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Functionality Distribution of Carboxyl- and Hydroxyl-Terminated Polybutadiene

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Functionality Distribution of Carboxyl- and Hydroxyl-Terminated Polybutadiene

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ABSTRACT

Elution from silica gel was used to fractionate liquid polymers according to the number of chemically reactive groups per molecule (the functionality). Methods are presented for the functionality fractionation of high and low functionality carboxyl-terminated polybutadiene (CTPB). Results are also given on the fractionation of low functionality hydroxyl-terminated polybutadiene (HTPB) and of high functionality HTPB using a new elution series employing about half the solvent volume of that used in previous work. Calculated average functionalities agree reasonable well with those obtained on the whole polymer by other methods.
The high functionality HTPB averaged a functionality of 2.51 with variations between 2.43 and 2.63, while values of 2.53 and 2.57 were obtained by gel point methods. Recovery from the columns was 89 to 97%. Little or no nonfunctional material was found and usually about 10% monofunctional. Molecular weight of the monofunctional was about 1000; of the difunctional 4000 to 4500; and of the trifunctional 2000 to 2500 in agreement with the elution results of Muenker. It was concluded that HTPB did not change on the columns over a 72-hr period.

With high functionality CTPB, molecular weight tended to increase as the functionality increased and in one case, a molecular weight fractionation showed an increasing functionality with increasing molecular weight of the fractions. Material with functionality above three was difficult to remove from the columns, and in general the older the sample the lower the recovery. It is postulated that the high functionality material results from coupling of lower molecular weight molecules either by oxidation or during the polymerization process.

INTRODUCTION

The silica-gel elution method for the determination of prepolymer functionality distribution was first demonstrated by Muenker and Hudson [1] and used for the functionality fractionation of saturated liquid hydroxyl- and carboxyl-terminated hydrocarbon polymers of functionality two and below. Subsequently, the method was expanded to include fractionation of unsaturated hydroxyl-terminated prepolymers of functionality above two [2]. The technique was further extended by Law [3]. Adequate functionality fractionation of carboxyl-terminated unsaturated hydrocarbon prepolymers of functionality above two does not seem to have been achieved.

In the present work, methods are presented for the functionality fractionation of high and low functionality carboxyl-terminated polybutadiene (CTPB). Results are also given on the fractionation of high and low functionality hydroxyl-terminated polybutadiene (HTPB) using a new elution series that employs about half the solvent volume of that used in previous work [2]. Calculated average functionalities agree reasonably well with those obtained on the whole polymer by other methods.

The method is based on the adsorption of prepolymer on activated silica-gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. This technique can effectively separate prepolymers into non-, mono-, di-, and polyfunctional components. The initial work followed that of Muenker and Hudson [1, 2] as modified by the General Tire and Rubber Company [4] but with changes dictated by the high adsorption of the carboxyl group. Davidson Grade 81 silica gel was employed. This grade proved to be better suited for the purpose than Grade 62 or Grade 923 employed by Muenker [5]. Two lots of Grade 81 gel gave similar results.

DISCUSSION

Materials and Methods

Materials fractionated in this study were carboxyl- and hydroxyl-terminated polybutadienes from various sources. Samples of CTPB were obtained from the Phillips Petroleum Company (Butarez CTL-I and II), the General Tire and Rubber Company (Telagen CT), and Thiokol Chemical Company (HC-434). HTPB was obtained from Arco Chemical Company (R45M and R45HT), from the General Tire and Rubber Company (Telagen HT), and from Phillips Petroleum Company (Butarez HTS). Silica gel, Grades 62, 81, and 923, was obtained from the Davison Chemical Division of W. R. Grace and Company. CTPB and HTPB samples are referred to by letter codes.

Molecular weights were determined by gel permeation chromatographic methods using calibrations reported elsewhere [6]. Carboxyl contents were determined on thin films by IR techniques [7] at 1708 cm^{-1} using the 1434 cm^{-1} methylene peak as a standard. Hydroxyl groups were determined in CS_2 solution at 3615 cm^{-1} [7]. The peak height was sometimes measured on this spectrum, but if the shape of the curve indicated hydrogen bonding, the band area was measured between 3200 and 3700 cm^{-1}.

A minimum of about 250 mg was required for both molecular weight and equivalent weight measurements. Functionality was calculated by dividing molecular weight by equivalent weight. In some cases the weight average functionality was calculated from the proportion of reactive groups reacted at the gel point [8]. When the functionality of the eluted fractions was found, it was generally the case that the values were not whole numbers though often close to whole numbers. The functionality distribution was calculated by assuming that each fraction consisted only of material of whole functionality number immediately above and below the average value. A further assumption was that the molecular weight in each fraction was constant.

All together, three solvent elution series were used in the work which are described in some detail in the Appendix of this report (described as Series I through III). To make sure that no change or retention of material occurred during the elution process, all the fractions of one sample were collected after elution, combined, evaporated to dryness, and run on the GPC. The resulting distribution curve was compared with the distribution curve of the sample before elution (see Fig. 1). Weight- and number-average molecular weights before elution were 9168 and 7060, while after elution the combined fractions showed weight and number averages of 8389 and 6646. Curves before and after elution were similar although some high molecular weight material was retained on the silica columns.

Hydroxyl-Terminated Polybutadiene

The first work was on the fractionation of low functionality HTPB called Class 2 HTPB, and employed solvent Series III, see Appendix. A typical result is shown for HTPB-GC in Tables 1 and 2 and Fig. 2. The results on a repeat of this sample were 7.0% for Fraction A, 6.1% for Fraction B, and 82.7% for Fraction C.

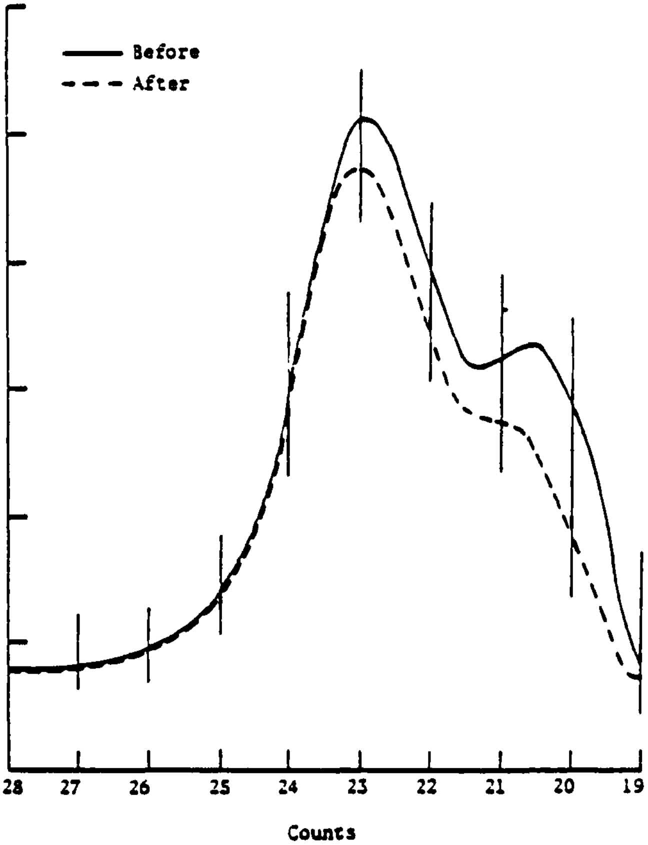

FIG. 1. GPC curves of CTPB before and after elution from silica gel.

Others have previously presented methods for functionality fractionation of HTPB with average functionality 2.0 or below [1]. It was soon found that fractionation of HTPB of average functionality above 2.0, called Class 1 HTPB, presented problems. Nearly all of the trifunctional material eluted with the difunctional. In one case when fractionating HTPB-GJ, 0.6% below functionality two was found and 87% eluted during the next step. In another case 94% of the sample eluted in this step although the average functionality of this prepolymer is 2.57.

A search was made for a solvent elution system which would allow separation of the major fraction of HTPB-GJ found in the third step of

TABLE 1. Functionality Fractionation of Various Prepolymers[a]

Sample	Fraction	Weight	Molecular weight	Carboxyl or hydroxyl equiv weight	Functionality
HTPB-GC	A	8.2	1100	-	0
	B	10.4	2379	2576	0.92
	C	80.6	1708	924	1.85
		99.2	2180	1040	
HTPB-FC	A	30.2	6537	10559	0.62
	B	12.4	5141	4341	1.18
	C	54.0	4598	2032	2.26
		96.6	5000	3100	
CTPB-FA-1	A	26.7	4500	-	0
	B	52	6000	2810	2.1
	C	2.7	-	-	-
	D	14.7	6000	2050	2.9
		96.1		3980	
CTPB-FB	A	3.3	-	-	-
	B	70.0	5600	2730	2.05
	C	6.1	9480	3440	2.75
	D	17.9	9480	2650	3.6
		97.3	4900	3850	
CTPB-FL	A	2.8	-	-	-
	B	68.5	5500	1940	2.8
	C	7.6	6100	2260	2.69
	D	15.8	8750	2230	3.9
		94.7		1960	

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[a] Molecular weights and reactive group equivalent weights beneath the lines are experimental results on the whole polymer.

TABLE 2. Functionality Distribution of Various Prepolymers[a]

	Sample					
		CTPB-FR				
Functionality	HTPB-GC	From GPC fractions	From SiO_2 column	CTPB-FA-1	CTPB-FB	CTPB-FL
0	9.0	7.1	6.5	26.6	3.3	2.8
1	21.7	0.3	0	0	0	0
2	68.5	52.8	66.7	48.5	68.1	16.1
3	-	28.8	12.0	18.3	15.2	61.6
4	-	7.6	9.8	-	10.7	14.2
5	-	3.3	-	-	-	-
	99.2	99.9	95.0	93.4	97.3	94.7
No. average functionality from above	2.05	2.22	2.06	1.5	2.2	2.8
Weight average functionality from above	2.20	2.56	2.36	2.33	2.39	2.96
Weight average functionality from above	1.95	2.60	2.60	2.35	2.62	2.64

[a] By elution from silica gel in all cases except one.

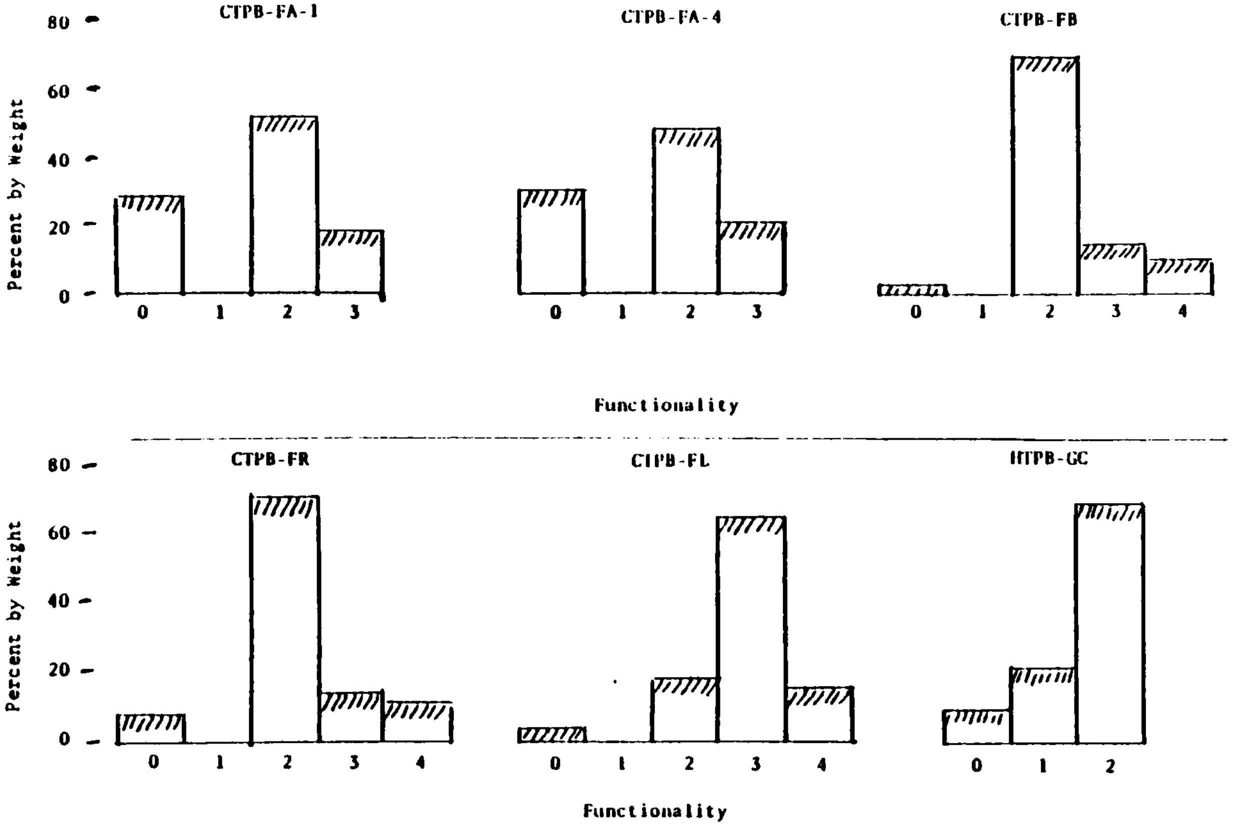

FIG. 2. Functionality distribution of prepolymers.

the procedure which utilized ethanol, chloroform, and benzene as the eluting solvent. The approach was to reduce and finally eliminate the polar constituents of this mixture. Elution with benzene alone reduced the proportion removed in this step to 33 to 36% of the whole. Further removal was then effected by elution with benzene containing successively increasing proportions of ethanol and chloroform. The procedures used are shown as solvent Series II in the Appendix. The solvent series is somewhat different from that described by Muenker [2] and employs only about half the solvent volume. Reproducibility of the elution procedures is shown in Table 3. Precision is not bad.

High functionality HTPB, samples of GJ and GL, was found to contain little or no nonfunctional material and usually less than 15% monofunctional material. Hence it was considered that the first step in elution Series II, use of 5% ether in hexane, might be omitted. When this was done, separation was clean cut and working up the fractions was faster. Five lots of HTPB-GJ and one of HTPB-GL were fractionated in this way with results as shown in Table 4 and Fig. 3. However, on fractionating two of these lots using the hexane-ether solvent, it was found that use of this solvent changed the results somewhat. A comparison is shown in Table 5 and Fig. 3. Use of hexane-ether yields a lower calculated average functionality and a higher proportion of monofunctional material. Experimental results on the whole polymer seem to agree more closely with those on the fractions found using the hexane-ether step than without.

The results on functionality fractionation of HTPB-GJ indicated about 10 to 15% monofunctional material of molecular weight about 1000, the rest being di- and trifunctional with molecular weights 4000 to 4500 and 2000 to 2500, respectively. Average functionality was calculated to be about 2.5.

Whereas molecular weight and functionality increase together for carboxyl-terminated polybutadiene fractions (CTPB), we have found that molecular weight of hydroxyl-terminated polybutadiene (HTPB-GJ) fractions decreased for the three-functional material as compared with the two-functional. Lockheed Propulsion Company has reported in joint work with Esso Corporation [9] that molecular weight increased as functionality increased for the material. They used a precipitation fractionation method. One explanation for the conflicting findings might be that a change in the polymer takes place on the silica column.

Using HTPB-GJ, Lot 006131, all the fractions were collected immediately after silica elution, combined, evaporated to dryness, and run on a gel permeation chromatograph (GPC). The resulting distribution curve was compared with the distribution curve of the sample before elution (see Fig. 4). Another sample of the same lot was held on the silica gel for over 72 hr and then eluted using the same procedure. The fractions were collected after elution, combined, evaporated to dryness, and run on the GPC. Molecular weight results are shown in Table 6.

TABLE 3. Reproducibility of Elution Fractionation

	Percent eluted						Functionality		
	A	B	C	D	E	Total	A	B	C
HTPB-GJ 006131	1.28	47.75	4.87	37.4	4.3	95.6	0	1.89	2.73
	1.54	47.91	6.30	37.72	3.42	96.9	0	1.91	2.56
	1.70	47.44	5.04	38.50	2.91	95.6	0	1.84	2.61
HTPB-GJ 006131	-	35.8	7.4	45.2	4.6	93.0	-	-	-
	-	32.1	8.5	47.9	5.3	93.8	-	-	-
CTPB-FB	3.3	70.0	6.1	17.9	-	97.3	-	-	-
	1.9	70.3	4.2	23.6	-	95.0	-	-	-
CTPB-FA-2	25.9	35.9	1.7	21.7	-	85.2	0	2.30	2.75
	26.7	38.4	2.5	23.1	-	90.7	0	2.38	2.83
CTPB-FA-3	30.3	43.7	2.5	17.9	-	94.4	0	2.22	2.75
	29.9	44.8	3.2	18.1	-	96.0	0	2.26	2.76

TABLE 4. Functionality Distribution of HTPB-GJ[a]

Lot No.	Elution recovery	Wt%, functionality				Calcd average functionality
		1	2	3	Sum	
001251	93.6	4.3	47.3	29.8	81.4	2.43
806301	89.3	9.6	21.3	47.1	78.0	2.63
909061	95.8	10.1	31.5	36.2	77.8	2.47
006131	93.4	6.2	31.1	43.5	80.8	2.60
106012 HT	97.4	8.1	34.9	40.4	83.4	2.54
805201	95.2	14.5	30.0	36.1	80.6	2.41
805181[a]	91.7	17.5	28.1	36.8	82.5	2.38

[a] Determined without hexane-ether solvent except for Lot 805181.

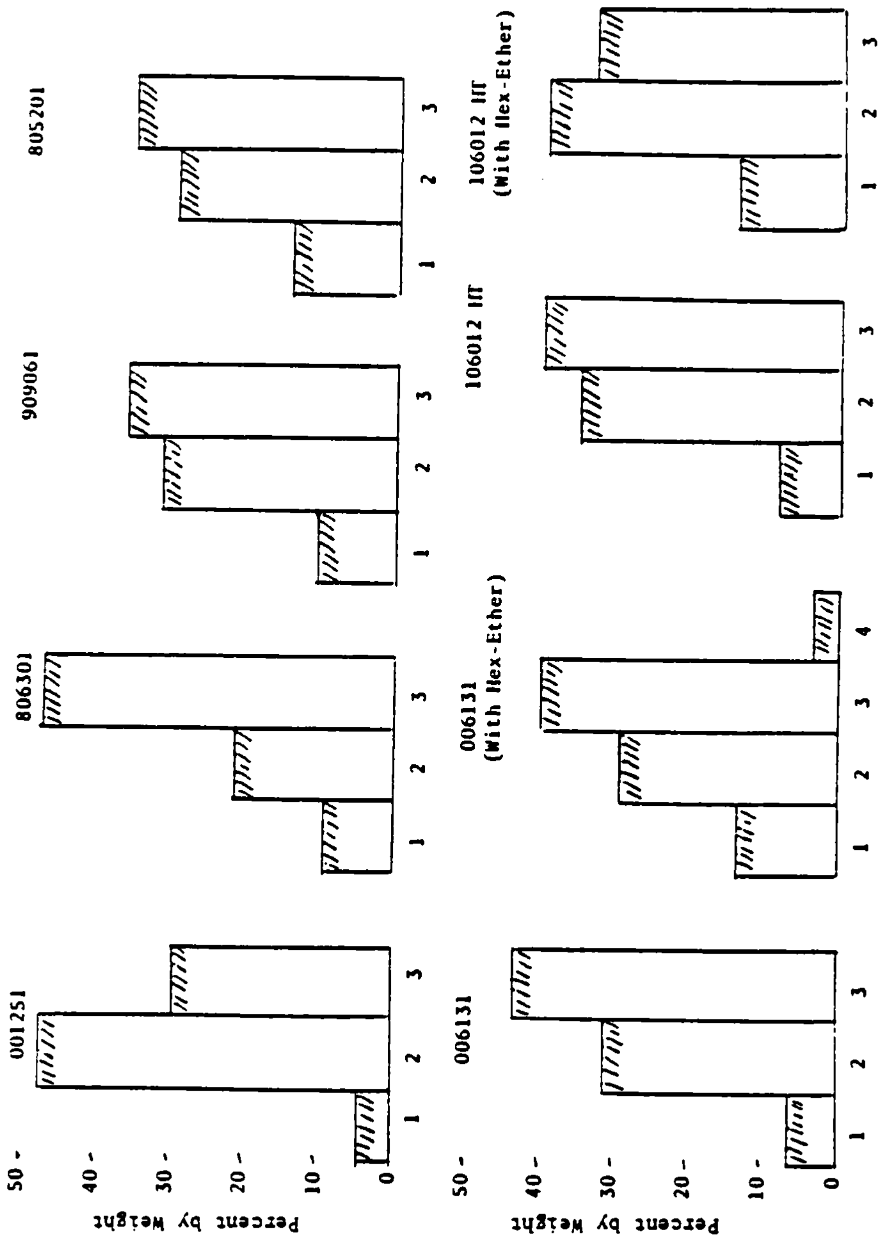

FIG. 3. Functionality distribution of HTPB-G.I.

TABLE 5. Fractionation of HTPB with and without Hexane-Ether Elution

		A	B			C	D			E	Total
		(wt%)	Wt%	M_n	Equiv wt	(wt%)	Wt%	M_n	Equiv wt	(wt%)	recovery (%)
HTPB-GJ	With hexane-ether	1.7	43.4	4087	2429	4.7	40.0	2028	656	2.7	92.5
006131	Without hexane-ether	-	33.9	4827	2540	7.9	46.5	2374	810	5.0	93.4
HTPB-GL	With hexane-ether	1.7	37.6	3632	2225	16.4[a]	33.0	1955	682	6.0	94.8
106012	Without hexane-ether	-	32.3	4386	2508	6.8	51.1	2262	810	7.2	97.4

		Wt% function				Whole polymer, calcd			Whole polymer, expt		
		1	2	3	Sum	M_n	Equiv wt	Average functionality[b]	M_n	Equiv wt	Average functionality[b]
HTPB-GJ	With hexane-ether	15.4	29.5	40.0	85.1	2749	1058	2.60	2932	1200	2.44
006131	Without hexane-ether	6.2	31.1	43.5	80.8	3021	1136	2.65	-	-	-
HTPB-GL	With hexane-ether	14.4	39.8	33.3	87.5	2635	1107	2.39	2875	1192	2.40
106012	Without hexane-ether	8.1	34.9	40.4	83.4	2785	1098	2.54	-	-	-

[a] This fraction had a molecular weight of 2835 and an equivalent weight of 1230.

[b] Molecular weight divided by equivalent weight.

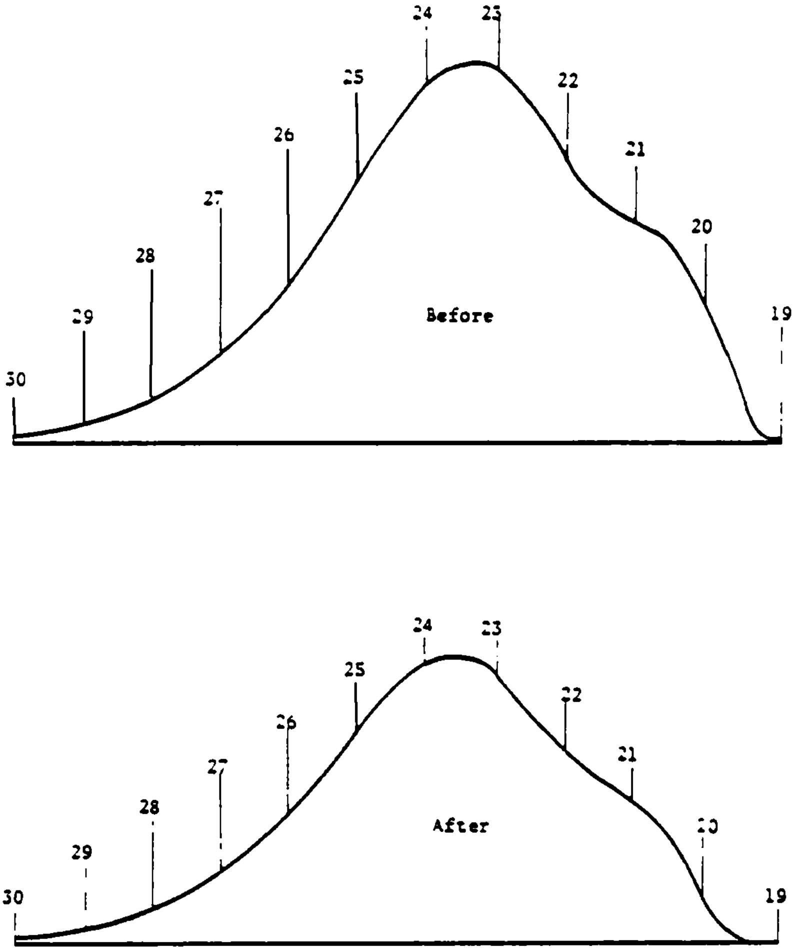

FIG. 4. GPC distribution of HTPB-GJ before elution and after elution and recombination.

In order to check GPC and vapor pressure osmometer (VPO) results with each other, this lot of HTPB-GJ was fractionated four times by elution from silica. The four approximately difunctional fractions were combined and the molecular weight was determined by GPC and VPO techniques. By GPC, M_w was 5342 and M_n 4305. By VPO, M_n was 4210. The equivalent weight by IR methods was 2372, yielding a functionality of 1.81.

TABLE 6

HTPB-GJ 006131	Before elution	After immediate elution and recombination	After 72 hr elution and recombination
M_n	3099	3144	3014
M_w	4681	4705	4583
M_w/M_n	1.51	1.50	1.52

From these results one must conclude that HTPB-GJ elutes from silica gel (Grade 81) with no polymerization or degradation.

Carboxyl-Terminated Polybutadiene

When CTPB is fractionated by the methods used above for HTPB, a part of the sample is retained on the column. It was found, however, that this portion could be removed in most cases if a little acetic acid was added to the final elution solvent. See Series I in the Appendix. It is necessary in this case to pump off the acetic acid from the final dry fraction of the sample exhaustively before determination of carboxyl content.

During the elution process the last fraction washed out by acetic acid and chloroform usually showed a double peak when this fraction was put through the GPC. In other words, the elution process gave fractions containing two molecular weight species. This result gives more confidence in the elution method for separation by functionality and the GPC process for separation by size.

Results found for various types of CTPB are shown in Tables 1 and 2 and Fig. 2. Agreement between calculated average functionalities and those determined from gel point measurements was not too good in some cases. Results on six samples of recently produced Butarez CTL-I averaged 28.9% nonfunctional material out of 30% presumed to be present with an average total recovery of 95.4%.

In the case of CTPB, molecular weight tended to increase as the functionality increased and in one case, shown in Table 2, a molecular weight fractionation showed an increasing functionality with increasing molecular weight of the fractions.

As information accumulated on the fractionation of a number of samples of CTPB using the Series I solvents but with lower volumes than given in the Appendix, examples of low recovery from the columns were found. Instead of the 95.4% mentioned above, in one case 79% was

TABLE 7. Effect of Sample Age on Recovery of CTPB

Type CTPB	Approx age (yr)	Recovery of fractions (%) A	B	C	D	Total
I	0-1	30.2	43.1	8.1	17.8	99.1
	1	29.7	44.2	2.1	18.5	94.5
	2	26.7	52.0	2.7	14.7	96.1
	2	28.1	43.8	2.9	19.1	93.8
	2	29.1	40.8	2.2	21.3	93.3
	3	27.5	39.5	3.5	21.0	91.5
	4	23.0	47.8	4.0	18.6	90.5
	6	22.1	45.5	2.5	17.4	87.5
II	4	3.5	63.3	3.4	22.9	93.1
	4	2.7	62.3	2.4	22.6	90.9
	4	1.6	60.1	2.4	22.5	86.6
	5	2.3	51.7	2.9	22.5	79.4

recovered and in others 87%. On arranging these samples in order of age, it was found that recovery tended to decrease with age of the sample (see Table 7). Specifically, the samples showed less non- and difunctional material without a change in the proportion of trifunctional material as they became older. In an effort to increase the recovery of these samples from the columns, the major parameters of the process were varied using a single 6-year old Type I sample, as shown in Table 8. The silica gel to polymer ratio was increased from 50/1 to 133/1 using a 26-mm i.d. column as well as a 20-mm column, and in one case the proportions of eluting solvents were increased to the amounts given in Series I in the Appendix. Recovery increased from 87.5 to 94.8%. A further experiment showed a slight decrease in recovery when using silica gel which had been stored at 65% R.H. Of more importance, the functionality separation of Fractions B and D almost vanished when using the moist silica but was reasonably high when a dry gel was used in the 26-mm column at a 133/1 gel to polymer ratio (see Table 8).

Some years ago NAVORDSTA reported that a proportion of some CTPB prepolymers was insoluble in pentane and presented a test which could rate each prepolymer for pentane insolubles in terms of a number.

TABLE 8. Fractionation of an Old CTPB Sample

Gel/polymer (g/g)	Column diam (mm)	Conditions	Percent eluted					Functionality			Ratio functionality D/B
			A	B	C	D	Total	A	B	D	
50/1	20		22.1	45.5	2.5	17.4	87.5	0	2.39	2.40	1.04
80/1	20		27.9	35.9	3.7	20.7	88.2	0	2.45	2.44	1.00
62/0.75	26		28.6	35.2	2.0	21.9	87.7	0	2.14	2.73	1.28
100/0.75	26		26.3	36.8	2.1	21.8	87.0	0	1.88	2.89	1.53
100/1	20	Solvent increased	28.3	41.0	5.6	19.4	94.3	0	2.33	2.77	1.18
100/0.75	26	Gel stored 65% R.H.	26.9	33.2	2.6	23.8	86.5	0	2.51	2.55	1.02
50/1	20	Pentane insol removed	31.7	43.6	2.5	17.0	94.8	0	2.34	2.72	1.16

[Prepolymer (2.50 g) was weighed into a 50-ml beaker and dissolved in pentane. The solution was added to a 100-ml graduated centrifugal cup (Fisher 5-622) and pentane added to a total volume of 100 ml. The cup was allowed to remain overnight at 25°C and the volume of lower layer was read off.] In 1966 it was found that this number for the lot of CTPB used to obtain the data in Table 8 was 0.5. However, on rerunning the test in 1971, the value was found to have increased to 2.0. Pentane insolubles were isolated from a lot of CTPB and found to have the same carboxyl content as the whole polymer but with much higher viscosity. In a few days the material hardened in air and became solid. In the present work the pentane insolubles were removed from a large sample of the lot used for the data in Table 8. The pentane insolubles were found to have a molecular weight of 10,200 and a functionality of 3.53. The portion remaining after removal of the insolubles was then fractionated using the Series I procedure. Recovery was nearly 95% with a reasonable functionality separation of Fractions B and D. One can postulate that the high functionality material results from coupling of low molecular weight molecules by an oxidation process.

Two procedures were thus needed for functionality fractionation of CTPB. In order to minimize differences between the procedures, the solvent volumes used in both were placed at the same high level and 25-mm columns were employed in both. The remaining differences were then in sample size and in the cut-off point for collection of one of the fractions. It was decided to use the pentane insolubles test as a means of classifying CTPB samples according to the particular procedure to be used. Based on results of this test applied to a number of samples, a value of 0.50 ml pentane insolubles was set as the dividing point between two classes of CTPB. Details are described in the Appendix.

CONCLUSION

Methods have been presented for reproducibly separating carboxyl- and hydroxyl-terminated butadiene polymers into fractions which vary according to the number of reactive groups per molecule. Considering the number of steps involved and the difficulties of the work, precision is fairly good. Separation does seem to be by functionality. Molecular weight of CTPB was found to increase with functionality, but on the contrary the molecular weight of high functionality HTPB (Sample GJ) showed lower molecular weight for the high functionality fractions than for the low. This result is in contradiction to that of another group [9] and also appears a little illogical. Nevertheless, extensive efforts failed to show any significant errors in this work.

APPENDIX

This method is for the determination of the distribution of functionalities of liquid carboxyl-terminated polybutadiene (CTPB) of 20 to 30% vinyl content and of liquid hydroxyl-terminated polybutadiene (HTPB) of 20 to 30% vinyl content.

1. CTPB samples are divided into two classes as follows: 2.50 g of sample are weighed into a 50-ml beaker and dissolved in n-pentane. The solution is added to a 100-ml graduated centrifugal cup and pentane added to a total volume of 100 ml. A stopper is placed in the top of the cup and the mixture shaken to homogeneity. The cup is allowed to remain overnight at 25°C and the volume of any lower layer is read off estimating to one hundredth of a milliliter. Samples yielding 0 to 0.50 ml are designated Class 1 and treated as described in Paragraphs 1.1 below. Those yielding 0.51 ml or more lower layer are designated Class 2 and treated as described in Paragraphs 1.2 below.

1.1. Fractionation of Class 1 CTPB

1.1.1. Prepare a 3-1/2% by volume solution of diethyl ether in hexane by mixing 965 ml of hexane and 35 ml of diethyl ether. Weigh 100 g of silica gel (Grace-Davison, Grade 81) into a 600-ml beaker and add 300 ml of the ether-hexane solution with stirring. Pour sea sand into the bottom inch of a 25-mm by 3 ft demountable chromatographic column fitted with a course sintered glass disk. The slurried silica gel is transferred into the column as rapidly as possible. Drain the solvent to the top of the gel bed and add 1/2 in. of sea sand to keep from disturbing the gel when the sample and solvents are added.

1.1.2. Measure 400 ml of the 3-1/2% ether-hexane solution into a graduated cylinder and pour into a 1-liter separatory funnel. Weigh 1.00 g of CTPB sample into a 6-dram vial. Add 10 ml of the ether-hexane solution taken from the funnel to dissolve the polymer. Transfer the dissolved sample quantitatively to the column, rinsing several times with small amounts of solvent from the separatory funnel. Drain the solvent from the column until the sample liquid reaches the top of the sand.

1.1.3. Additional solvent is added to the column from the separatory funnel. The funnel is fitted with a stopper and secured in place above the column with a ring clamp. Flow rate of solvent through the column should be adjusted at the beginning of elution process to 12 ml/min by regulating the opening of the column stopcock. The flow rate will change during the run because the different solvents have different densities and viscosities. However, the stopcock opening should not be changed once it is set. The complete elution series is as follows:

Series I:

A	Diethyl ether 3.5, hexane 96.5	400 ml
B	Ethanol 25, chloroform 10, benzene 65	300 ml
C-I	Ethanol 10, chloroform 90	300 ml then
C-II	Chloroform	300 ml
D	Chloroform 99, acetic acid 1	600 ml

Proportions are in percent by volume. Collect the fractions in a 250-ml graduated cylinder so the volumes can be measured. Then transfer to 500 ml Erlenmeyer flasks. Do not let the column run dry at any time during the elution series.

1.1.4. Fraction A, Paragraph 1.1.3, should contain 570 ml. Start collecting Fraction A when the sample is added to the column. Continue collecting until the solvent front from Solvent B has reached the bottom of the column. This front can be seen because of the difference in refractive index of the two solvent combinations.

1.1.5. Prepare Solvent B, Paragraph 1.1.3, by mixing 195 ml benzene, 75 ml of ethanol, and 30 ml of chloroform. Add 300 ml of Solvent B to the separatory funnel. When Fraction A, Paragraphs 1.1.3 and 1.1.4, reaches the sand, begin adding Solvent B to the column from the funnel. Collect 300 ml of Fraction B.

1.1.6. As each solvent drains from the funnel, add the next solvent combination in the series, Paragraph 1.1.3. Solvent C-I contains 270 ml chloroform and 30 ml ethanol. Solvent C-II is 300 ml chloroform. For fraction C, collect 650 ml.

1.1.7. Solvent D, Paragraph 1.1.3, contains 594 ml chloroform and 6 ml glacial acetic acid. Collect Fraction D which will amount to 450 ml by letting the column drain completely.

1.1.8. Set up a rotary evaporator connected with two Dry Ice-acetone traps in series and then a vacuum pump. Carefully evaporate the solvent from each fraction using a 250-ml round-bottom flask at first, and then when the volume has decreased transfer the material to a previously tared 50 ml round-bottom flask, rinsing several times with a small amount of solvent. When the solvent has evaporated, place the flasks in a heated vacuum desiccator or vacuum oven and pump for 2 hr at 60° C. Weigh the flasks and calculate the weight percent of each fraction using the relationship:

weight percent of fraction = 100 × (weight flask plus sample - weight flask)

1.1.9. For each fraction in Paragraph 1.1.8 having a weight of 150 mg or more, determine the molecular weight using the procedures in "A Cooperative Molecular Weight Distribution Test" [6].

1.1.10. For each fraction in Paragraph 1.1.8 having a weight of 150 mg or more, determine the carboxyl equivalent weight by the procedures in "Infrared Determination of Carboxyl and Hydroxyl Contents of Functionally Terminated Polybutadiene" [7].

1.1.11. Report as the results of the test the weight percent of each fraction from Paragraph 1.1.8, the molecular weight of each fraction from Paragraph 1.19, and the carboxyl equivalent weight of each fraction from Paragraph 1.1.10.

1.2. Fractionation of Class 2 CTPB

1.2.1. The procedure for the functionality fractionation of Class 2 CTPB is the same as that described in Paragraphs 1.1 above for Class 1 CTPB with the following exceptions:

a. In Paragraph 1.12, change the CTPB sample size to 0.75 g.

b. In Paragraph 1.1.6, collect 600 ml of Fraction C instead of 650 ml.

c. In Paragraph 1.17, 500 ml of Fraction D will be obtained when the column is drained.

d. In Paragraph 1.1.8, the calculation for the weight percent of the fractions will be:

weight percent of fraction = 133.3 × (weight flask plus sample - weight flask)

2. HTPB samples are divided into two classes. In Class 1 are those materials which average more than two hydroxyl groups per molecule. Members of this class are treated as described in Paragraphs 2.1 below. In Class 2 are those materials which average two or less hydroxyl groups per molecule. Members of this class are treated as described in Paragraph 2.2 below.

2.1. Fractionation of Class 1 HTPB.

2.1.1. A 5% by volume solution of diethyl ether in hexane is made by mixing 950 ml of hexane and 50 ml diethyl ether. Weigh 50 g of silica gel (Grace-Davison, Grade 81) into a 450-ml beaker and add 150 ml of the ether-hexane solution with stirring. Pour sea sand (washed and ignited) into the bottom inch of a 20-mm by 3 ft demountable chromatograph column fitted with a sintered glass disk. Then pour the slurried silica gel into the column as rapidly as possible. Drain the solvent to the top of the gel bed and add 1/2 in. of sea sand to keep from disturbing the gel when the sample and solvents are added.

2.1.2. Measure 300 ml of the 5% ether-hexane solution and pour into a 1-liter separatory funnel. Weigh 1.00 g of HTPB sample in a 6-dram vial and dissolve in 10 ml of solvent from the funnel. Transfer the dissolved sample quantitatively to the column, rinsing the vial several times with small amounts of solvent from the separatory funnel. Drain solvent from the column until the sample liquid reaches the top of the sand.

2.1.3. Additional solvent is added to the column from the separatory funnel. The funnel is fitted with a stopper and secured in place above the column with a ring clamp. Flow rate of solvent through the column should be adjusted at the beginning of the elution process to 10 ml/min by regulating the opening of the column stopcock. The flow rate will change during the run because the different solvents have different densities and viscosities. However, the stopcock opening should not be changed once it is set. The complete elution series is as follows:

<u>Series II:</u>

A	Diethyl ether 5, hexane 95	300 ml
B	Benzene	500 ml
C	Ethanol 5, chloroform 5, benzene 90	200 ml

D	Ethanol 10, chloroform 10, benzene 80	200 ml
E	Ethanol 25, chloroform 10, benzene 65	200 ml

Proportions are in percent by volume. Collect the fractions in a 250-ml graduated cylinder so the volumes can be measured. Then transfer to 500 ml Erlenmeyer flasks. Do not let the column run dry at any time during the elution series.

2.1.4. Fraction A, Paragraph 2.1.3, should contain 350 ml. Start collecting Fraction A when the sample is added to the column. Continue collecting until the solvent front from Solvent B has reached the bottom of the column. This front can be seen because of the difference in refractive index of the two solvent combinations.

2.1.5. Add 500 ml of benzene to the funnel. This is Solvent B, Paragraph 2.1.3. When Fraction A reaches the sand, begin adding Solvent B to the column. Collect 500 ml of Fraction B.

2.1.6. As each solvent drains from the funnel, add the next solvent combination in the series. Solvent C, Paragraph 2.1.3, contains 10 ml ethanol, 10 ml chloroform, and 180 ml benzene. For Fraction C, collect 150 ml.

2.1.7. Solvent D, Paragraph 2.1.3, contains 20 ml of ethanol, 20 ml chloroform, and 160 ml of benzene. Collect 250 ml of Fraction D.

2.1.8. Solvent E, Paragraph 2.1.3, contains 50 ml of ethanol, 20 ml of chloroform, and 130 ml of benzene. Fraction E should contain 200 ml and drain the column.

2.1.9. Set up a rotary evaporator connected with two Dry Ice-acetone traps in series and then a vacuum pump. Carefully evaporate the solvent from each fraction using a 250-ml round-bottom flask at first and then when the volume has decreased, transfer the material to a previously tared 50 ml round-bottom flask, rinsing several times with a small amount of solvent. When the solvent has evaporated, place the flasks in a heated vacuum desiccator or vacuum oven and pump for 2 hr at 60°C. Weigh the flasks and calculate the weight percent of each fraction using the relationship:

weight percent of fraction = 100 × (weight flask plus sample - weight flask)

2.1.10. For each fraction in Paragraph 2.1.9 having a weight of 150 mg or more, determine the molecular weight using the procedures in "A Cooperative-Molecular Weight Distribution Test" [6].

2.1.11. For each fraction in Paragraph 2.1.9 having a weight of 150 mg or more, determine the hydroxyl equivalent weight by the procedures in "Infrared Determination of Carboxyl and Hydroxyl Contents of Functionally Terminated Polybutadienes" [7].

2.1.12. Report as the results of the test the weight percent of each fraction from Paragraph 2.1.9, the molecular weight of each fraction from Paragraph 2.1.10, and the hydroxyl equivalent weight of each fraction from Paragraph 2.1.11.

2.2. Fractionation of Class 2 HTPB.

2.2.1. The procedure for the functionality fractionation of Class 2 HTPB is the same as that described in Paragraphs 2.1 above for Class 1 HTPB with the following exceptions:

a. In Paragraph 2.1.1, change the volumes of all solvents and the weight of the silica gel to one-half that required in Paragraph 2.1.1.

b. In Paragraph 2.1.2, change the 300-ml volume of the 5% ether-hexane solution to 100 ml and 1.00 g of HTPB sample to 0.50 g.

c. In Paragraph 2.1.3, change the complete elution series to the following:

<u>Series III</u>:

A	Diethyl ether 5, hexane 95	100 ml
B	Diethyl ether 5, hexane 95	200 ml
C	Chloroform 10, ethanol 25, benzene 65	220 ml

d. Change Paragraph 2.1.4 to the following: Fraction A, Paragraph 2.2.1c, should contain 100 ml. When this 100 ml has been collected, add 200 ml more of the 5% ether-hexane solution into the 1-liter separatory funnel and add this to the column (Solvent Mixture B). Collect 200 ml of Fraction B.

e. Change Paragraph 2.1.5 to the following: Mix Solvent C, Paragraph 2.2.1a, consisting of 62.5 ml ethanol, 25 ml chloroform, and 162.5 ml benzene and add to the funnel. When Fraction B reaches the sand, begin adding Solvent C to the column. Collect 250 ml of Fraction C, draining the column.

f. Change Paragraph 2.1.6 to the following: As each solvent drains from the funnel, add the next solvent combination in the series, Paragraph 2.2.1c.

g. Paragraph 2.1.7, omit.

h. Paragraph 2.1.8, omit.

i. In Paragraph 2.1.9, the weight percent of fraction = 200 × (weight flask plus sample - weight flask).

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