 30°C, 93% conversion, 0.27 mole-% AIBN. It is noticed that after heat treatment (90°C for 10 min) the second peak was eliminated and the fraction of intermediate molecular weights was increased. The hatched area in Figure 2a represents the change in the area of the second peak caused by heat treatment and is proportional to the mass of aggregates. It is believed that such heat treatment would not lead to polymer-chain degradation.<sup>5-7</sup>

### Use of Different Initiators

It was of interest to study the effect of different initiators on the heat stability of the aggregates. Beside AIBN, the following initiators were

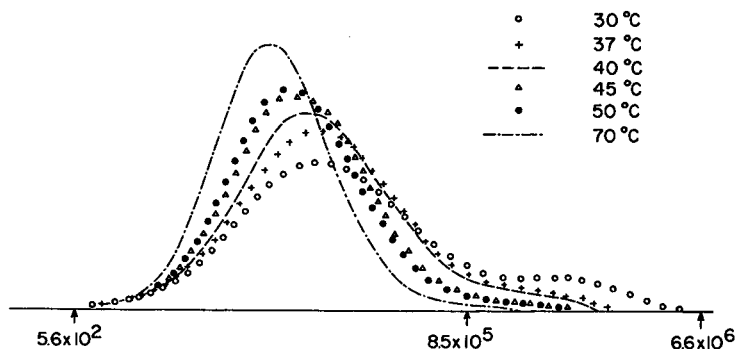


Fig. 1. GPC chromatograms for samples prepared at different temperatures.

used: IPP, dicyclohexyl peroxydicarbonate (A), di(*sec*-butyl)peroxydicarbonate (B), and di(2-ethylhexyl)peroxydicarbonate (C). Polymers were prepared at 93% conversion, 0.27 mole-% initiator, at 30°C. Solutions of the polymers in THF were injected before and after heating at 90°C for 10 min. It was possible to differentiate between two types of behavior. In Figure 2a and b, the results for AIBN and IPP are shown; almost complete elimination of the second peak is observed.

For the same heat treatment, however, the other initiators show different behavior. Figure 3 indicates that the aggregates formed with these initiators are more stable toward heating (elimination of the second peak was not complete). Initiator B gives aggregates having a greater stability than the others. Whether the physical properties of PVC produced by these various initiators are significantly different, as suggested by our measurements, is not known. Further work is required to answer this question.

The arrows in Figures 2 and 3 indicate the apparent molecular weight. These figures show that the aggregates have a molecular weight of the order of one million; a value of  $10^8$  was reported by Kratochvil<sup>11</sup> using light scattering.

### Use of GPC to Measure Tacticity

To date, NMR is the only reliable tool to obtain tacticity data for PVC. In the present work it is shown that such data can also be obtained by using GPC. Samples prepared at different temperatures were analyzed by NMR. Tacticity data were obtained in the form of diads and are shown in Table I. The Arrhenius plot of the tacticity data is shown in Figure 4,

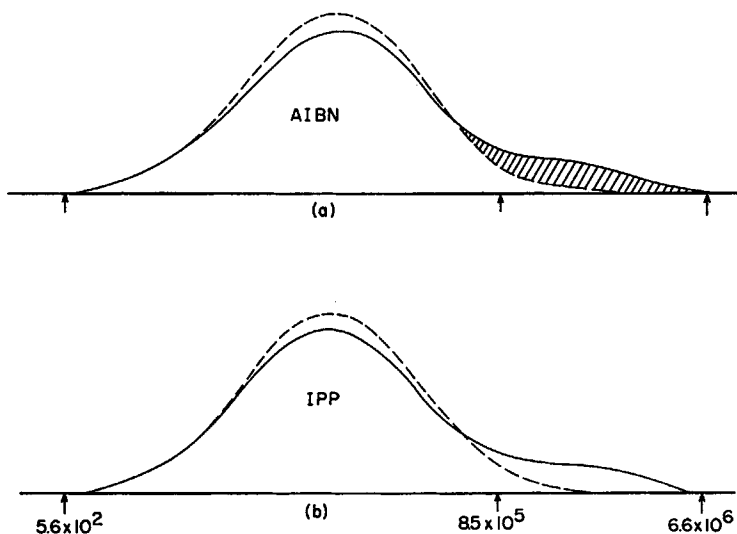


Fig. 2. Effect of heating on GPC chromatogram for samples prepared at 30°C: (a) initiated by AIBN; (b) initiated by IPP; (---) after heating; (—) before heating.

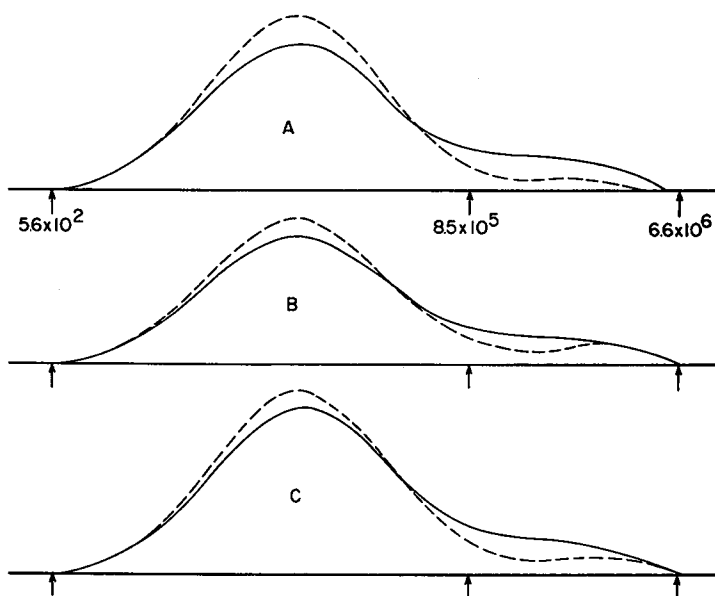


Fig. 3. Effect of heating on GPC chromatograms for samples prepared at 30°C, using different initiators.

TABLE I  
Measured  $S$  and  $A$  at Different Temperatures\*

Temp., °C	$S$ , %	$A$ , %
30	57.6	10.98
37	57.0	3.85
40	56.8	2.51
45	56.5	1.22
50	55.9	—
70	54.4	—

\*  $A$  = Fraction of hatched area (Fig. 2a) to total chromatogram;  $S$  = fraction of syndiotactic placements.

where  $\ln(1 - S)/S$  is plotted versus  $1/T$ ,  $S$  being the syndiotactic fraction:

$$\ln \frac{1 - S}{S} = \frac{\Delta(\Delta S_p)^*}{R} - \frac{\Delta(\Delta H_p)^*}{R} \cdot \frac{1}{T}$$

From this plot, values of the difference in enthalpy and entropy of activation for isotactic and syndiotactic monomer placement were obtained. It was found that

$$-\Delta(\Delta H_p)^* = \Delta H_t^* - \Delta H_s^* = 689 \text{ cal/mole}$$

$$-\Delta(\Delta S_p)^* = \Delta S_t^* - \Delta S_s^* = 1.67 \text{ eu.}$$

These values are compared with literature values in Table II.

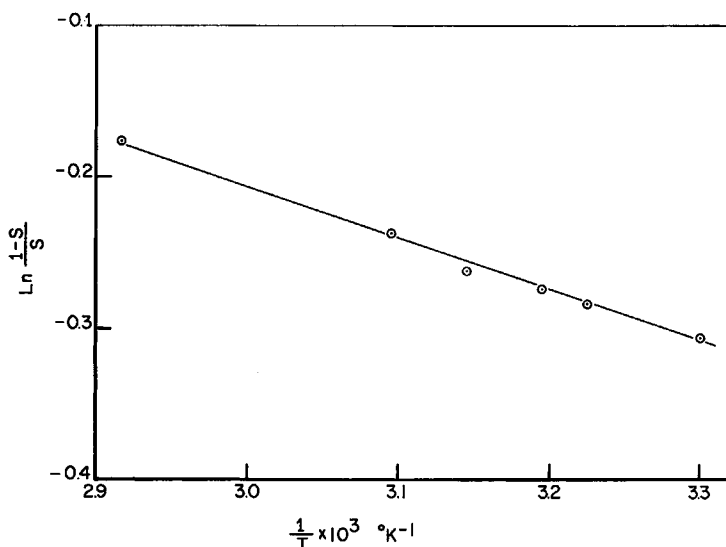


Fig. 4. Arrhenius plot for tacticity data;  $S$  is syndiotactic fraction.

TABLE II  
 $\Delta(\Delta H_p)^*$  and  $\Delta(\Delta S_p)^*$  for PVC

Reference	$-\Delta(\Delta H_p)^*$ , cal/mole	$-\Delta(\Delta S_p)^*$ , eu
Fordham et al. <sup>14</sup>	600	—
Bovey et al. <sup>15</sup>	310	0.6
Cavalli et al. <sup>13</sup>	630	1.5
Present work	689	1.67

It is believed that the aggregates found in PVC are made of relatively stable supermolecular structures linked together by crystalline bonds.<sup>9</sup> It is the syndiotactic placement that is responsible for the formation of these crystallites.<sup>12</sup> As the polymerization temperature decreases, the fraction of syndiotactic placements increases,<sup>13</sup> giving rise to a higher content of crystallites and therefore more aggregates. This explains the appearance of a second peak at the high molecular weight end in GPC chromatograms for PVC samples prepared at relatively low temperatures. It was noticed in Figure 1 that as the polymerization temperature increases, the second peak gradually decreases until it is almost absent at 70°C; this is in agreement with the above discussion.

The hatched area in Figure 2a is proportional to the mass of aggregates. This area should correlate the syndiotacticity of the polymer. If we define the quantity  $A$  as the fraction of the hatched area to the total chromatogram area, then we can make an Arrhenius plot for  $\ln(1 - A)/A$  versus  $1/T$ , similar to that of tacticity data in Figure 4.

The measured values of  $A$  at different temperatures are shown in Table I, and the Arrhenius plot, in Figure 5. The straight line of Figure 5 has a

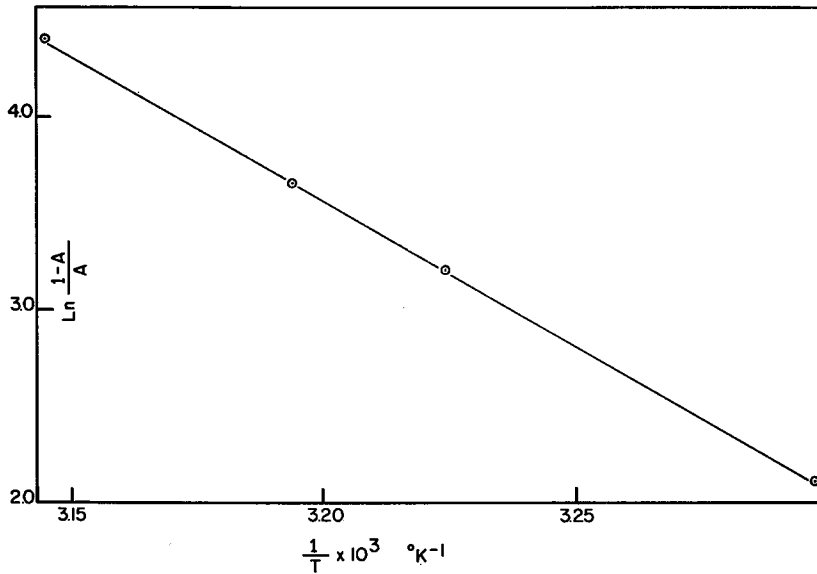


Fig. 5. Arrhenius plot for GPC data;  $A$  is fraction of total chromatogram area due to aggregates.

slope of  $-1.48 \times 10^4$  and an intercept of 50.87, while the slope of the tacticity data line, Figure 4, has a value of  $-3.47 \times 10^3$ . This big difference shows that  $A$  is much more sensitive to temperature than  $S$ . If the linear relations between  $\ln (1 - A)/A$  and  $\ln (1 - S)/S$  with  $1/T$  are represented as follows:

$$\ln \frac{1 - S}{S} = a + \frac{b}{T}$$

$$\ln \frac{1 - A}{A} = c + \frac{d}{T}$$

then these two equations would give

$$\left( \frac{1 - A}{A} \right) = k \left( \frac{1 - S}{S} \right)^h$$

where  $h = d/b$  and  $k = \exp(c - h \cdot a)$ . A plot of this equation on a log-log scale is shown in Figure 6. The slope  $h = 42.7$  and the intercept  $(c - h \cdot a) = 15.2$ . Such a relationship between  $A$  and  $S$  enables one to use the GPC to measure  $A$  and tacticity.

The use of our GPC technique could be extended to polymer processing. This would depend upon the existence of a correlation between physical properties of PVC and weight fraction of aggregates as measured by GPC. Further research is required to develop this application.

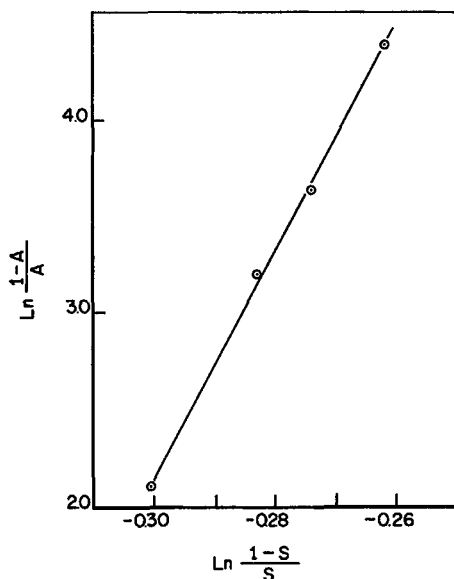


Fig. 6. Relation between NMR and GPC data.

### Nomenclature

- A* fraction of the total GPC chromatogram area due to aggregates, i.e., fraction of hatched area in Figure 2a
- R* gas constant
- S* fraction of syndiotactic placements
- T* absolute temperature, °K
- $\Delta H^*$  activation enthalpy change
- $\Delta S^*$  activation entropy change

### Subscripts

- i* refers to isotactic placement
- S* refers to syndiotactic placement
- p* refers to placement

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