

## STUDY ON LONG CHAIN BRANCHING IN POLYBUTADIENES BY GPC COUPLED WITH CAPILLARY VISCOMETER

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### ABSTRACT

The long chain branching of polybutadienes (PB) was measured with gel permeation chromatography coupled to an automatically recording capillary viscometer. In this method the experimental relation  $[\eta] (V)$  was translated into the calibration curve  $[\eta] (V_R)$  for the monodisperse species.

The curve is combined with the universal calibration so that the molecular weight distribution and an additional parameter, e.g. the average branching factor of this samples may be obtained. Long chain branching molecular weight changes with polymerization conditions.

### INTRODUCTION

Since the discovery of the technique of GPC coupled with capillary viscometer (GPC-Au.V) as a useful tool in determining the molecular weight ( $MW$ ), molecular weight distribution ( $MWD$ ) and branching parameters of branched polymers, it has been widely used in this field of research.

In this work with the aid of theoretical treatment the experimental relation  $[\eta] (V)$  was translated into the calibration curve  $[\eta] (V_R)$ . When this curve was combined with the universal calibration curve, most promising parameters, e.g. branching factor of every count  $g_i$  and average branching factor  $\langle g \rangle$  may be obtained. Ambler et al.<sup>[1]</sup> has discussed branching of polybutadiene. In a previous work<sup>[2]</sup> we also studied the long chain branching of polybutadiene by means of Drott, Kurada's method<sup>[3,4]</sup>, which assumes that the probability of the occurring of branching in the polymers is the same as the polymers with  $MW$ . However our work has pointed out that for polybutadienes there exists a critical  $MW^{[5]}$ , at which long chain branching molecules appear. This critical  $MW$  varies with polymerization conditions.

Since the determination of long chain branching by GPC-Au.V technique is also based on that the dimension of random coil is affected by branching. Therefore, whether there is another factor affecting the coil size should not be considered. Park and Graessley<sup>[6]</sup> did not correct the separation and column dispersion effects when they used this technique to study long chain branching. The results of our work indicate that the experimental relation do not agree with that from the calibration curve.

In this work the calibration curve  $[\eta] (V_R)$  for polybutadiene was obtained according to

the principle reported in our previous work<sup>[7,8]</sup>, and also a series of branching parameters, the effect of the dead volume of the connecting tube and the residual volume of the syphone tube on the branching parameters was discussed, which has not appeared in literature yet. Discussion on experiment to theoretical treatment was made; and satisfactory results were obtained.

### EXPERIMENTAL

The experimental procedure used is the same as that employed in our previously work<sup>[7,8]</sup>. The PB samples were provided by Shengli Chemical Works (Beijing). Their *cis*, *trans* and vinyl structure contents are listed in Table 1.

Table 1 Contents of *cis*, *trans* and vinyl structure in polybutadiene samples

| Sample | <i>Cis</i> (%) | <i>Trans</i> (%) | Vinyl (%) |
|--------|----------------|------------------|-----------|
| PB-1   | 95.94          | 2.12             | 1.94      |
| PB-2   | 94.90          | 3.15             | 1.95      |
| PB-3   | 94.39          | 3.52             | 2.08      |
| PB-4   | 95.20          | 2.29             | 2.51      |

A JNZ-900 GPC coupled with an automatic viscometer was used in this work. In order to minimize concentration effects on the peak position the concentration of the solution of PB in THF was less than 3 mg/ml. The flow rates of solvent through a set of four silica gel columns were 1 ml/min. GPC operation was carried out under room temperature, while the viscometer was kept at 30°C by a thermostat bath, the temperature of which was controlled within  $\pm 0.01^\circ\text{C}$ . The syphon was kept at the same temperature. The solvent from the capillary was carried off through a hole in the bottom of the thermostat. With this fully automatic device the variation in the flow time of pure solvent was 0.01 second, a reproducibility within 0.005%.

### RESULTS AND DISCUSSION

The automatic capillary viscometer as a molecular size detector when coupled with GPC can be used to evaluate the degree of long chain branching of macromolecules.

This coupling technique is a powerful means for the characterization of branched polymers. Satisfactory results have been obtained in our laboratory by using the following method.

The intrinsic viscosity of fraction *i* in GPC is given by Eq. (1):

$$[\eta] = \sqrt{2(\eta_{sp} - \ln \eta_r)} / C \quad (1)$$

where  $\eta_r$  is the relative viscosity, expressed by  $t_i/t_0$ , while  $t_i$  and  $t_0$  are the flow time of the solution and solvent in the viscometer respectively; *C* is the concentration.

Through correction of the dead volume of the connecting tube and the residual volume of

the syphon tube, the concentration of fraction  $i$ ,  $C_i$  (g/ml), can be defined by Eq. (2):

$$C_i = C_0 \frac{V_0}{V_s} W_i \quad (2)$$

where  $C_0$  is the concentration of sample;  $V_0$  is the total amount of injected polymer solution;  $V_s$  is the volume of the syphon tube;  $W_i$  is the weight fraction of the samples within count  $i-1$  and  $i$  in GPC, which may be obtained from GPC chromatogram  $F(V)$ . When the dead volume ( $\Delta V$ ) of the connecting tube is considered, the weight fraction certainly can be defined by Eq. (3):

$$W_{i,\text{corr}} = \int_{V_{i-1}-\Delta V}^{V-\Delta V} F(V)dV / \int_0^\infty F(V)dV \quad (3)$$

Again, if consideration of the residual volume of the syphon tube is given, the concentration  $C_i$  can be defined by Eq. (4).

$$C_{i,\text{corr}} = \sum_{j=1}^i \delta^{i-j} (1-\delta) C_j \quad (4)$$

where  $\delta$  is the ratio of total volume of syphon tube to its residual volume. In practical calculation, only the influence of the first two counts is considered. Then Eq. (4) can be rewritten as follows:

$$C_{i,\text{corr}} = C_0 \frac{V_0}{V_s} (1-\delta) [W_{i,\text{corr}} + \delta W_{i-1,\text{corr}} + \delta^2 W_{i-2,\text{corr}}] \quad (5)$$

Substitute  $C_{i,\text{corr}}$  into Eq. (1), accurate value of intrinsic viscosity can be obtained by using the method reported in our previously work<sup>[6]</sup>, the elution volume  $V_{\eta_i}$ , which corresponds to  $[\eta_i]$  in GPC, may be calculated. Thus the experimental relation  $[\eta](V)$  can be written as

$$\ln[\eta] = \bar{A}_\eta - \bar{B}_\eta V_{\eta_i} \quad (6)$$

where  $\bar{A}_\eta$  and  $\bar{B}_\eta$  are the intercept and slope respectively of the uncorrected experimental relation. With the aid of theoretical treatment the retention volume  $V_R$  derived is given by

$$V_R = V_C + \xi^2 (V_{\eta_i} - V_C) \quad (7)$$

where  $\xi^2$  is a parameter of dispersion defined as

$$\xi^2 = (\delta_T^2 - \sigma_0^2) / \sigma_T^2 \quad (8)$$

in which  $\sigma_T^2$  and  $\sigma_0^2$  are the variances of the experimental chromatogram  $F(V)$  and of the spreading factor respectively;  $V_C$  is the point of intersection of experimental relation  $[\eta](V)$  with calibration function  $[\eta](V_R)$ , and is given by

$$V_C = \bar{V} - \frac{1}{2} \bar{B}_\eta \sigma_T^2 \quad (9)$$

where  $\bar{V}$  is the average count of GPC chromatogram  $F(V)$ , with  $V_C$  and  $\xi^2$  the retention volume  $V_R$  may be obtained by Eq. (7). Then the corrected calibration relation is

$$\ln[\eta] = A_\eta - B_\eta V_R \quad (10)$$

From Fig. 1, it may be seen that the difference between  $[\eta](V)$  and  $[\eta](V_R)$  is quite obvious. The difference between the branching parameters obtained from  $[\eta](V)$  and  $[\eta](V_R)$  amounts to 2–3%. Therefore, it is proper that  $[\eta](V)$  should be translated into  $[\eta](V_R)$  before

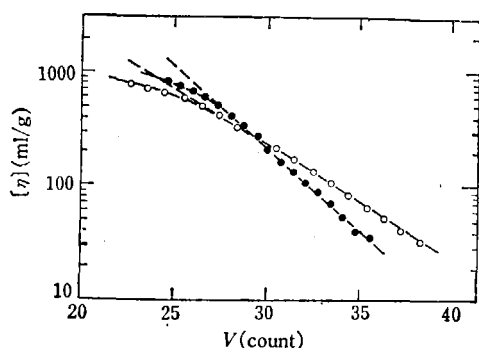


Fig. 1 The experimental relation  $[\eta] (V)$  and calibration curve  $[\eta] (V_R)$  of sample PB-4

discussion of long chain branching. The intrinsic viscosity of the linear molecules  $[\eta_{Li}]$  corresponding to the whole of each count can be obtained from the linear portion and its extension of  $[\eta] [V_R]$ .

The intrinsic viscosity of the branched molecules  $[\eta_{bi}]$  is obtained experimentally from GPC-Au.V technique. The factor of branching then may be obtained from  $[\eta_{bi}]$ ,  $[\eta_{Li}]$ .  $M^*$  represents the critical molecular weight, as mentioned above, at which branching starts to form. When  $M \leq M^*$ ,  $[\eta_{Li}] = [\eta_{bi}]$ . Use the principles of universal calibration relation<sup>[9]</sup>, a general relationship between  $[\eta_{Li}]$  and  $[\eta_{bi}]$  can be expressed as

$$[\eta_L] M_L = [\eta_b] M_b \quad (11)$$

The ratio of MW for branched and linear molecules of the same hydrodynamic volume is expressed by  $G_v$

$$\left( \frac{M_L}{M_b} \right)_v = \left( \frac{[\eta_b]}{[\eta_L]} \right)_v = G_v \quad (12)$$

However the value  $G_v$  thus obtained is different from the ratio when the molecular weights are the same.

From Eq. (12) expression  $M_b = \frac{M_L}{G_v}$  can be obtained. When this relation is substituted to Mark-Houwink equation resulting in Eq. (13):

$$([\eta_L])_{M_b} = K M_b^\alpha = K \left( \frac{M_L}{G_v} \right)_v^\alpha = \frac{(K M_L^\alpha)_v}{G_v^\alpha} = \frac{([\eta_L])_v}{G_v^\alpha} \quad (13)$$

Naturally, when number of fraction is  $V$ , MW is  $M_b$ . Hence

$$([\eta_b])_{M_b} = ([\eta_b])_v \quad (14)$$

With Eqs. (13) and (14), the following equation is resulted.

$$G = \left( \frac{[\eta_b]}{[\eta_L]} \right)_{M_b} = \left( \frac{[\eta_b]}{[\eta_L]} \right)_v G_v^\alpha$$

or finally,

$$G = G_v^{1+\alpha} \quad (15)$$

When this ratio is related to the ratio of squares of gyration

$$g = \left[ \frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_L} \right]_M \quad (16)$$

The relation between parameters  $G$  and  $g$  may be got

$$G = G(g) = g^\varepsilon$$

The value of the exponent  $\varepsilon$  is dependent on the branching structure. For random branching  $\varepsilon$  equals 0.5<sup>[10]</sup>. Thus

$$g = G^2 = G_V^{2(1+\alpha)} \quad (17)$$

From Eq. (17) the branching factor  $g_i$  of every count in GPC can be obtained, while the average  $MW$  and  $MWD$  are calculated from the following relation, which is obtained from Eq. (12)

$$M_b = \frac{M_L}{G_V} = \left( \frac{[\eta_L]}{K} \right)^{\frac{1}{\alpha}} / G_V \quad (18)$$

Number average and weight average molecular weights may be obtained by Eqs. (19) and (20) respectively.

The Mark-Houwink constants for polybutadiene used in the present work were  $k=0.0251$ ,  $\alpha=0.725$ .

$$\langle M \rangle_w = \sum_i M_{bi} H_i / \sum_i H_i \quad (19)$$

$$\langle M \rangle_n = \sum_i H_i / \sum_i H_i / M_{bi} \quad (20)$$

$$\langle [\eta] \rangle = \sum_i [\eta_i] H_i / \sum_i H_i \quad (21)$$

With these relationship, the average branching parameter can be defined as the following equation

$$\langle G_V \rangle = \frac{\langle [\eta_b] \rangle}{\langle [\eta_l] \rangle} = \frac{\sum_i [\eta_{bi}] H_i}{\sum_i [\eta_{li}] H_i} \quad (22)$$

Combining this relation Eq. (22) with Eq. (17) the average branching factor  $\langle g \rangle$  can be obtained. The average intrinsic viscosities obtained through calculation using Eq. (21) are compared with those determined in the normal way with an Ubbelohde viscometer. Both data are given in Table 2. The variance is within 1–3% for all the samples.

Table 2 Comparison of intrinsic viscosities obtained by two different methods

| Sample | [ $\eta$ ] (ml/g) |           |
|--------|-------------------|-----------|
|        | Ubbelohde         | GPC-Au. V |
| PB-1   | 214               | 206       |
| PB-2   | 210               | 212       |
| PB-3   | 202               | 201       |
| PB-4   | 246               | 243       |

From the list, it may be seen that the two sets of  $[\eta]$  are in good agreement, which illustrates

that the method is reliable and satisfies the accuracy requirement and that samples are not degraded during GPC determination. The various results from GPC-Au.V determination of sample PB-4 as well as those calculated with Eqs. (1), (10), (17) and (18) are shown in Table 3.

Table 3 The retention volume, intrinsic viscosity, branching factor and  $MW$  of sample PB-4

| Count | $V_{\eta_i}$ | $V_R$ | $[\eta_i]$ | $g_i$ | $M_{bi} \cdot 10^{-4}$ |
|-------|--------------|-------|------------|-------|------------------------|
| 22—23 | 22.71        | 24.86 | 780        | 0.243 | 417                    |
| 23—24 | 23.59        | 25.46 | 730        | 0.381 | 280                    |
| 24—25 | 24.54        | 26.10 | 652        | 0.528 | 191                    |
| 25—26 | 25.52        | 26.76 | 590        | 0.787 | 126                    |
| 26—27 | 26.51        | 27.44 | 500        | 0.930 | 88.0                   |
| 27—28 | 27.51        | 28.11 | 400        | 0.939 | 65.3                   |
| 28—29 | 28.50        | 28.78 | 315        | 0.974 | 47.8                   |
| 29—30 | 29.50        | 29.45 | 261        | 0.985 | 35.1                   |
| 30—31 | 30.49        | 30.13 | 212        | 1.030 | 25.6                   |
| 31—32 | 31.49        | 30.81 | 171        | 1.045 | 18.8                   |
| 32—33 | 32.48        | 31.48 | 136        | 1.006 | 14.0                   |
| 33—34 | 33.47        | 32.15 | 112        | 1.025 | 10.0                   |
| 34—35 | 34.46        | 32.82 | 90.4       | 1.020 | 9.3                    |
| 35—36 | 35.45        | 33.49 | 72.2       | 1.023 | 5.5                    |
| 36—37 | 36.43        | 34.15 | 56.8       | 1.00  | 4.2                    |
| 37—38 | 37.83        | 34.83 | 44.2       | 0.992 | 3.2                    |
| 38—39 | 38.42        | 35.50 | 35.0       | 1.00  | 2.4                    |
| 39—40 | 39.31        | 36.10 | 16.4       | —     | 1.7                    |

In order to understand the influence of the dead volume of the connecting tube ( $\Delta V$ ) and the residual volume fraction of syphon tube  $\delta$ , calculation of the experimental data under different combination of  $\Delta V$  and  $\delta$  were carried out. The results are listed in Table 4.

Table 4 The influence of  $\Delta V$  and  $\delta$  on the calculated items

| Calculated items                     | $\Delta V$ ( $\delta=0.05$ ) |       |       | $\delta$ ( $\Delta V=0.62$ ) |       |       |
|--------------------------------------|------------------------------|-------|-------|------------------------------|-------|-------|
|                                      | 0                            | 0.62  | 1     | 0                            | 0.05  | 0.1   |
| $\langle [\eta] \rangle$ (ml/g)      | 187.6                        | 187.6 | 187.6 | 187.6                        | 187.6 | 187.6 |
| $\langle g \rangle$                  | 0.832                        | 0.825 | 0.862 | 0.873                        | 0.825 | 0.837 |
| $\langle M \rangle_w \times 10^{-4}$ | 28.87                        | 30.93 | 31.09 | 28.86                        | 30.93 | 31.09 |
| $\langle M \rangle_n \times 10^{-4}$ | 12.15                        | 11.28 | 11.56 | 11.77                        | 11.28 | 11.38 |

It can be seen from the table that the variation of  $\Delta V$  and  $\delta$  had no influence on the calculated intrinsic viscosities, but it affects the calculated value of  $\langle g \rangle$ ,  $\langle M \rangle_w$  and  $\langle M \rangle_n$ , which is not negligible. Therefore, accurate determination of  $\Delta V$  and  $\delta$  is of practical importance to the calculation of branching factor.  $\Delta V$  and  $\delta$  are constants, being 0.62 count and 0.05 respectively in our case. The relation between  $M_{bi}$  and  $g_i$  from Table 3 is shown in Fig. 2.

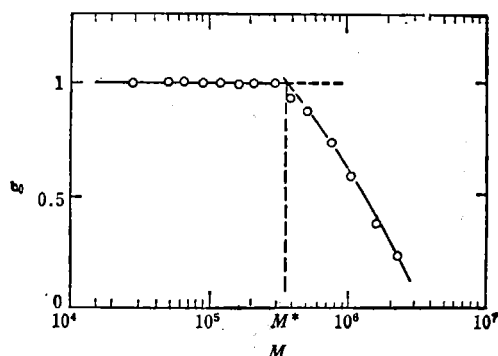


Fig. 2 Relation between  $MW$  and branching factor (PB-4)

The figure shows that the  $MW$  at the point of  $g_i$  which is next to but smaller than 1 is the critical molecular weight  $M^*$ . Long chain branching exists in molecules with  $MW > M^*$ , but not in those with  $MW < M^*$ . The calculated values of  $\langle M \rangle_w$ ,  $\langle M \rangle_n$ ,  $M^*$  and  $\langle g \rangle$  of all samples are listed in Table 5.

Table 5 Average molecular weights and branching parameters

| Sample | $\langle M \rangle_w \cdot 10^{-4}$ | $\langle M \rangle_n \cdot 10^{-4}$ | $M^* \cdot 10^{-4}$ | $\langle g \rangle$ |
|--------|-------------------------------------|-------------------------------------|---------------------|---------------------|
| PB-1   | 31.35                               | 15.30                               | 20.5                | 0.688               |
| PB-2   | 31.22                               | 15.18                               | 29.9                | 0.735               |
| PB-3   | 21.53                               | 13.67                               | 28.9                | 0.825               |
| PB-4   | 29.05                               | 13.93                               | 35.6                | 0.965               |

Then the relation of number of branching  $n_w$  with branching factor can be expressed by Zimm-Stockmayer<sup>[11]</sup> equation of polydisperse and three functional branching, if the long chain branching in every GPC fraction are considered as three functional and polydisperse

$$\langle g \rangle = \frac{6}{\bar{n}_w} \left[ \left( \frac{2 + \bar{n}_w}{4\bar{n}_w} \right)^{\frac{1}{2}} \ln \frac{(2 + \bar{n}_w)^{\frac{1}{2}} + \bar{n}_w^{\frac{1}{2}}}{(2 + \bar{n}_w)^{\frac{1}{2}} - \bar{n}_w^{\frac{1}{2}}} - 1 \right] \quad (23)$$

where  $\bar{n}_w$  is weight average number of branching point in one molecule. Hence the degree of branching  $\bar{\lambda}$  is defined as

$$\bar{\lambda} = \frac{\bar{n}_w}{\langle M \rangle_w} \quad (24)$$

The branching parameters of the polybutadienes studied are given in Table 6.

Table 6 Branching parameters of polybutadienes

| Sample | $\langle g \rangle$ | $\overline{n}_w$ | $\overline{\lambda} \times 10^5$ |
|--------|---------------------|------------------|----------------------------------|
| PB-1   | 0.688               | 2.64             | 0.84                             |
| PB-2   | 0.735               | 2.05             | 0.66                             |
| PB-3   | 0.825               | 1.15             | 0.53                             |
| PB-4   | 0.965               | 0.18             | 0.062                            |

Data in Tables 5 and 6 show that two PB samples characterized have various degrees of long chain branching but the number of branching points was very little. However the influence on the hydrodynamic volume was remarkable. Another advantage of this method is that the distribution of long chain branching could be obtained by only one run of experiment, as shown in Fig. 3.

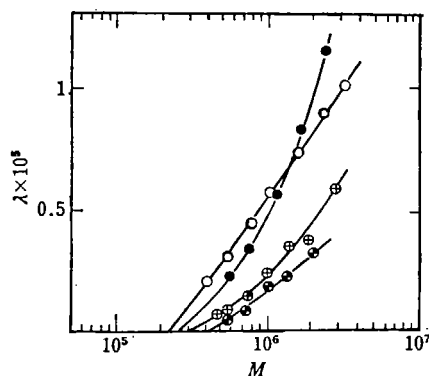


Fig. 3 Distribution of long chain branching of PB

Fig. 3 illustrates that the distributions of long chain branching of the four different samples are different; for the samples the degree of branching increases with the increase in molecular weight; the critical molecular weight of these samples are all greater than  $2 \times 10^5$ , but different among each other in actual values.

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