

Functionality Distribution of Hydroxyl-Terminated Polybutadienes Using Gel Permeation Chromatography. II. Measurements for Commercial Polymers

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Synopsis

The functionality averages, functionality distribution, hydroxyl equivalent weight, molecular weight averages, and molecular weight distribution of three commercial hydroxyl terminated polybutadienes have been determined using a dual-detector GPC method used to analyze the polymers before and after derivatization with phenyl isocyanate. The values of these parameters are compared with existing literature data. The determined number-average functionalities were in reasonable agreement with previously published values. However, the distribution of functionality as a function of molecular weight differs from distribution data obtained by column fractionation techniques. Our distribution data appears to be generally consistent with the distribution expected from the polymerization mechanisms. The differences in the variation of hydroxyl content with molecular weight obtained from the dual-detector GPC method and the column fractionation procedures should be resolved since a combination of these procedures could provide additional information regarding the actual amounts of mono-, di-, and polyfunctional polymer and their molecular weight distributions. The dual-detector GPC method should be applicable for the determination of the distribution of a variety of functional groups provided a selective derivatization reaction is available or a second detector which can directly and accurately determine the concentration of the functional group is available.

INTRODUCTION

The study of molecular weight and functionality parameters of telechelic hydrocarbon-based prepolymers has received much attention in recent years¹⁻⁶ owing to the influence that these parameters exert on the vulcanization and product properties. An excellent review of these systems has been presented by French.⁷

Previous work has been limited to the determination of the average functionality of the whole polymer or of fractions obtained by some appropriate fractionation procedure. Muenker² and Law,⁵ for instance, used extensive column elution techniques for separating the various species and then determined the average functionality of the fractions.

In the previous paper,⁸ we described a dual-detector gel permeation chromatography (GPC) method for simultaneously determining the molecular weight averages, molecular weight distribution, hydroxyl equivalent weight, functionality averages, and functionality distributions of hydroxyl-terminated polybutadienes. The method is based on the simultaneous use of a differential refractive index and ultraviolet GPC detectors to analyze the polymers before and after derivatization of the hydroxyl groups with phenyl isocyan-

ate. In this paper, the method will be utilized to determine these parameters for several commercial hydroxyl-terminated polybutadiene prepolymers and to compare the data with existing literature values.

EXPERIMENTAL

Two hydroxyl-terminated polybutadienes were obtained from the Arco Chemical Company, and one-hydroxyl terminated polybutadiene was obtained from the Phillips Petroleum Company. All polymers were used as received. Reagent-grade phenyl isocyanate from Matheson, Coleman and Bell was used to derivatize the hydroxyl-terminated polybutadienes. The phenyl isocyanate was vacuum distilled before use and stored under nitrogen pressure in a sealed, dark polymerization bottle.

Approximately 0.4 g of the polymer was weighed into a small, dry, high-pressure polymerization tube which was subsequently sealed with a Crown cap and a Teflon-lined Viton septum. The polymerization tube was evacuated by inserting a needle connected to a vacuum pump through the septum. The tube was placed in a sand bath at 80°C and evacuated for approximately ½ hr to remove volatile impurities from the polymer. The needle attached to the vacuum pump was removed and the tube pressured to 15 psi with prepurified nitrogen. A 100% excess of phenyl isocyanate required for derivatization of the hydroxyl groups, based on previous hydroxyl equivalent weight data, was carefully syringed into the polymerization tube containing the polymer. The phenyl isocyanate was mixed into the polymer by rotating the tube, and the mixture was allowed to react for 16–18 hr at 70–80°C. Excess phenyl isocyanate was removed by inserting the needle attached to the vacuum source through the septum of the heated tube and evacuating the tube for an additional ½ hr.

The polymer was analyzed using a previously described⁸ gel permeation chromatograph equipped with an ultraviolet detector. The molecular weight calibration for hydroxyl-terminated polybutadienes is described by the following equation:

$$\log M = 7.9292 - 0.1786C$$

when M is the molecular weight and C is the GPC elution volume expressed as GPC counts. Since derivatization of the hydroxyl-terminated polybutadienes resulted in only insignificant changes in the molecular weight averages and molecular weight distribution, the differential refractive index data of the underivatized polymer were used for the functionality calculation.

A Mechrolab Model 302 vapor pressure osmometer was used for the determination of number-average molecular weight. Hydroxyl equivalent weights were obtained by a previously described⁸ acetic anhydride titration method.

RESULTS AND DISCUSSION

The GPC data for sample 1 from Arco Chemical Company is shown in Figure 1. In the previous paper, we indicated that the number-average molecular weight of this polymer increased only by the expected amount after derivatization with phenyl isocyanate. Figure 1 shows both the differential re-

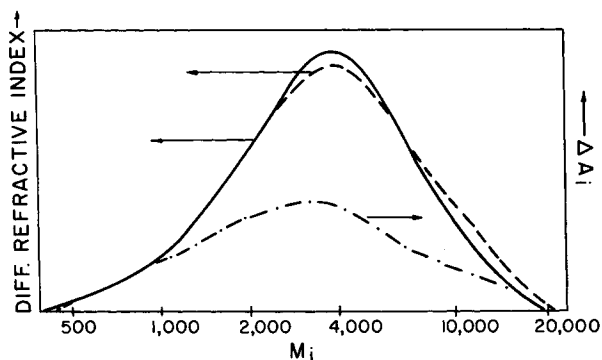


Fig. 1. GPC chromatogram of sample 1: (—) base polymer Δ RI chromatogram; (---) Δ RI chromatogram of polymer after derivatization with phenyl isocyanate, (-·-·) difference in UV absorbance between derivatized and underivatized polymer (A_i).

fractive index GPC chromatograms of the base polymer and the base polymer after derivatization with phenyl isocyanate. Very little difference is noticed between the two chromatograms. In fact, the M_n of the base polymer was 2680 g/mole, while the derivative had an M_n of 2860 g/mole. This 6.7% increase may show the addition of the phenyl isocyanate moieties to the polymer backbone, but this increase in molecular weight is well within the observed experimental error.⁹ Molecular weight data for all the samples shown in Table I indicated that the reaction of the hydroxyl groups with phenyl isocyanate resulted in only insignificant changes in molecular weight averages and molecular weight distribution.

The GPC UV difference curve shown in Figure 1 is the difference in UV chromatograms between the base polymer and the polymer after derivatization with phenyl isocyanate shifted to account for the volume of tubing between the two detectors. The total UV area of the underivatized polymer was quite small, amounting to approximately 6% of the total area observed for the derivatized polymer.

The GPC data for sample 2 from Arco Chemical Company and sample 3 from Phillips Petroleum Company are shown in Figures 2 and 3, respectively. Contrary to the results obtained with sample 1, both of these polymers have bimodal molecular weight distributions. We are unsure if this is indicative of poor column resolution or is real and due to the polymerization mechanism or process.

Some of the problems involved in determining the molecular weight averages of hydroxyl-terminated polybutadiene using GPC analysis have been discussed in the previous paper.⁸ In addition, the coefficients of variation for

TABLE I
GPC Molecular Weight Data

Polymer	Before derivatization		After derivatization	
	M_n	M_w/M_n	M_n	M_w/M_n
Sample 1	2680	1.66	2860	1.66
Sample 2	3946	1.80	3760	1.86
Sample 3	3980	1.26	3844	1.28

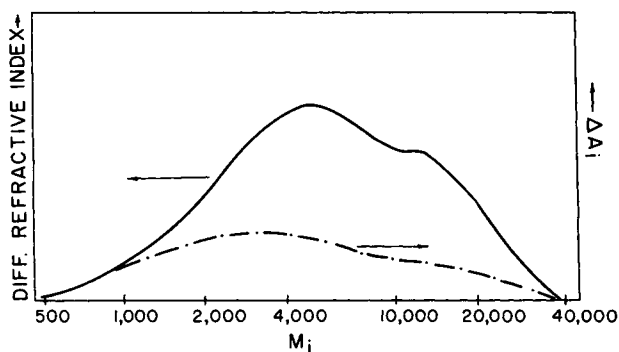


Fig. 2. GPC chromatogram of sample 2: (—) Δ RI chromatogram; (---) difference in UV absorbance between derivatized and underivatized polymer (A_i).

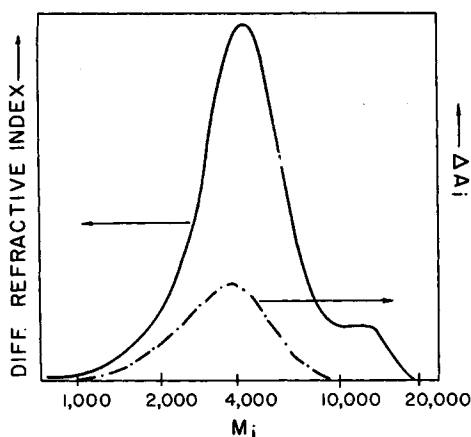


Fig. 3. GPC chromatogram of sample 3: (—) Δ RI chromatogram; (---) difference in UV absorbance between derivatized and underivatized polymer (A_i).

M_n and polydispersity indices for GPC data from eight different laboratories have been previously determined.⁹ The coefficient of variation for number-average molecular weights of hydroxyl-terminated polybutadienes were approximately 7%, and a coefficient of variation of approximately 2% to 5% was observed for the polydispersity index based on the mean value. However, the calibration constant for VPO determinations of M_n have also recently been observed to vary with molecular weight.¹⁰ In addition, VPO determinations of number-average molecular weights are quite sensitive to low molecular weight impurities. In spite of these problems, reasonable agreement was found between the M_n values determined by GPC and those obtained by VPO measurements with the exception of the values for sample 3. Our number-average molecular weights and polydispersity indices for the three polymer studied are shown in Table II with values obtained by other workers.^{2,6,9,11}

The functionality distribution data for sample 1 and 2 are shown in Figures 4 and 5, respectively. These figures are plots of functionality versus the logarithm of molecular weight. These two polymers have similar functionality distributions which show that the functionality increases with molecular weight.

TABLE II
Comparison of Molecular Weight Data of Different Investigators

Polymer	M_n	M_w/M_n	Method	References
Sample 1	2993	1.54	GPC	9
	3350	2.24	VPO; GPC	11
	3000	—	osmometry	6
	2800	—	osmometry	2
	2680	1.66	GPC	this work
	2770	—	VPO	this work
Sample 2	3700	—	osmometry	6
	3400	—	osmometry	2
	3760	1.86	GPC	this work
Sample 3	4734	1.15	GPC	9
	3844	1.28	GPC	this work
	2950	—	VPO	this work

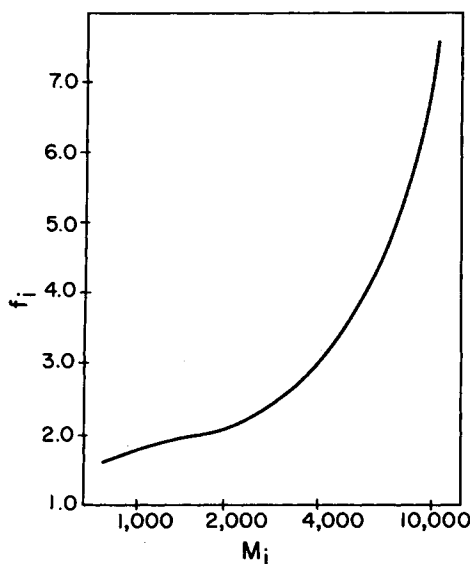


Fig. 4. Functionality distribution of sample 1.

The functionality distribution data for sample 3 are shown in Figure 6. The functionality was reasonably constant with a value slightly less than two for the major portion of the polymer but shows a rapid decrease at the high molecular weight end. This decrease in functionality corresponds to the high molecular weight shoulder in the GPC chromatogram shown in Figure 3, suggesting that this portion of the polymer has a very low functionality value. The value for the functionality actually reaches zero, however, the error involved in determining functionality is at a maximum at the molecular weight extremes.

The hydroxyl equivalent weight data for the three hydroxyl-terminated polybutadienes are shown in Table III with equivalent weight values determined by the titration procedure. We have also included literature values for the equivalent weight of these polymers.^{2,6,12} The maximum difference between our GPC and titrimetric hydroxyl equivalent weights was observed

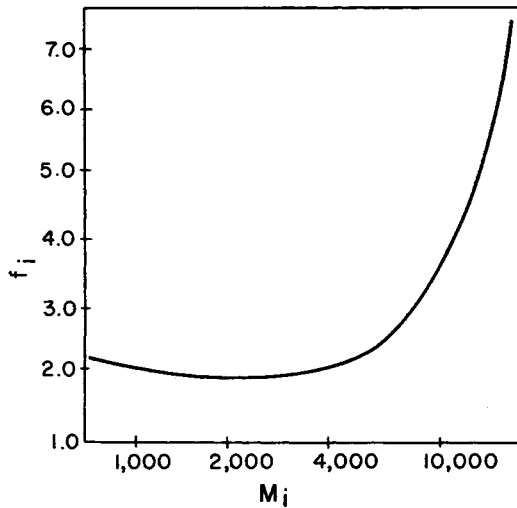


Fig. 5. Functionality distribution of sample 2.

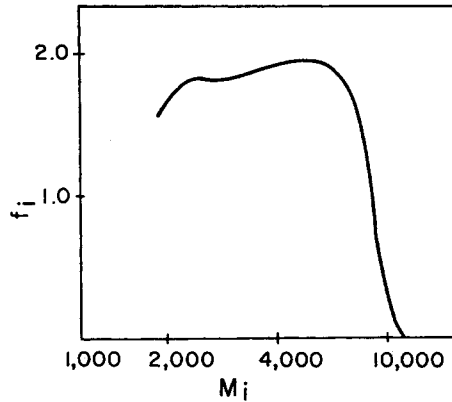


Fig. 6. Functionality distribution of sample 3.

TABLE III
Hydroxyl Equivalent Weights of Hydroxyl-Terminated Polybutadienes

Polymer	Hydroxyl equivalent weight			References
	GPC	Titration	Literature value	
Sample 1	1130	1220	1330	6
			1130, 1190, 1220	2
Sample 2	1630	1330	1430	6
			1380	2
Sample 3	2320	2560	1960	12

for sample 1, with the titrametric value being approximately 18% lower than the GPC value. The GPC method should be insensitive to low molecular weight hydroxyl-containing impurities which would result in lower hydroxyl equivalent weight values when the equivalent weight is determined using the titration procedure. However, we cannot attribute the difference in these

TABLE IV
Functionality Averages of Hydroxyl-Terminated Polybutadienes

Polymer	f_n	f_w	f_w/f_n
Sample 1	2.38	3.57	1.50
Sample 2	2.42	3.11	1.29
Sample 3	1.71	1.68	0.92

values solely to hydroxyl-containing impurities since, for two of the three samples shown in Table III, the GPC hydroxyl equivalent weights were approximately 10% lower than our titrametric values.

The determined values for the number-average and weight-average functionalities are shown in Table IV. The number-average functionality (f_n), which is equal to the ratio of the number-average molecular weight to the hydroxyl equivalent weight, is the value usually quoted in the literature. The f_n values for samples 1 and 2 are significantly greater than 2, and the values for sample 3 is slightly less than 2. The ratio of f_w to f_n can be indicative of how the functionality is skewed as a function of molecular weight.⁸ The f_w/f_n ratios of sample 1 and 2 are 1.50 and 1.29, respectively. The values are greater than unity, suggesting that the functionality is greater in the high molecular weight portion of the polymer. The functionality distribution data shown in Figures 4 and 5 indicate that this is the case. The f_w/f_n value for sample 3 is only slightly less than unity, suggesting a reasonably uniform distribution with the high molecular weight portion of the polymer having a lower functionality as shown in Figure 6.

A comparison of the number-average functionality of sample 1 determined by the dual-detector GPC method with literature values is included in the previous paper.⁸ Our value, 2.42, for the number-average functionality of sample 2 compares favorably with the literature values of 2.6⁶ and 2.48.² We are unaware of a literature value for the number-average functionality of sample 3. However, a number-average functionality can be calculated using the suppliers value for the hydroxyl equivalent weight, 1960 g/equiv, and the number-average molecular weights shown in Table II. The functionality calculated using our GPC number-average molecular weight and the suppliers hydroxyl equivalent weight is 1.96. The functionality value calculated using the GPC number-average molecular weight determined in the cooperative study⁹ was 2.42, which is quite large, particularly if this polymer was prepared using a difunctional initiator. Using our VPO molecular weight value, an f_n value of 1.51 was obtained.

We have found that the functionality of both samples 1 and 2 increases with increasing molecular weight. This increase in functionality is reflected in the ratios of the weight-average to number-average functionality. Since both polymers are believed to be prepared by the same free radical-catalyzed process,² it was expected that they would have similar functionality distributions. Reed¹³ has observed that the functionality of hydroxyl-terminated polybutadienes prepared with the free-radical initiator 4,4' - azobis(4 - cyano - *n* - pentanol) increased as the number-average molecular weight increased. It is reasonable to expect that for a polymerization which involves a radical-chain transfer process that the functionality of the polymer would increase

with increasing molecular weight. The polymer chains with higher molecular weights would have a higher probability of participating in the chain transfer reaction.

Muenker² found that trifunctional prepolymer was a major component in both samples 1 and 2, and no measurable quantities of non- and monofunctional prepolymer were found using a column fractionation technique. Sample 2 appeared to have a higher difunctional content than sample 1. However, the amount of trifunctional prepolymer was lower in the high molecular weight fractions, which is contrary to our observations. Refinements in the column fractionation technique have recently been made by Law,⁵ who also measured the functionality distribution of four hydroxyl-terminated polybutadienes by using GPC to analyze the fractions. According to Law, all four of the prepolymers contained measurable quantities of non-, mono-, di-, and trifunctional prepolymers. Three of the polymers also contained tetrafunctional prepolymer, and one of the polymers contained pentafunctional material. However, none of the polymers showed an increase in functionality with increasing molecular weight such as we have observed with samples 1 and 2. A direct comparison of our data with the data of Law is not possible, since the samples used by Law are not adequately identified, but it is reasonable to assume that his samples included one of these polymers which we have investigated.

We must conclude that for these polymers there is a definite discrepancy in the functionality distribution as determined by the dual detector GPC method and column fractionation techniques. We are presently unable to explain these discrepancies. A possible explanation for this difference, suggested by a referee, is that separation by column fractionation may involve the geometric arrangement of the active sites as well as the number of active sites. Surely, some variation could be explained by variations between lots of the same polymer, but we are convinced that the differences are too large for this to be the only explanation.

We also determined the functionality distribution of sample 3, a hydroxyl-terminated polybutadiene believed to have been prepared using an anionic catalyst.⁷ A bimodal molecular weight distribution was observed (Fig. 3). The major portion of the polymer had a relatively uniform functionality distribution increasing slightly as the molecular weight increased. This would be compatible with the preparation of the polymer using a difunctional anionic initiator with partial termination occurring during polymerization. The high molecular weight portion of the polymer consists of a small amount of material of low functionality. We are unable to offer any mechanistic explanation for this result. However, these data are comparable to the results of Law⁵ obtained for a sample of a hydroxyl-terminated polybutadiene designated HTPB-2. The results of Law indicated that the high molecular weight fraction of HTPB-2 was a mixture of mono- and nonfunctional polymer.

We believe that the dual detector GPC method is a promising method of determining the functionality distribution of a polymer as a function of molecular weight. Our data for the functionality distribution of hydroxyl-terminated polybutadienes is generally consistent with the results expected from the methods believed to have been used for the preparation of these polymers. Several problems are involved with the method. The principal

problem involves the molecular weight calibration of the GPC and the effect of functional groups on the calibration. This problem is discussed in detail in the previous paper.⁸ It was also difficult to obtain complete derivatization of the hydroxyl groups with phenyl isocyanate. However, complete derivatization is not required if the equivalent weight of the polymer can be determined by an alternate method. However, if complete derivatization is not obtained, it is necessary to assume that the derivatization reaction is random and independent of the molecular weight of the polymer chains and the location of the hydroxyl group in a particular chain.

Our results differ from the data obtained using column fractionation techniques by which the polymers are partially separated according to functionality.^{2,3,5} We believe that it is important that the differences in the results obtained by these two methods be resolved since a combination of the dual-detector GPC method and the column fractionation technique could provide additional information concerning the relative amounts of mono-, di-, and polyfunctional polymers and their molecular weight distributions.

The dual-detector GPC method should also be applicable for the determination of the functionality distribution of other polymers having functional groups other than hydroxyl. The adaptation of the method would require a molecular weight calibration of the GPC and a selective derivatization reaction which would result in sufficient UV absorptivity for detection. Detectors which are capable of determining the concentration of the functional group without derivatization would, of course, be preferred.

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