

# Functionality Distribution of Hydroxyl-Terminated Polybutadienes Using Gel Permeation Chromatography. I. The Method and Calibration Procedure

J. N. ANDERSON, S. K. BACZEK, H. E. ADAMS, and L. E. VESCELIUS,  
*Central Research Laboratories, The Firestone Tire and Rubber Company,  
Akron, Ohio 44317*

## Synopsis

A method for simultaneously determining the molecular weight averages, molecular weight distribution, hydroxyl equivalent weight, functionality averages, and functionality distribution of hydroxyl-terminated polybutadienes using GPC has been developed. The method is based on the preparation of a UV absorbing derivative of the hydroxyl group and GPC analysis using dual differential refractive index and UV detectors. In order to determine the hydroxyl equivalent weight, quantitative derivatization of the hydroxyl group is required. If the equivalent weight can be determined by an independent method, the derivatization reaction can be less than quantitative if sufficient UV absorptivity can be obtained. The procedure used for calibrating the GPC columns and UV detector are presented. Equations for calculating number- and weight-average functionalities from GPC data were also developed. The number-average functionality is independent of the functionality distribution, but the weight-average functionality is dependent upon the distribution of functionality. The ratio of the weight-average to number-average functionality is indicative of how the functionality is skewed as a function of molecular weight.

## INTRODUCTION

In recent years, considerable attention has been focused on the structural characterization of functionally terminated hydrocarbon prepolymers used in propellant binders and other applications.<sup>1</sup>

The molecular weight averages and molecular weight distributions of hydroxyl- and carboxyl-terminated polybutadienes have been determined<sup>2</sup> using gel permeation chromatography (GPC). The functionality distribution of these prepolymers has also been previously studied using column fractionation<sup>3,4</sup> and a procedure<sup>5</sup> combining GPC and column fractionation of the polymer by stepwise elution from silica gel. The carboxyl or hydroxyl equivalent weights of the fractions were determined using infrared or near-infrared spectroscopy. The fractionation procedure is quite laborious, and multiple peaks were observed in the elution profile making it difficult to decide how the fractions were to be grouped for subsequent analysis.

Previously, a technique for determining the distribution of unsaturation in copolymers containing a small number of double bonds as a function of GPC elution volume was developed.<sup>6</sup> The technique utilized a GPC equipped with UV photometer and differential refractometer detectors to determine the ratio of the weight fraction of olefinic bonds to the weight fraction of

polymer by GPC analysis of the polymer after derivatization of the double bonds with 2,4-dinitrobenzenesulfonyl chloride. It was suggested that the technique should be applicable for the determination of the distribution of other functional groups with the choice of suitable reagents for derivatization.

The purpose of this investigation was to attempt to extend our previous study to simultaneously determine the molecular weight averages, molecular weight distribution, hydroxyl equivalent weight, functionality averages, and functionality distribution of hydroxyl-terminated polybutadienes using a GPC technique.

## EXPERIMENTAL

A Waters Associates Model 200 gel permeation chromatograph equipped with an automatic sample injector system and a auxiliary du Pont Model 410 photometer operating at 254 nm was used for this investigation. The GPC solvent was THF. A set of four columns with permeabilities of  $10^4$  Å, 2000–5000 Å, 700–2000 Å, and 100–350 Å was used and operated at room temperature with a solvent flow rate of 1 ml/min. The GPC was connected to a minicomputer system (Lockheed Mac 16 computer with an 8 K core).

The GPC eluent was first directed through the UV detector and then through the refractive index detector. Because of the volume of the tubing between the two detectors, it was necessary to correct the UV response data by shifting the data to a higher elution volume or GPC count. The exact shift of the UV data was determined by injecting a polystyrene standard into the GPC. The areas of the differential refractive index and UV peaks were normalized and plotted using a CALCOMP plotter. The UV data were shifted to progressively higher elution volumes until the two plots were identical. It was found that a shift of 0.43 counts to a higher elution volume was required. Our data acquisition system allows one to introduce this shift factor before the data are stored in the minicomputer by delaying the acquisition of the UV data by a predetermined count interval. All data were sampled at 0.2-count intervals and punched on IBM cards for subsequent calculations. Computer programs were written and used for the described functionality calculations.

The VPO molecular weight data were obtained in toluene using a Mechrolab Model 302 osmometer. Benzil was used as the primary standard. Data were obtained at four concentrations and extrapolated to infinite dilution.

Hydroxyl equivalent weights were determined by acetylation of the hydroxyl groups with an excess of acetic anhydride in pyridine, followed by titration of the excess acetic anhydride and the resulting acetic acid with alcoholic KOH. A mixture of thymolphthalein and alizarin yellow R was used as indicator. Hydroxyl equivalent weights were also frequently determined by infrared analysis by measuring the absorbance at 2.75 microns and obtaining the equivalent weight from a standard calibration curve prepared using cetyl alcohol as a standard.

The UV detector was calibrated using solutions prepared by successive dilutions of a  $1/16$  wt-% solution of the phenylurethane derivative of *n*-propanol, isopropanol, or hydroxyl-terminated polybutadiene in THF. The com-

puter-integrated areas of the UV peaks were plotted versus the sample size. The slopes of the plots (area units/g) were multiplied by the hydroxyl equivalent weight (g/meq) to obtain the calibration constants (area units/meq).

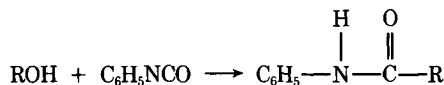
The nonfunctional polybutadienes were prepared for use as calibration standards at 30°C using butyllithium as the catalyst and previously described<sup>7</sup> bottle polymerization techniques.

The phenyl urethane derivatives of *n*-propyl and isopropyl alcohols were prepared according to the method described by Shriner, Fuson, and Curtin<sup>8</sup> and purified by repeated recrystallization.

The hydroxyl-terminated polybutadiene used for calibration of the UV detector after derivatization with phenyl isocyanate was prepared using an acetal-substituted alkylolithium<sup>9</sup> initiator. After polymerization of the butadiene was complete, the "living" polymer was reacted with ethylene oxide to produce a monoacetal-hydroxyl-terminated polybutadiene. The hydroxyl equivalent weight of the polymer as determined by infrared analysis was 3570. The hydroxyl functionality of this polymer was 0.51.

## RESULTS AND DISCUSSION

In our previous investigation,<sup>6</sup> the usefulness of derivatization to alter a functional group of a polymer to one which could be readily and selectively detected using a UV photometer in order to determine the distribution of these functional groups using dual detector GPC analysis was illustrated. It was expected that a similar technique could be developed for the determination of the distribution of hydroxyl groups in hydroxyl-terminated polymers, particularly polybutadiene. We believed that phenyl isocyanate could effectively be used for derivatization of the hydroxyl groups resulting in the formation of a urethane:



This reaction was expected and found (see Table III, ref. 10) to be essentially quantitative and to provide a product with sufficient UV absorptivity for detection during GPC analysis.

The weight fraction of polymer  $(F_p)_i$  eluting at GPC count  $i$  is equal to the normalized refractive index peak height at count  $i$ :

$$(F_p)_i = \frac{g_i}{\sum g_i} \quad (1)$$

where  $g_i$  is the peak height at count  $i$  as measured from the GPC refractive index peak at constant count intervals, and  $\sum g_i$  is the summation of the peak heights.

If the underivatized hydroxyl-terminated polymer has no UV absorbance at the particular wavelength used for analysis, the equivalent fraction of hydroxyl groups,  $(F_{\text{OH}})_i$ , eluting at GPC count  $i$  is equal to the normalized UV absorbance of the derivatized polymer at count  $i$ :

$$(F_{\text{OH}})_i = \frac{A_i}{\sum A_i} \quad (2)$$

where  $A_i$  is the UV absorbance at count  $i$  obtained at constant count intervals, and  $\Sigma A_i$  is the summation of these values. If the underivatized polymer has UV absorption at the wavelength used for analysis, the following equation must be used to calculate the fractional equivalents of hydroxyl groups eluting at GPC count  $i$ :

$$(F_{\text{OH}})_i = \frac{\Delta A_i}{\Sigma \Delta A_i} \quad (3)$$

In the equation,  $\Delta A_i$  is the difference in UV absorbance between the derivatized and underivatized polymer at GPC count  $i$ .

The functionality ( $f$ ) of a telechelic polymer is usually defined<sup>3-5</sup> as the ratio of the number-average molecular weight ( $M_n$ ) of a polymer to its equivalent weight ( $Z$ ):

$$f = \frac{M_n}{Z} \quad (4)$$

The equivalent weight of hydroxyl-terminated polybutadienes can be readily determined using titration and spectroscopic methods.<sup>3,5</sup> Since the hydroxyl-terminated polybutadienes are derivatized with phenyl isocyanate before GPC analysis, the total area of the UV absorption measured by the UV detector would be expected to be proportional to the total hydroxyl content if the reaction of the polymer with the phenyl isocyanate was quantitative. The actual hydroxyl content of the polymer could be determined from these data after appropriate calibration of the UV detector. The total hydroxyl content of the polymer expressed as equivalents of hydroxyl per gram of polymer is equal to the reciprocal of the equivalent weight of the polymer.

To calibrate the UV detector, phenyl isocyanate derivatives of *n*-propyl and isopropyl alcohols were prepared. Both of these urethanes were used to determine if different calibrations would be required for primary and secondary hydroxyl groups. By injecting known quantities of these urethanes into the GPC and measuring the UV peak areas, a calibration of the detector was obtained. These data are shown in Figure 1. It is apparent that no significant difference in the linear calibrations exist between primary and secondary alcohols.

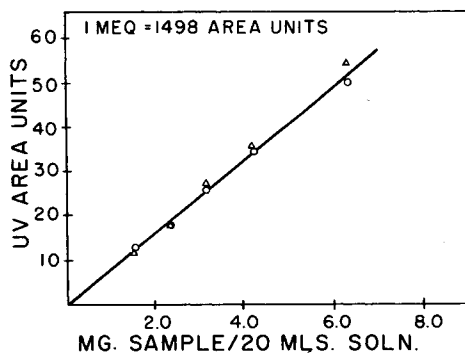


Fig. 1. Calibration of the UV detector with phenylurethane derivatives of *n*-propanol ( $\Delta$ ) and isopropanol (O).

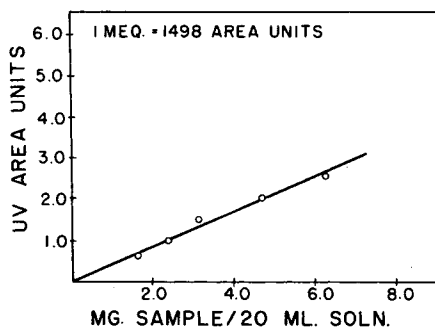


Fig. 2. Calibration of the UV detector with a phenylurethane derivative of a hydroxyl-terminated polybutadiene.

To provide data to substantiate the applicability of this calibration to hydroxyl-terminated polybutadienes, we also calibrated the detector with a phenylurethane derivative of a hydroxyl-terminated polybutadiene for which the hydroxyl content had been determined using a titration technique. These data are shown in Figure 2 and further illustrate the applicability of our calibration data obtained with the simple alcohols since both sets of data indicate an identical detector response for a given hydroxyl concentration. Consequently, the total area of the GPC peak obtained using the UV detector can be used to determine from these calibrations the number of equivalents of hydroxyl in the sample injected into the GPC. If one injects a known weight of polymer into the GPC, the equivalent weight of the whole polymer can be readily determined since the equivalent weight is equal to the grams of polymer ( $W_t$ ) per equivalent of hydroxyl ( $E$ ):

$$Z = \frac{W_t}{E} \quad (5)$$

If one assumes that the reaction of the phenyl isocyanate with the hydroxyl groups is random and independent of the molecular weight of the individual polymer chains or the location of the hydroxyl group in a particular chain, quantitative derivatization is not required for subsequent functionality calculations, providing that (1) the degree of derivatization results in adequate UV absorptivity and (2) the equivalent weight of the polymer is determined by an independent method.

Once the equivalent weight of the whole polymer has been determined from the previous procedure, or any independent method, the equivalent weight of the polymer eluting at GPC count  $i$  can be determined using the following relationship:

$$Z_i = \frac{Z(F_p)_i}{(F_{OH})_i} \quad (6)$$

where  $Z_i$  is the equivalent weight of the polymer eluting at GPC count  $i$ .

If the GPC has also been calibrated so that the molecular weight of the hydroxyl-terminated polybutadiene is known as a function of elution volume, the functionality of the polymer as a function of elution volume or molecular

weight can be determined. The functionality at GPC count  $i$ ,  $f_i$ , is calculated from the following equation:

$$f_i = \frac{M_i}{Z_i} \quad (7)$$

where  $M_i$  is the molecular weight at count  $i$ , and  $Z_i$  is the equivalent weight at count  $i$ .

Once the functionality of the polymer as a function of molecular weight has been determined, these data may be used to determine the functionality of the whole polymer. The number-average functionality  $f_n$  can be calculated using the following relationship:

$$f_n = \frac{\sum \left[ \frac{(F_p)_i}{M_i} \right] f_i}{\sum \left[ \frac{(F_p)_i}{M_i} \right]} \quad (8)$$

The weight of polymer at count  $i$ ,  $W_i$ , can be calculated from

$$W_i = (F_p)_i W_t \quad (9)$$

where  $W_t$  is the total weight of the sample injected into the GPC. Since

$$f_i = M_i \frac{E_i}{W_i} \quad (10)$$

where  $E_i$  is the number of  $W_i$  equivalents of hydroxyl at count  $i$ , it may be seen by substitution of (10) into eq. (8) that

$$f_n = \frac{\sum (F_p)_i \left[ \frac{E_i}{W_i} \right]}{\sum \frac{(F_p)_i}{M_i}} \quad (11)$$

Substituting eq. (9) into (10) gives

$$f_n = \frac{\sum \frac{E_i}{W_t}}{\sum \frac{(F_p)_i}{M_i}} \quad (12)$$

Since

$$M_n = \frac{1}{\sum \frac{(F_p)_i}{M_i}} \quad (13)$$

it may be seen that

$$f_n = M_n \frac{\sum E_i}{W_t} \quad (14)$$

Using eq. (5) leads to

$$f_n = \frac{M_n}{Z} \quad (15)$$

which shows that the functionality defined in eq. (4) is actually a number-average functionality. This indicates that  $f_n$  is independent of the functionality distribution.

We next defined the weight-average functionality  $f_w(\text{OH})$  by the following relationship:

$$f_w = \sum (F_p)_i f_i \quad (16)$$

Since

$$f_i = \frac{M_i E_i}{(F_p)_i W_i} \quad (17)$$

the substitution of eq. (17) into (16) gives the following relationship:

$$f_w = \frac{1}{W_t} \sum M_i E_i \quad (18)$$

This equation indicates that the weight-average functionality is dependent upon the functionality distribution of the copolymer. We have found that if the high molecular weight portion of the copolymer has a greater functionality than the low molecular weight portion,  $f_w$  would be greater than  $f_n$ . Conversely, we have found that if the low molecular weight portion of the copolymer has a higher functionality,  $f_w$  would be less than  $f_n$ . The ratio  $f_w/f_n$  appears to be a measure of how the functionality distribution is skewed as a function of molecular weight (see appendix).

From the previous discussion, it is obvious that one of the critical considerations in accurately determining the functionality distribution of hydroxyl-

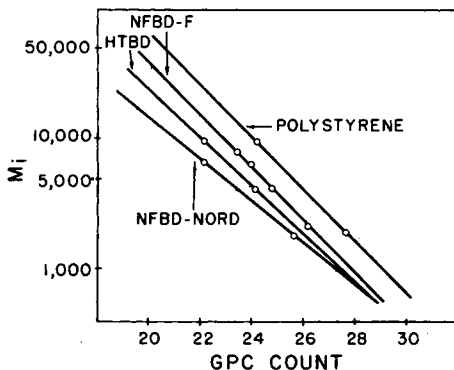


Fig. 3. GPC calibration for polystyrene, hydroxyl-terminated polybutadiene (HTBD), and nonfunctional polybutadiene (NFBBD). Firestone calibration for nonfunctional polybutadiene, (NFBBD-F). Calibration for nonfunctional polybutadiene from Naval Ordnance Station study (NFBBD-NORD).

TABLE I  
Microstructure and VPO Molecular Weights of Nonfunctional Polybutadienes

Sample no.	Microstructure			$M_n$
	% cis-1, 4	% trans-1, 4	% 1, 2	
1	31.5	52.1	16.4	2297
2	35.0	55.0	10.1	4382
3	36.8	54.8	8.4	6660
4	34.4	57.5	8.1	8122

TABLE II  
Comparison of Molecular Weight Data for a Hydroxyl-Terminated Polybutadiene

	GPC <sup>a</sup>	Reference 11
$M_n$	3600	3350
$M_w$	7200	7500
$M_w/M_n$	2.00	2.24

<sup>a</sup> Calculated using nonfunctional polybutadiene GPC calibration obtained using prepared standards.

TABLE III  
Functionality of the Hydroxy Polybutadiene

Reference	$f_n$
3	2.30 to 2.48
15	2.2
This work	{ 2.20 <sup>a</sup> 2.38 <sup>b</sup>

<sup>a</sup>  $f_n = M_n(\text{GPC})/Z(\text{titration})$ .

<sup>b</sup>  $f_n = M_n(\text{GPC})/Z(\text{GPC})$ .

terminated polybutadienes is the molecular weight calibration of the GPC for these polymers. This laboratory participated in a cooperative program<sup>2</sup> which had as its primary objective the measurement of the molecular weight distribution of hydrocarbon prepolymers, including hydroxyl-terminated polybutadienes using the GPC technique. We observed, as did others,<sup>2,11</sup> that the resolution of the suggested column set was poor at higher molecular weights and a shoulder was observed on the high molecular weight side of the GPC peaks. After completing the cooperative program, the column set was changed to improve resolution by changing one of two 700–2000 Å columns to a 10<sup>4</sup> Å column. The revised column set included four columns with 10<sup>4</sup> Å, 2000–5000 Å, 700–2000 Å, and 100–350 Å permeabilities. This column change eliminated the high molecular weight shoulder previously observed for a hydroxyl-terminated polybutadiene manufactured by the ARCO Chemical Company. This column set was then calibrated according to the procedure outlined in the cooperative program.

Ahad<sup>11</sup> has published data indicating that the choice of the column set used in the cooperative study results in polydispersity index ( $M_w/M_n$ ) values which are too low. From light scattering, VPO, and GPC data, he concludes



that the correct value for  $M_w/M_n$  for the hydroxyl-terminated polybutadiene is between 2.24 and 2.44. We obtain a value of 1.66 for the dispersity of this sample of hydroxyl polybutadiene. This raises some question about the accuracy of the calibration of the GPC for functional hydroxyl-terminated polybutadienes.

A calibration curve for nonfunctional polybutadienes was also presented in the cooperative investigation.<sup>2</sup> A significant difference between the calibrations obtained for the hydroxyl-terminated polybutadienes and nonfunctional polybutadiene was observed. This is illustrated for our column set in Figure 3.

It is not immediately obvious that a polybutadiene with terminal hydroxyl groups should have a GPC calibration significantly different than the calibration for nonfunctional polybutadienes. One could rationalize such a difference on the basis of polymer chains associating through hydrogen bonding of the terminal hydroxyl groups. Such association would be expected to decrease with increasing dilution and the ability of the solvent to participate in hydrogen bonding as an acceptor of donor molecule. In view of the small concentration of hydroxyl groups in the solutions of the telechelic polymers used for VPO molecular weight determinations or GPC analysis, it is questionable<sup>12</sup> if association could be a significant factor. After derivatization of a hydroxyl-terminated polybutadiene with phenyl isocyanate to form a urethane derivative, the molecular weight of this derivative as calculated from GPC data using the hydroxyl polybutadiene calibration was increased only by the amount expected. Although polyisocyanates<sup>13</sup> are known to associate through hydrogen bonding, the degree of association of the terminal urethane derivative would be expected to differ from hydroxyl polybutadiene. Yet the urethane and hydroxyl-terminated polymers appear to have very similar GPC calibrations.

In view of these questions, we prepared a series of polybutadienes using a butyllithium catalyst to confirm the calibration for the nonfunctional polybutadienes and to determine if the calibration differed significantly from that of the hydroxyl polybutadienes. Characterization data for these polymers are shown in Table I. The GPC calibration data are also shown in Figure 3 and differ significantly from the calibration data obtained for nonfunctional polybutadienes and hydroxyl-terminated polybutadienes in the cooperative program. Our calibration data are in better agreement with data previously obtained by Runyon.<sup>14</sup> When our calibration for nonfunctional polybutadienes is used to calculate the molecular weight distribution of the hydroxyl polybutadiene, the number- and weight-average molecular weights and the polydispersity index agree well with values previously published by Ahad<sup>11</sup> for this polymer. These values are compared in Table II. This suggests that perhaps the nonfunctional and hydroxyl-terminated polybutadienes have a common GPC calibration. But when this GPC number-average molecular weight and the equivalent weight determined from titration data are used to determine the number-average functionality, a significantly larger value ( $f_n = 2.95$ ) than the values previously reported<sup>3,15</sup> for this polymer and shown in Table III was obtained. However, the number-average functionality ( $f_n = 2.20$ ) determined from the GPC number-average molecular weight calculated using the hydroxyl-terminated polybutadiene calibration is in excellent

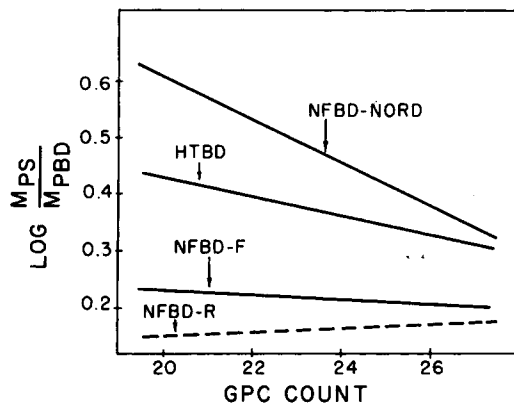


Fig. 4. Difference in calibrations between polystyrene and hydroxyl-terminated (HTBD) and nonfunctional (NFBD) polybutadienes. NFBD-R is extrapolated data from reference 14.

agreement with previously published values. Therefore, if the nonfunctional polybutadienes and hydroxyl-terminated polybutadienes have the same GPC calibration, it is likely that the more accurate calibration is that used for the hydroxyl-terminated polymers.

We are presently unable to explain the difference in the calibrations obtained for nonfunctional polybutadienes in the cooperative study with the Naval Ordnance Station and this investigation. Perhaps the fact that the column set used in the original Naval Ordnance Station study did not resolve the high molecular weight material is responsible for this difference. These data are also shown in Figure 4 as a plot of difference in the equations relating logarithm of molecular weight to GPC elution volume, expressed in counts, for polystyrene and polybutadiene. We have also included similar data obtained by Runyon for polybutadiene and the data for hydroxyl-terminated polybutadiene for comparison. It is interesting to note that the data obtained for the hydroxyl-terminated polybutadienes is approximately the mean obtained for the nonfunctional polybutadiene at our laboratories and the Naval Ordnance Station. It is not likely that the observed variation can be attributed to differences in the microstructure of the polymers used to obtain the calibrations.<sup>16</sup>

Ahad<sup>11</sup> has found that the hydrodynamic volume<sup>11</sup> of a hydroxyl-terminated polybutadiene is identical to that of the same polybutadiene with acetate groups. Furthermore, we have found that the hydrodynamic volume of a hydroxyl-terminated polybutadiene is nearly identical to that of the same polybutadiene with phenylurethane groups. This indicates that these functional groups are unimportant in determining the hydrodynamic volume of the polymer. We have, therefore, chosen to assume that the nonfunctional and hydroxyl-terminated polybutadienes have a common GPC calibration. If this assumption is incorrect, it would be necessary to determine the functionality distribution of a hydroxyl-terminated polybutadiene before one could calculate either a molecular weight or molecular weight distribution from GPC data. From a comparison of the calculated values of  $f_n$  for a hydroxyl-terminated polybutadiene obtained using number-average molecular weights calculated from GPC calibrations for hydroxyl-terminated and nonfunctional

polybutadienes and the equivalent weight obtained from titration data, we concluded that the GPC calibration based on hydroxyl-terminated polybutadienes was the more accurate calibration.

Another factor which can influence<sup>17</sup> the molecular weight and molecular weight distribution obtained from GPC data is the variation of the refractive index of a polymer with molecular weight. However, data for the variation of the refractive index of polybutadiene or hydroxyl-terminated polybutadienes with molecular weight are currently unavailable. Using the observed variation of refractive index with molecular weight for polyisobutylene<sup>18</sup> and correcting the GPC data obtained for a polybutadiene with a GPC  $M_n$  of 2900 and a GPC polydispersity index ( $M_w/M_n$ ) of 1.53, a corrected  $M_n$  of 2700 and a polydispersity index of 1.60 were obtained. This illustrates the relative importance of this correction which should be considered for a more rigorous treatment of the data; but until more precise and accurate GPC calibration data are obtained and the relationship of the refractive index of hydroxyl-terminated polybutadiene and molecular weight determined, such a correction would be superfluous.

### Appendix

The purpose of this appendix is to present some theoretical justification for the statement that the ratio  $f_w/f_n$  is a measure of how the functionality distribution is skewed as a function of molecular weight.

The weight  $W_i$  of polymer at count  $i$  can be expressed as

$$W_i = N_i M_i \quad (19)$$

where  $N_i$  is the number of moles of polymer at count  $i$ . If  $N$  is the total number of moles of polymer, then dividing (19) by  $N W_t$  and using eq. (9) gives

$$\frac{(F_p)_i}{M_i} = \frac{N n_i}{W_t} \quad (20)$$

where  $n_i$  is the mole fraction of polymer ( $n_i = N_i/N$ ). Substituting (20) into (8) gives the following simple and convenient expression for  $f_n$ :

$$f_n = \sum n_i f_i \quad (21)$$

Remember that

$$f_w = \sum (F_p)_i f_i \quad (16)$$

Assume the functionality can be given by

$$f_i = f_0 + ik \quad (22)$$

where  $f_0$  and  $k$  are constant functionalities. If  $k > 0$  ( $k < 0$ ), the functionality is monotonically increasing (decreasing). Now

$$f_n = f_0 + k \sum i n_i \quad (23)$$

and

$$f_w = f_0 + k \sum i (F_p)_i \quad (24)$$

It is clear that if the functionality is constant (i.e.,  $k = 0$ ), then  $f_n = f_w$ . When  $k \neq 0$ , the relation of  $f_n$  and  $f_w$  will depend upon the molecular weight distribution as well as the functionality distribution. Without rigorous proof, let it be stated that

$$\sum i n_i < \sum i (F_p)_i \quad (25)$$

Then, if  $k > 0$  (functionality skewed to high molecular weight),

$$k \sum i n_i < k \sum i (F_p)_i \quad (26)$$

and

$$f_n < f_w \quad (27)$$

If  $k < 0$  (functionality skewed to low molecular weight),

$$k \sum i n_i > k \sum i (F_p)_i \quad (28)$$

and

$$f_n > f_w \quad (29)$$

It can be shown that eq. (25) is certainly true for log normal distributions. In that case,

$$(F_p)_i = b \exp - \left( \frac{\log M_i - \log M_0}{\sqrt{2}\sigma} \right)^2 \quad (30)$$

where  $\sigma$  is the standard deviation of the distribution and  $b$  is a normalization constant adjusted so that  $\sum (F_p)_i = 1$ . Equations (20) and (30) can be juggled to give

$$n_i = (W_i b/N) b \exp - \left[ \left( \frac{\log M_i - \log M_0}{\sqrt{2}\sigma} \right)^2 + \log M_i \right] = b' \exp - \left[ \frac{\log M_i - (\log M_0 - \sigma^2)}{\sqrt{2}\sigma} \right]^2 \quad (31)$$

which shows that the number distribution is also log normal with its peak appearing at  $(\log M_0 - \sigma^2)$ . Since both the number and weight distributions are symmetric, it is easy to perform the summations in eq. (25). For instance, if the number distribution is indexed in such a manner that

$n_1 = n_N, n_2 = n_{N-1}, n_3 = n_{N-2}, \dots$  then

$$\begin{aligned} \sum i n_i &= n_1 = N n_N + 2n_2 + (N-1)n_{N-1} + \dots \\ &= (N+1)n_1 + (N+1)n_2 + \dots \\ &= (N+1) \sum_{i=1}^{N/2} n_i \\ &= \frac{N+1}{2} \end{aligned} \quad (32)$$

and this is just the index number appearing at the peak of the number distribution. If the same procedure is followed for  $\sum i (F_p)_i$ , the result will be the index appearing at the peak of the weight distribution. Equations (30) and (31) show that this will be larger than  $\sum i n_i$ , verifying eq. (25). (The small error in this procedure, resulting from the conflicting necessities that both summations must use the same index system and both must be indexed symmetrically, can be made negligibly small by indexing far out on the tails of the number and weight distributions.)

These relationships have been developed for monotonic functionalities and log normal molecular weight distributions. Other functionalities and molecular weight distributions must be investigated separately.

The VPO molecular weights were determined by Mr. C. O. Jones, and Mrs. J. L. Young obtained the titrametric hydroxyl equivalent weights. We also wish to acknowledge the laboratory assistance of Mr. D. B. Diehl and to thank The Firestone Tire and Rubber Company for permission to publish these data.

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