

DETERMINATION OF BRANCHING DISTRIBUTION IN HIGH *cis*-1,4-POLYBUTADIENE BY GPC AND AUTOMATIC VISCOMETRY*

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ABSTRACT

Based on the methods reported by Ambler and Kraus, a method has been developed for the determination of long-chain branching distribution in polymers by the combined use of GPC and intrinsic viscosity data of polymer fractions. In this method, g_i , λ_i , G_i , m_i , the weight percentage of polymer that is branched, etc. can be used simultaneously to characterize the distribution, degree and content of branching in polymers. Some relations between molecular weight polydispersity and branching polydispersity in Nickel-based high *cis*-1,4-polybutadiene samples are discussed. It was found that the number of long branches λ per unit molecular weight is a function of molecular weight and all of the samples are highly branched at a molecular weight of about 10^6 .

INTRODUCTION

Some methods can be used for determining long-chain branching in polymers, such as the methods of light scattering, intrinsic viscosity, sedimentation-velocity and gel permeation chromatography (GPC) etc. But the method by means of GPC and viscometry is widely used^[1-13]. Examples are the studies of branching by Drott and Mendelson^[1-3] on low-density polyethylene (LDPE), by Ambler et al.^[6] on polystyrene (PS), styrene-butadiene copolymer (SBR) and polybutadiene (PB), by Kraus and Stacy^[7] on PB and SBR, and by Constantin^[13] on LDPE.

Whether the number of long branches λ per unit molecular weight is a constant is a matter in dispute. Drott et al.^[3,6] made an assumption that λ is a constant independent of molecular weight within any one sample. This assumption is expressed by eq. (1),

$$\lambda = n/M \approx \text{constant} \quad (1)$$

where λ is the long-chain branching frequency, n is the number of branches per molecule, and M is molecular weight. The data reported on λ were obtained generally under the condition of weight-average molecular weight less than 10^6 . However, some data reported on λ for fractions from LDPE^[13] and Lithium-based PB^[7] samples showed that λ is not a constant, but varies appreciably with molecular weight, and the variation is particularly remarkable at high molecular weights.

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A vast amount of data on λ for fractions obtained from some polymers, such as LDPE, randomly branched PS, star-branched SBR, and Lithium-based PB, etc. have been reported. The branching distributions in Nickel-based high *cis*-1,4-polybutadiene has not been found yet. In order to find the relation between long-chain branching distribution and molecular weight distribution, in the present work an experimental technique of GPC combined with viscometry is used. Since high *cis*-1,4-PB has a broad molecular weight distribution, it is necessary to know whether there is a tendency for λ to approach a steady value at high molecular weight.

METHOD

The method used in the present investigation is based on the methods reported by Ambler^[6] and Kraus^[7]. The results of the molecular weight distribution and the long-chain branching distribution in polymer can be obtained simultaneously with this method which regards λ as a function of molecular weight M but not a constant. The long-chain branching distribution in polymer can be characterized simultaneously by some parameters such as the branching function g , the branching frequency λ , the branching factor G and the number of branch points per molecule m . The long-chain branching frequency of the i th fraction λ_i can be calculated in combination of the intrinsic viscosity of the i th fraction and GPC data. The computation is simple and straightforward. The results of g_i and λ_i calculated is unique solution, and can be solved directly without iteration. Therefore, the method is more advantageous for the study of the relation between long-chain branching distribution and molecular weight distribution in polymer.

Following basic assumptions are made for the method: (a) the concept of hydrodynamic volume and the universal calibration technique are valid; (b) the *cis*-1,4-PB is a polydisperse polymer having randomly distributed trifunctional branch points as indicated by ¹³C-NMR^[14]; (c) each fraction separated by GPC for viscosity measurement is monodisperse in molecular weight^[15]; (d) short-chain branching is neglected since its effects on reducing viscosities are less than long-chain branching^[16].

Thus the following equations were obtained:

$$[\eta]_i = [(\eta_{sp}/C)_i + (\ln \eta_r/C)_i] / 2 - kC_i \quad (2)$$

$$[\eta] = \sum_i W_i [\eta]_i \quad (3)$$

$$g_i = K^{-2} J_i^{-2\alpha} [\eta]_i^{2(1+\alpha)} \quad (4)$$

$$\bar{M}_w = K^{-\frac{1}{1+\alpha}} \sum_i W_i J_i^{\frac{1}{1+\alpha}} g_i^{-\frac{1}{2(1+\alpha)}} \quad (5)$$

$$\bar{M}_n = K^{-\frac{1}{1+\alpha}} / \sum_i W_i J_i^{\frac{1}{1+\alpha}} g_i^{\frac{1}{2(1+\alpha)}} \quad (6)$$

$$\bar{M}_z = K^{-\frac{1}{1+\alpha}} \sum_i W_i J_i^{\frac{2}{1+\alpha}} g_i^{-\frac{1}{1+\alpha}} / \sum_i W_i J_i^{\frac{1}{1+\alpha}} g_i^{-\frac{1}{2(1+\alpha)}} \quad (7)$$

$$M_i = J_i / [\eta]_i \quad (8)$$

$$\lambda_i = \left\{ \left(\frac{8M_i g_i^{-2}}{9\pi} + \frac{M_i}{7} \right) - \left[\left(\frac{8M_i g_i^{-2}}{9\pi} + \frac{M_i}{7} \right)^2 - 4 \left(\frac{16M_i^2}{81\pi^2} \right) (g_i^4 - 1) \right]^{1/2} \right\} / \frac{32M_i^2}{81\pi^2} \quad (9)$$

$$G_i = [\eta]_i / [\eta]_{i_0} \quad \text{With } [\eta]_{i_0} = KM^\alpha \quad (10)$$

where K is the Mark-Houwink coefficient, α is the Mark-Houwink exponent, $[\eta]$ is the intrinsic viscosity and W_i is the weight fraction of the i th fraction. The universal calibration parameter J has been defined as the product of the intrinsic viscosity and molecular weight.

The branching function is a function of the number type of long-chain branch points in a molecule, and it has been defined as the ratio of the mean-square radius of gyration of the branched molecules to that of linear one with equal M :

$$g = \langle r_{br}^2 \rangle / \langle r_L^2 \rangle \quad (11)$$

The relation between g and the number of branched points has been derived by Zimm and Stockmayer^[17].

The branching factor G has been defined as the ratio of the intrinsic viscosity of the branched polymer to that of linear polymer with same molecular weight (see eq. (10)). Theoretically the branching factor is related to the branching function, and may be represented by

$$G \approx g^{\frac{1}{2}} \quad (12)$$

for most cases^[18, 19].

Eq. (2) is a new "one point" formula for the calculation of intrinsic viscosity, where k is a correction factor and C_i is the concentration of the i th fraction. This equation is rather simple and convenient to use, the calculated results with eq. (2) is nearly the same as those calculated with the equation given by Maron^[20]

$$[\eta] = (\eta_{sp} + \gamma \ln \eta_r) / (1 + \gamma) C \quad (13)$$

as shown in Table 2.

The other parameters, such as the lowest molecular weight of branched polymer that can be measured, M^* ; the number of branch points in a branched molecule, m ; the weight percentage of polymer that is branched, can be calculated from the same equations given by Ambler^[16].

An electronic computer program for solving above equations with ALGOL-60 language is developed.

Table 1

Sample	[η] (dl / g)	
	From $\sum_i W_i [\eta]_i$	Measured
A	2.48	2.48
B	2.91	2.91
C	2.73	2.67

EXPERIMENTAL

Separations were performed with a modified Model SN-01A gel permeation chromatograph with a refractive index detector which was made in China. The operating temperature was 25°C. A flow rate of 1 cc/min and injection volumes of 1.9 cc were used. In all experiments, tetrahydrofuran (THF) was used as a solvent. To measure the flow time for

Table 2 (Data on fractionated sample A)

Fraction No.	t_i ($t_0=165.403$)	$(\eta_r)_i$	$(\eta_{sp})_i$	W_i	C_i	$[\eta]_i$ (dl / g)	
						From eq. (2) $k = 0.341$	From eq. (13) $r = 2.14$
27	165.407	1.000024	0.000024				
28	165.417	1.000085	0.000085				
29	166.073	1.00405	0.00405	0.00570	0.000715	5.66	5.66
30	167.626	1.0134	0.0134	0.0143	0.00179	7.48	7.47
31	168.619	1.0194	0.0194	0.0221	0.00277	6.97	6.96
32	168.888	1.0211	0.0211	0.0264	0.00331	6.35	6.34
33	169.078	1.0222	0.0222	0.0313	0.00393	5.62	5.61
34	169.174	1.0228	0.0228	0.0363	0.00456	4.98	4.97
35	169.148	1.0226	0.0226	0.0406	0.00509	4.41	4.41
36	169.092	1.0223	0.0223	0.0449	0.00563	3.94	3.93
37	168.873	1.0210	0.0210	0.0484	0.00607	3.44	3.43
38	168.781	1.0204	0.0204	0.0527	0.00661	3.07	3.07
39	168.583	1.0192	0.0192	0.0563	0.00706	2.71	2.70
40	168.432	1.0183	0.0183	0.0605	0.00759	2.40	2.40
41	168.204	1.0169	0.0169	0.0634	0.00795	2.11	2.11
42	167.923	1.0152	0.0152	0.0655	0.00822	1.84	1.84
43	167.634	1.0135	0.0135	0.0670	0.00840	1.60	1.60
44	167.210	1.0109	0.0109	0.0655	0.00822	1.32	1.32
45	166.920	1.0092	0.0092	0.0620	0.00777	1.18	1.18
46	166.595	1.0069	0.0069	0.0556	0.00697	0.986	0.988
47	166.246	1.0051	0.0051	0.0470	0.00590	0.862	0.864
48	165.957	1.0033	0.0033	0.0378	0.00474	0.695	0.696
49	165.771	1.0022	0.0022	0.0299	0.00375	0.585	0.586
50	165.627	1.0014	0.0014	0.0228	0.00286	0.489	0.490
51	165.556	1.0009	0.0009	0.0171	0.00214	0.419	0.420
52	165.485	1.0005	0.0005	0.0121	0.00152	0.329	0.329
53	165.399	0.9999	0.0001	0.00855	0.00107		
54-60				0.00641			
$\sum_i W_i = 1.00$					$\sum_i W_i [\eta]_i$	2.48	2.48
					$[\eta]_{\text{measured}} = 2.48$		

each fraction, a high accuracy automatic capillary viscometer with optical fibres as cold light source has been constructed. The viscometer has a capillary of 0.35 mm in diameter and a length of 170 mm. The flow time of pure THF at 25°C is about 170 sec. The fluctuations of flow time of the solvent in this capillary viscometer are less than $\pm 4 \times 10^{-3}$ sec. The temperature of the viscometer was controlled at 25°C, and the bath temperature was maintained constant within $\pm 5 \times 10^{-4}$ °C. A detailed description of this instrument is to be presented separately.

Three commercial Nickel-based high *cis*-1,4-PB samples were used in this study. Sample A has Mooney viscosity value of 45, and sample B 42.5. Both of them were produced in China. Sample C has a Mooney viscosity value of 45, and was produced in Japan.

The measured flow times of fractions were used to calculate the intrinsic viscosities by eq. (2). These intrinsic viscosity data, together with the normalized weight fractions W_i , were then used to calculate the intrinsic viscosity of the original whole polymer by eq. (3). The results listed in Table 1 are in reasonable agreement with the values actually measured on the whole polymer. Taking an example by sample A, the full results were listed in Table 2.

RESULTS AND DISCUSSIONS

Calculation of the branching content in polymer

The presence of branching in a polymer has been most readily determined from a reduction in the intrinsic viscosity. Although fractions of a linear polymer will fit the normal plot in the familiar Mark-Houwink straight-line relationship, fractions of a branched sample of the same polymer will coincide this relationship only at low molecular weights, and will fall below the normal linear plot at high molecular weight^[21]. We use the reduction in intrinsic viscosity as our criterion for indicating branching in polymers. The weight percentage of polymer that is branched and the lowest molecular weight of branched polymer measured (M^*) can be obtained from the relation between GPC results and Mark-Houwink plot for branched polymer. The results obtained are summarized in Table 3.

Table 3

Sample	$M^* \times 10^{-5}$	(wt. %) Branched
A	1.71	32.3
B	8.26	12.5
C	11.9	12.8

Variation of g , λ , m with molecular weight

With the described device and the reported equations, some curves of the variation of long-chain branching parameters with molecular weight were obtained experimentally.

Figure 1 shows the curves of the variation of g with molecular weight for the three samples.

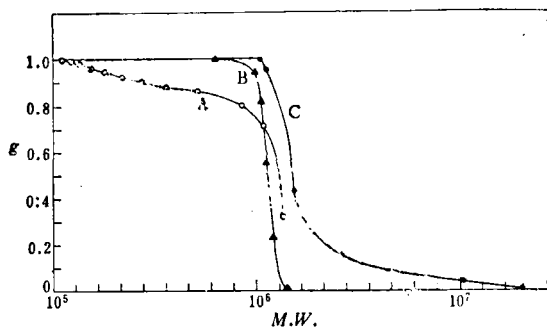


Fig. 1 Variation of long-chain branching function with molecular weight
Sample A ○; Sample B ▲; Sample C ●.

Figure 2 shows the curves of the variation of λ with molecular weight for the three samples.

Figure 3 shows the curves of the variation of m with molecular weight for the three samples.

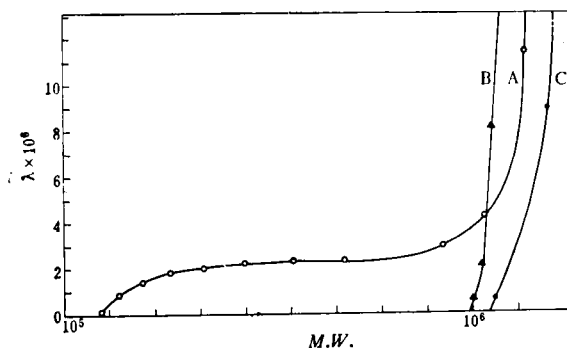


Fig. 2 Variation of long-chain branching frequency with molecular weight
Sample A ○; Sample B ▲; Sample C ●.

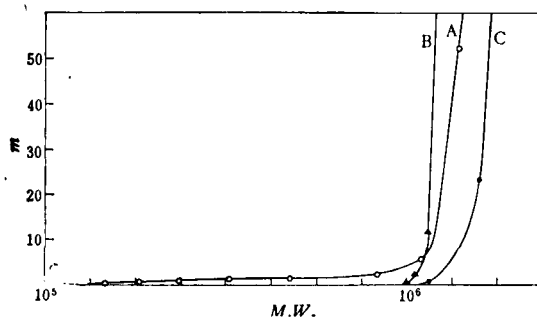


Fig. 3 Variation of the number of branch points in a branched molecule with molecular weight
Sample A ○; Sample B ▲; Sample C ●.

From the distribution curves the following regularities are found: (a) In the case of molecular weight less than 10^6 , branching is present for sample A to a small extent, no branching is observed on the whole for samples B and C. (b) At a molecular weight of about 10^6 , variations in g , λ , m among the three samples are appreciable and they are highly branched. (c) In the case of molecular weight more than 10^6 , there is a decrease in the dependence of degree of braching on molecular weight.

Distribution of G with molecular weight

The degree of branching in fractions of polymer can be indicated by the values of G_i . It can be determined experimentally and requires no prior knowledge of the functional relation between branching frequency and molecular weight (see eq. (10)). Figure 4 shows the curves of the variation of G with molecular weight for these three samples. As can be seen from the figure, the G distribution curves show the same general trend as the g , λ and m distribution curves.

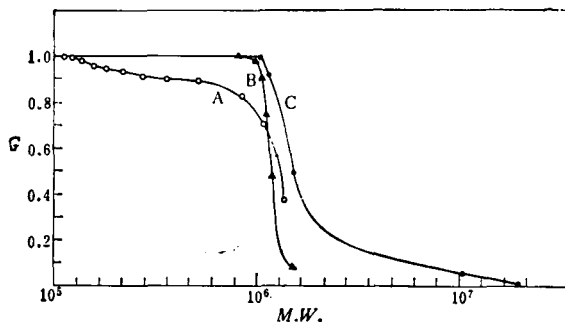


Fig. 4 Variation of long-chain branching factor with molecular weight
Sample A ○; Sample B ▲; Sample C ●.

CONCLUSION

It is concluded that the determination of branching is possible by using of GPC-intrinsic viscosities of polymer fractions. This method provides more information with respect to both molecular weight distribution and branching distribution, and should enable more comprehensive and precise characterization of long-chain branching in polymers. The measured values of λ from fractions of three high *cis*-1,4-PB samples indicate that the values of λ can vary with molecular weight, and have no tendency to approach a steady value at high molecular weights. Thus, the assumption of a constant value of λ in unfractionated samples is not generally valid. The values of g , λ , G , m for GPC fractions of the three high *cis*-1,4-PB samples show that all of them are highly branched at a molecular weight of about 10^6 .

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