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CHARACTERIZATION OF LOW-MOLECULAR-WEIGHT DIFUNCTIONAL POLYBUTADIENES

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SUMMARY

Hydroxyesterification and esterification reactions were made on α,ω -dicarboxy-polybutadiene polymers and the products characterized by both analytical and preparative gel permeation chromatography. The choice of a calibration curve to study transformation of polymers is discussed, as well as the reasons for adopting the MOORE calibration curve relating size of polymers to elution volume. An automatic Fortran program was used to calculate number-average and weight-average sizes of polymers from the chromatograms. Problems associated with changes in the distribution of a polymer during a reaction are examined. To relate sizes of polymers in solution to molecular weight, measurements were made by vapor phase osmometry, light scattering and viscosity. The constancy of the refractive index increments with polymer size has been verified. //

INTRODUCTION

Many problems are encountered in the characterization of low-molecular-weight polymers, polymers with molecular weight lower than about 5000. While the number average molecular weight (\overline{M}_n) can be measured easily by several well-known methods, the weight average molecular weight (\overline{M}_w) and the distribution of these polymers are very difficult if not impossible to obtain. Gel permeation chromatography (GPC) has become a well established technique for the characterization of high-molecular-weight polymers, and it is often possible to extract all the information required from only one chromatogram. It has been used with low-molecular-weight compound¹⁻⁶ but with less success, the main difficulty being the construction of a valid calibration curve.

The first part of this paper will deal with attempts to obtain a suitable calibration curve for low-molecular-weight polymers. In the second part, results obtained in analyzing some low-molecular-weight functionally terminated polybutadienes will be presented.

Calibration of GPC

The calibration of GPC for high-molecular-weight polymers has been fully

* In part.

described⁷. The calibration curve most often used relates the elution volume (V) to the logarithm of the molecular weight (M).

This calibration procedure presents two main difficulties. Firstly, well-characterized molecular weight standards are needed. These are not readily available for low-molecular-weight polymers. Secondly, a separate calibration curve is required for each polymer type studied. To solve this second problem, universal calibration curves have been proposed^{8,9} which, however, do not seem to be valid for low-molecular-weight polymers⁶.

The best solution so far proposed and used by most workers in this field is based on elution volume (V) versus molecular size (\AA) calibration curve. A typical calibration curve of this relationship obtained using four columns of 10^5 , 10^4 , 10^3 , and 10^2 \AA , respectively, is given in Fig. 1. Standard polystyrene and polyethers, from

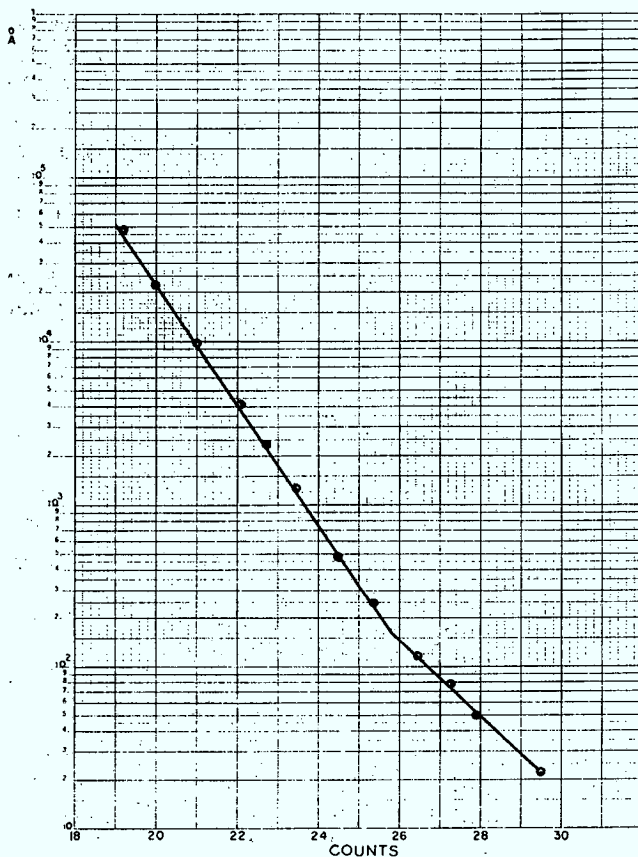


Fig. 1. Calibration curve.

Waters Associates, were used with an Ana-Prep instrument from the same company to obtain the curve. The reproducibility of this curve varied little from month to month giving only small parallel displacements. As can be seen, the curve is made up the most part of two straight line portions. A Fortran computer program was

used to calculate the number average molecular sizes (\bar{A}_n) (eqn. 1), and the weight average molecular sizes (\bar{A}_w) (eqn. 2), as defined by CAZES¹⁰.

$$\bar{A}_n = \Sigma H_i / \Sigma (H_i / A_i) \quad (1)$$

$$\bar{A}_w = \Sigma H_i A_i / \Sigma H_i \quad (2)$$

where

H_i = height of a given segment

A_i = Å size corresponding to this segment on the calibration curve.

This program used is quite similar to the one suggested by Waters¹¹ except that the baseline is found in a different manner. In our technique, the computer begins at the maximum of the peak of the chromatogram and considers values on each side of the distribution curve in a three point sequence until it encounters values which are either similar or increasing. The computer then compares separately the values obtained on both sides of the base and if these do not differ by more than 5% draws a straight line between them to give the base line. The computer does this with readings of the curve taken at 30 sec intervals by a digital curve translator.

The ratio of average sizes gives a measure of the polymer distribution (p) which is written with a subscript A (eqn. 3) to indicate that this distribution was obtained from measurements of the sizes of the polymer in solution. The terminology "volumetric distribution" is proposed for P_A .

$$P_A = \bar{A}_w / \bar{A}_n \quad (3)$$

To obtain an appreciation of the validity of the results from this method, some curve parameters were examined. The resolution factor (h) and the skewing factor (SK) were examined on calibration curves of standard monodisperse products. Our intention was to work under conditions where the resolution would remain constant and skewing negligible. To evaluate measurements on unknown polymers, changes in resolution and skewing must be considered but it is also important to check the constancy of the refractive index increment (dn/dc) over the entire molecular weight range studied.

Resolution and skewing

The Fortran program was extended to calculate the variance (σ) as well as the first and second moment (B_1 and B_2) of the distribution. The usual mathematical definition for these values are given in eqns. 4-6.

$$\sigma = \int_{-\infty}^{\infty} (x - \mu_1)^2 dF \quad (4)$$

$$B_1 = (b_1)^{1/2} = m_3 / m_2^{3/2} \quad (5)$$

$$B_2 = m_4 / m_2^2 \quad (6)$$

where

x = one point on the chromatogram

μ_1' = the arithmetic average of the theoretical distribution

$$F = \int_{-\infty}^{\infty} x(f(x)) dx$$

$$m_n = (1/N) \sum_i^N (x_i - \bar{x})^n$$

n = an integer

N = sampling size

$$\bar{x} = \text{arithmetic average of a sample with } N \text{ points} = \frac{1}{N} \sum_{i=1}^N x_i$$

In the equations above, the variance is related to the resolution of the system, the first moment, B_1 is a coefficient of symmetry equal to 0 for a perfect gaussian distribution, and the second moment B_2 is an acuity coefficient equal to 3 in an ideal case. The results of the calculation for the standard products are given in Table I. As usual, the reduced surface of the peak was also calculated to provide a check on the chromatogram.

TABLE I

POLYESTER AND POLYSTYRENE STANDARDS AT 0.1-0.15% IN TETRAHYDROFURAN

Samples (\AA)	Reduced surface (ml/mg)	σ	B_1	B_2	\bar{A}_n (\AA)	\bar{A}_w (\AA)
20 000	65.5	3.24	0.33	3.25	17 700	22 600
9 800	64.1	3.24	0.34	3.31	9 300	11 400
4 160	63.1	2.74	0.15	2.99	3 800	4 500
2 360	62.0	2.52	0.18	2.95	2 250	2 650
1 250	62.6	2.46	0.12	2.94	1 220	1 380
1 220	59.6	2.47	0.11	2.94	1 228	1 390
480	61.5	2.79	0.18	3.06	470	550
241	61.3	2.72	0.06	2.83	258	293
117	60.7	3.30	0.71	4.10	115	130
78	16.2	2.39	0.16	2.95	77	81
50.5	15.7	2.56	0.14	2.95	51	55

As can be seen, σ is fairly constant for the polystyrene standards smaller than 4160 \AA , except for the 117 \AA sample. In this range, 50.5 to 4160 \AA , B_1 is quite low giving an indication of a very small skewing effect toward the low-molecular-weight side of the distribution. B_2 is also very near to an ideal gaussian distribution. The overall results indicate that very small corrections are to be made. Nevertheless, as is shown in Table II, without any correction, the distributions p_A obtained are higher than the true distribution ($p(t)$) calculated from \bar{M}_n and \bar{M}_w measured by two independent techniques.

In order to obtain a better appreciation of the magnitude of the corrections that should be made for skewing and for the resolution power of the columns, the skewing factor (SK) and the resolution factor (h) were calculated as suggested by HAMIELEC¹² using eqns. 7-9 in their molecular size versions.

$$SK = \frac{A_1(t)}{A_1(\infty)} + \frac{A_2(t)}{A_2(\infty)} - 2 \quad (7)$$

$$h = 1/2\sigma^2 \quad (8)$$

$$A_k(h, SK) = A_k(\infty) \left(1 + \frac{SK}{2} \right) \exp(3 - 2K)D_2^2/4h \quad (9)$$

where

$A_1(t)$ = true average size at peak height for standard 1

$A_1(\infty)$ = measured size at peak height for standard 1

$K = 1, 2 \dots$ where $\bar{A}_1 = \bar{A}_n$ and $\bar{A}_2 = \bar{A}_w$

D_2 = slope of the calibration curve.

TABLE II

POLYETHER AND POLYSTYRENE STANDARDS AT 0.1-0.15% IN TETRAHYDROFURAN

Samples (\bar{A})	$p(t)$	P_A	$p(\infty)$
4160	1.05	1.18	1.06
2360	1.00	1.18	1.06
1250	1.04	1.13	1.02
1220	1.04	1.13	1.02
480	1.01	1.17	1.05
241	1.06	1.14	1.08
117	1.09	1.13	1.07
78	—	1.05	1.00
50.5	—	1.08	1.03

TABLE III

SKEWING FACTORS OF STANDARD PRODUCTS

$A_1(t)$ (\bar{A})	$A_2(t)$ (\bar{A})	SK
4160	2360	0
2360	1250	-0.055
1250	480	-0.08
480	244	-0.04
244	177	-0.05
117	78	-0.04
78	50.5	-0.01
		Average SK = -0.04

Table III gives the skewing factors obtained from two consecutive points along the valid part of the calibration curve. These results are the average of two determinations as calculated from eqn. 7. These values give for the skewing portion of the corrective eqn. 9 (*i.e.* $1 + SK/2$), an average value of 0.98 which, as was expected, is very small.

The resolution factors calculated with eqn. 8 for each standard product, as

determined from the chromatograms in the forward flow mode are given in Table IV and are constant at 2.25. However, the resolution portion of eqn. 9, exp. (3-2K) $D_2^2/4h$, gives different values because of the change in slope of the calibration curve. This gave values of 1.08 for A_n for the first part of the calibration curve with a slope (D_2) of 0.84, and a correction for symmetrical dispersion, and 0.92 for A_w . The second part of the calibration curve of slope 0.535 gave a correction of 1.03 A_n and 0.97 A_w .

TABLE IV

RESOLUTION FACTORS OF STANDARD POLYMERS FOUND IN THE FORWARD FLOW MODE

Samples (A)	<i>h</i> (from the chromatogram)
4160	2.04
2360	2.41
1250	2.58
480	1.88
244	1.92
117	—
78	2.52
50.5	2.41
Average <i>h</i> = 2.25	

However, if these values are used to obtain the true distribution, an overcorrection results giving distributions lower than unity. If the resolution constant is taken to be constant at about twice the value found in Table IV ($h = 4.5$), the results obtained for the distributions of the whole series would be very good as shown in Table II under $p(\infty)$.

Refractive index increment

The main conclusions that can be drawn from the results obtained with unknown polymers concern the constancy of dn/dc . For this, carboxyl-terminated and hydroxyl-terminated polybutadienes (OH polymer made from COOH polymer) were fractionated by preparative GPC in methylene chloride and their dn/dc measured at 25° with a differential refractometer (Model BP-2000 V, Phoenix Precision Instrument Company).

For the carboxyl-terminated polybutadiene, the results as shown in Table V

TABLE V

 dn/dc OF FRACTIONATED CARBOXYL-TERMINATED POLYBUTADIENE

Fraction No.	dn/dc THF	$[\eta]^a$	
		Benzene	THF
1	0.140	0.42	—
2	0.144	—	—
3	0.138	0.18	0.25
4	0.130	0.15	0.21
5	0.132	0.11	0.18
6	0.146	0.09	0.16

^a $[\eta]$: as determined by the one-point method.

indicate a nearly constant value of dn/dc . The intrinsic viscosity, as determined by the one-point method, is also given in this table.

The results for the hydroxyl-terminated polymer are given in Table VI. These are discussed in more detail in the second section. The first conclusion was that while separation against molecular sizes was obtained, it did not produce a polymer of significantly narrower distribution than the starting product. Secondly, the dn/dc is nearly constant for the first ten fractions obtained at about the same value as for the carboxyl-terminated polymer, but the remaining fractions gave values which are lower and scattered. This was probably caused by the presence of products formed during secondary reactions.

TABLE VI

dn/dc OF FRACTIONATED HYDROXYLESTER-TERMINATED POLYBUTADIENE

Fraction No	\bar{A}_n (Å)	\bar{A}_w (Å)	dn/dc THF	\bar{M}_n (VPO)
1	458	806	0.142	
2	387	588	0.147	
3	320	493	0.159	
4	284	477	0.140	
5	284	533	0.157	
6	308	560	0.104	
7	315	536	0.140	
8	314	539	0.137	4600
9	308	511	0.126	
10	288	470	0.133	
11	269	443	0.090	4200
12	240	397	0.097	4100
13	229	386	0.073	3700
14	204	347	0.095	3300
15	196	329	0.130	2900
16	181	307	0.100	2200
17	171	300	0.096	
18	157	268	0.142	

Finally, our study on the validity of the calibration curve has shown that a very small correction for skewing is needed. The resolution factor must be reevaluated but indications are that it is probably a constant. Quite good gaussian chromatograms were obtained with standard polymers in the 4160 Å to 50.5 Å range. The dn/dc ratio appeared to be constant in the molecular range of the polybutadienes examined.

APPLICATION OF GPC TO LOW-MOLECULAR-WEIGHT POLYBUTADIENE

Carboxyl-terminated polybutadiene

First the instrument was used to study lot-to-lot variation of carboxyl-terminated polybutadienes (HC-434) as received from the manufacturer (Thiokol Corporation). The results in Table VII show that lot 90M is quite different from the others because of a wider distribution. Lot 93M has average sizes slightly larger than the others in Table VII but has a narrow distribution. The six remaining lots show a slight

tendency towards narrower distributions especially in the last lots. These values are lower than those published⁴ for lot 30M (1.81, 2.07 and 1.73). In the latter work, however, the authors experienced some difficulties with absorption of the carboxyl-end-groups on the polystyrene gel.

TABLE VII

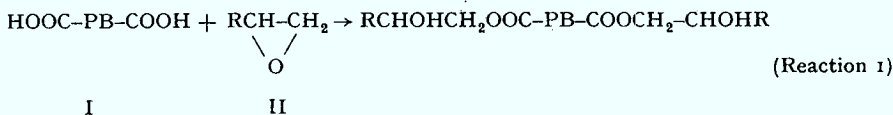
LOT-TO-LOT VARIATIONS FOR HC-434^a

Lot	\bar{A}_n (Å)	\bar{A}_w (Å)	P_A	M_n (VPO)
39M	234	376	1.61	3200
84M	247	423	1.71	3400
90M	253	491	1.94	3600
92M	235	402	1.71	
93M	259	412	1.59	
100M	249	410	1.66	
121M	238	374	1.57	
127M	233	354	1.52	

^a Four columns of respective pore sizes, 10³, 10³, 10⁴ and 10⁵ Å.

Hydroxyl-terminated polybutadienes

Difficulties arose during the development phase of a study initiated in our laboratory on the hydroxylesterification (reaction 1) of a carboxyl-terminated polybutadiene (PB) (I), using alkene oxides.



This reaction was first followed by acid number titration and bulk viscosity measurements on a Rotovisco Haake rotating viscometer giving the pattern shown in Fig. 2. In the first part of the reaction, the viscosity of the isolated polymer decreases slowly from an initial value of 200 P to about 150 P as the acid number is lowered to 2% of its initial value. Upon further reaction, the viscosity increases abruptly to 1000 P or more.

Various hypotheses are possible to explain this viscosity increase. However, GPC appeared to be a good technique to investigate what was happening to the polymer molecules as the reaction was proceeding.

If polymer I is reacted with ethylene oxide (II, R=H) and the resulting isolated polymer is analyzed by GPC at different reaction times, the changes of \bar{A}_n and \bar{A}_w shown in Fig. 3 are found.

These curves can be separated into two portions similar to the viscosity curve (Fig. 2). In the first part, small increases in sizes are measured as the \bar{A}_n is increased by 8 Å from the starting product to its extrapolated value at nil acidity number, and the \bar{A}_w increased by 33 Å. The second part shows an abrupt increase to 380 Å for \bar{A}_n and 845 Å for \bar{A}_w . An important aspect of the results, which is not possible to

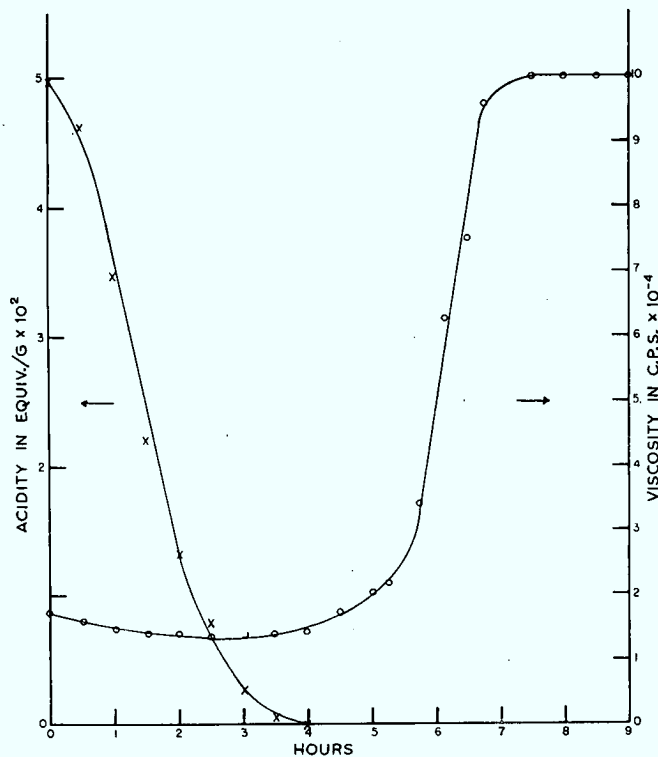


Fig. 2. Viscosity and acidity changes during hydroxyesterification reaction.

TABLE VIII

GPC OF THE PRODUCTS OF THE REACTION BETWEEN CARBOXYL-TERMINATED POLYBUTADIENE AND ETHYLENE OXIDE

Samples No.	Reduced surface (ml/mg)	σ	\bar{A}_n (Å)	\bar{A}_{10} (Å)	P_A
1	75.8	5.4	236	387	1.64
2	77.7	5.7	255	468	1.83
3	73.1	5.5	244	407	1.67
4	76.3	5.5	243	408	1.68
5	74.8	5.5	238	396	1.66
6	77.0	5.5	248	419	1.69
7	79.0	5.6	240	403	1.68
8	78.6	5.7	243	420	1.73
9	75.2	5.5	250	420	1.68
10	77.0	6.0	303	589	1.94
11	74.1	6.5	381	845	2.2

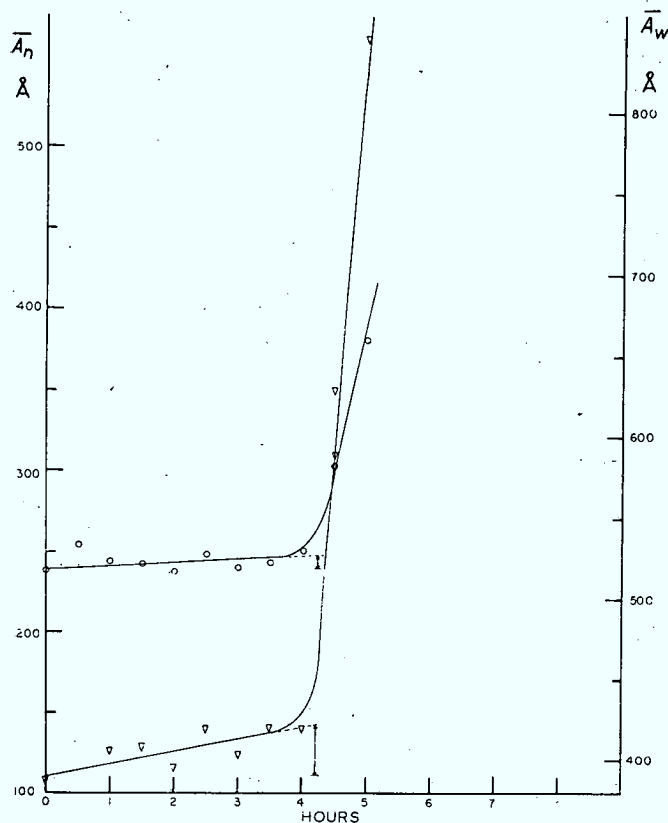


Fig. 3. Hydroxylesterification by ethylene oxide.

visualize from this figure but which is easily noted from Table VIII, is that the distribution values remain nearly constant, except for sample 2, from the first to the ninth sample, after which there was a sharp increase. This can also be observed with the variance of the chromatogram as the increase in size is accompanied by an increase of the width of the distribution curve.

Secondly the reaction with propylene oxide (II, $R=CH_3$) was examined. In this case, any possible effect of the solvent evaporation on reacted polymer was also investigated. The polymer fractions taken out of the reaction kettle at different reaction times were measured, both in the presence of solvent (unevaporated polymer) and after stripping out all volatile products (evaporated polymer). The results for the \bar{A}_n and \bar{A}_w are shown in Fig. 4.

It was found that the size values were always slightly higher for the evaporated polymers than for the unevaporated ones. However, this effect was so small and so regular that we were led to think that it could have been caused by a slight shifting in the calibration curve. In any case, these curves can also be divided into two portions. The first one shows an increase of 9 Å for the \bar{A}_n and 39 Å for the \bar{A}_w at zero acidity number. The second portion increases rapidly as was the case with the ethylene oxide adduct, but this time, as the reaction was investigated further, a leveling off appeared

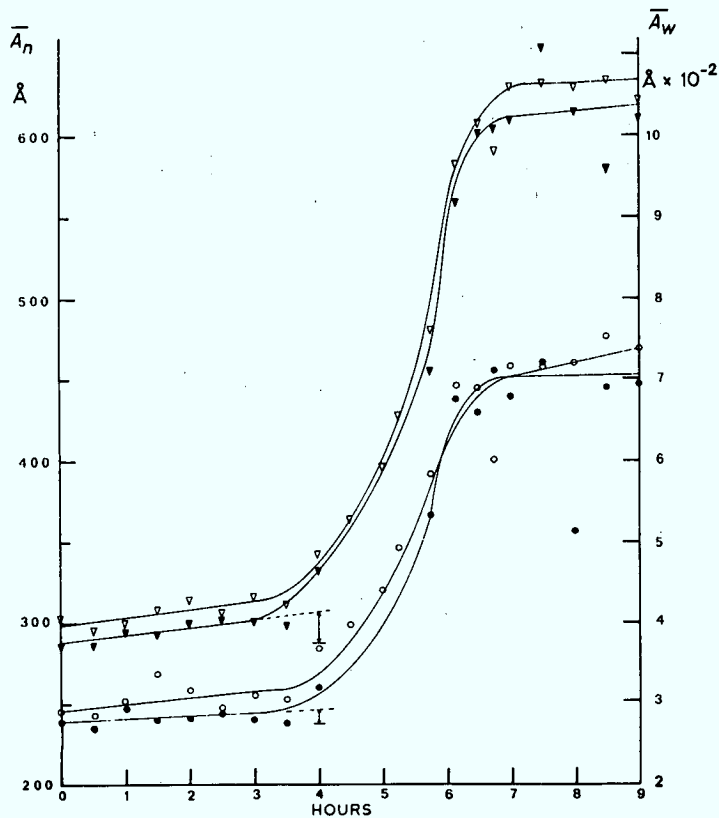


Fig. 4. Hydroxylesterification by propylene oxide. $\circ = \bar{A}_n$ not evaporated; $\bullet = \bar{A}_n$ evaporated; $\nabla = \bar{A}_w$ not evaporated; $\blacktriangledown = \bar{A}_w$ evaporated.

TABLE IX

GPC OF THE PRODUCTS OF THE REACTION BETWEEN CARBOXYL-TERMINATED POLYBUTADIENE AND PROPYLENE OXIDE

Samples No.	Reduced surface (ml/mg)	σ	\bar{A}_n (Å)	\bar{A}_w (Å)	P_A
1	73.7	5.1	239	371	1.55
2	76.3	5.2	248	396	1.60
3	74.1	5.5	241	403	1.67
4	77.1	5.5	241	406	1.68
5	77.0	5.8	260	468	1.80
6	73.5	5.9	367	712	1.94
7	74.8	6.6	430	1004	2.33
8	77.6	6.6	439	1021	2.33
9	82.1	7.6	357	1032	2.89
10	93.7	6.5	446	1022	2.29

for an \bar{A}_n of about 460 Å, which is almost double the initial value, and for an \bar{A}_w value of about 1050 Å. In Table IX, the distribution and variance values are seen to increase slowly from the first to the eighth sample before rising to a significantly higher value.

The same effect was noticed when the reaction with butylene oxide (II, R=C₂H₅) was considered. Fig. 5 summarizes these results. In this case, there was no evidence of an increase of molecular sizes caused by evaporation in the first portion of the curve, but large differences were noted in the leveling-off portion. The first part of the curve gives an increase in \bar{A}_n values of 14 Å and for \bar{A}_w , of 40 Å. The second part shows increases of about the same extent as those found for the propylene oxide transformed polymer at least for the unevaporated samples. Values of Table X show very small effects on the distribution from the first to the ninth sample. For the other sample, the distribution increases to a value higher than 2.

A summary of the GPC results is given in Table XI. These results, as well as the

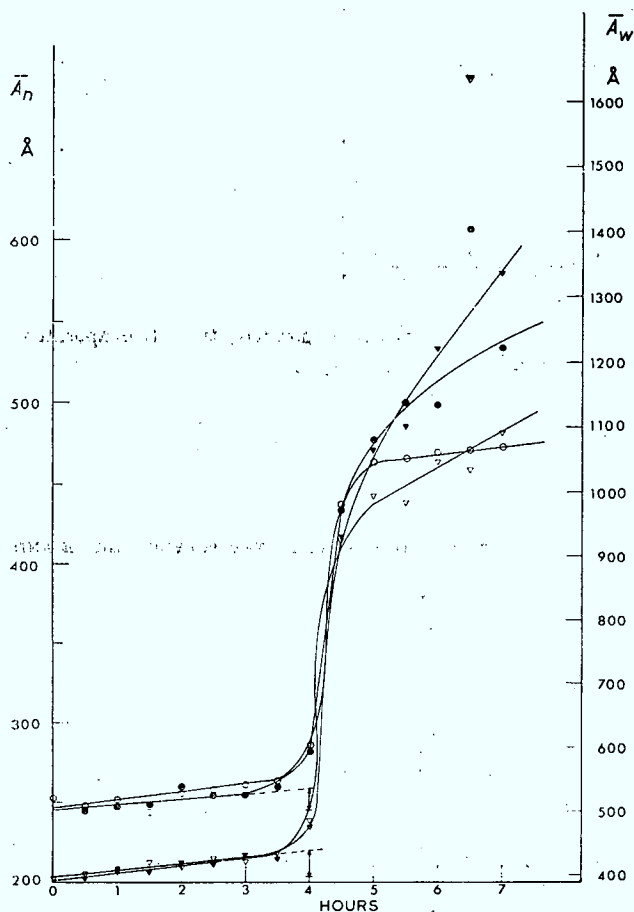


Fig. 5. Hydroxyesterification by butylene oxide. $\circ = \bar{A}_n$ not evaporated; $\bullet = \bar{A}_n$ evaporated; $\nabla = \bar{A}_w$ not evaporated; $\blacktriangledown = \bar{A}_w$ evaporated.

TABLE X

GPC OF THE PRODUCTS OF THE REACTION BETWEEN CARBOXYL-TERMINATED POLYBUTADIENE AND BUTYLENE OXIDE

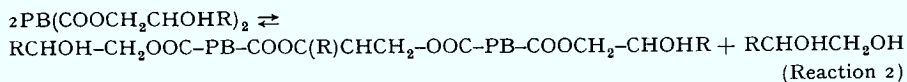
Samples No.	Reduced surface (ml/mg)	σ	\bar{A}_n (Å)	\bar{A}_w (Å)	P_A
1	77.8	5.3	245	395	1.61
2	81.3	5.4	248	409	1.65
3	77.4	5.4	248	404	1.63
4	75.8	5.2	260	419	1.61
5	77.0	5.3	257	416	1.62
6	80.0	5.5	255	433	1.70
7	76.5	5.3	260	425	1.63
8	77.9	5.5	283	487	1.72
9	75.1	6.2	435	932	2.14
10	75.0	6.4	477	1063	2.23
11	70.7	6.3	500	1100	2.20
12	75.5	6.7	498	1221	2.45
13	78.1	7.0	606	1641	2.71
14	71.9	6.8	533	1346	2.52

TABLE XI

SUMMARY OF THE RESULTS OF HYDROXYL ESTER-TERMINATED POLYBUTADIENES

Reacting epoxides	First part of the curves			Final equilibrium state		
	$\Delta\bar{A}_n$ (Å)	$\Delta\bar{A}_w$ (Å)	P_A	\bar{A}_n (Å)	\bar{A}_w (Å)	P_A
Ethylene	8	33	1.7	—	—	—
Propylene	9	39	1.7	460	1050	2.3
Butylene	14	40	1.7	470	=1050	2.3

fact that almost identical infrared and NMR spectra are obtained for all these products, agree with the hypothesis that the first portion of the curves corresponds to the hydroxyl esterification reaction. As the acidity decreases close to zero, a secondary transesterification reaction (reaction 2) takes place rapidly doubling the molecular sizes and widening the distribution until an equilibrium state is reached.



The summary of Table XI does point out some additional problems. It must be emphasized at this point that the results are presented at their present stage of study, and not fully resolved.

The increases in size were calculated from the values of HENDRICKSON AND MOORE¹ and HENDRICKSON³ with the hypothesis that the polymer is difunctional and that every functional group reacts ideally. The calculated increases in sizes were compared to measured values in Table XII. The comparison is very good considering the

TABLE XII

SIZES OF THE SUBSTITUENTS

Substituents	Calculated (\AA)	Measured (\AA)
$-\text{CH}_2\text{CH}_2\text{O}-$	11.6	8
$-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$	14.2	9
$-\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{O}-$	16.6	14

possibility of changes in the association between solvent molecules and functional groups. However, if the reaction were to take place in the ideal manner as these first results indicate, it would lead to corresponding calculated increases of \overline{A}_w situated between 4 to 8 \AA . These values are lower than the ones obtained (33–40 \AA).

The obvious answer to this lack of agreement is that near the end of the hydroxyl esterification a transesterification reaction begins to take place and by doubling molecular sizes, it produces a more noticeable effect on the \overline{A}_w than on the \overline{A}_n , as the \overline{A}_w is more sensitive to high-molecular-weight polymers. More information on the initial stage of the transesterification reaction is needed to resolve the statistical calculations.

It was thought that more information could be obtained by not only looking

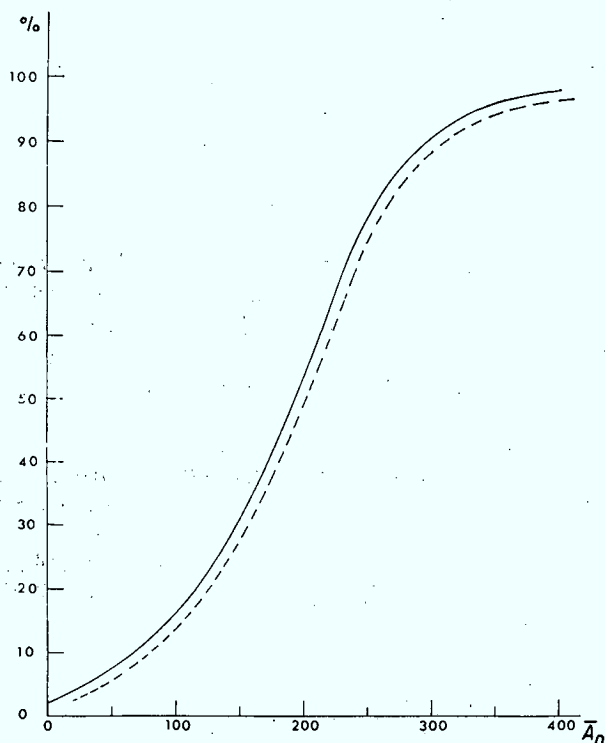


Fig. 6. Ideal change in distribution curve.

at the added results of the average sizes but by looking at the changes in sizes all along the distribution curves. Ideally (Fig. 6) two parallel distribution curves should be obtained, or at least the differences between the distribution of the starting product and that of a polymer obtained at a given stage of the reaction should vary regularly. However, the results of Fig. 7 were obtained showing important irregularities in the curves.

Evidently, it is important to determine if these irregularities are technical artifacts or if they are significant. To get a clearer picture of the reaction mechanism a model reaction was needed, and an esterification of carboxyl groups by an excess of alcohol was chosen.

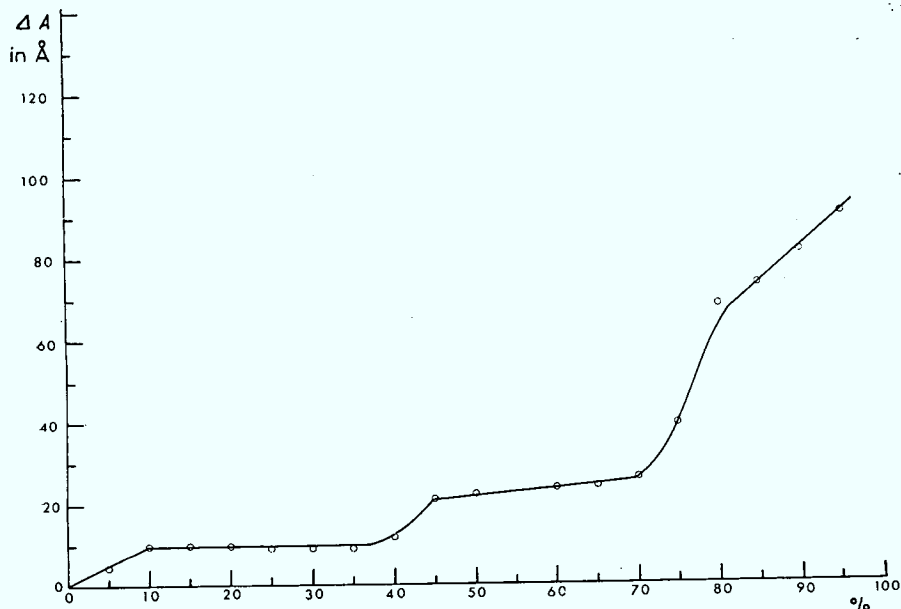


Fig. 7. Distribution difference between initial and isolated polymer.

Ester-terminated polybutadiene

GPC studies on the methylesters of various carboxyl-terminated polybutadienes have been published². They give increased or decreased sizes after esterification depending on the polymer used, but good reproducibility of distribution values are obtained.

Two different carboxyl-terminated polybutadienes (HC-434, Thiokol Corporation and Telagen CT 2000, General Tire) were esterified with various alcohols. The GPC results on the esterified HC-434 are given in Table XIII. With the exception of the ethyl ester product, it is seen that the sizes increase slowly with the length of the ester chain. However, the size decreases with the more compact end-groups such as alcohol containing side substituents. The results of the esterified Telagen are in Table XIV. Again mean sizes increased with the length of the ester chain but this time more slowly than was the case with HC-434. The butanol adduct does not reflect the general

TABLE XIII

GPC OF ESTERIFIED CARBOXYL-TERMINATED POLYBUTADIENES (HC-434)

Types of ester end-group	Reduced surface (ml/mg)	σ	\bar{A}_n (Å)	\bar{A}_{10} (Å)	P_A
—	75.18	5.4	237	399	1.68
Methyl	75.69	5.25	242	403	1.67
Ethyl	78.31	5.3	224	378	1.69
Propyl	71.62	5.2	251	423	1.69
Butyl	74.10	5.1	257	429	1.67
Isopropyl	78.00	5.2	229	379	1.65
sec.-Butyl	77.37	5.3	233	399	1.71
tert.-Butyl	71.56	5.3	235	395	1.68

TABLE XIV

GPC OF ESTERIFIED CARBOXYL-TERMINATED POLYBUTADIENE (TEL)

Types of ester end-group	Reduced surface (ml/mg)	σ	\bar{A}_n (Å)	\bar{A}_{10} (Å)	P_A
—	72.20	5.0	142	218	1.53
Methyl	72.35	4.6	143	206	1.44
Ethyl	74.05	4.8	144	216	1.50
Propyl	71.32	4.4	146	207	1.42
Butyl	72.20	5.0	142	218	1.53
Isopropyl	73.11	5.0	148	234	1.58
sec.-Butyl	71.12	4.5	149	212	1.42
tert.-Butyl	71.86	4.9	146	221	1.52

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trend. Surprisingly, compact end-groups (isopropanol, etc.) gave a greater increase of the total polymer size than other products.

Differences all along the distribution curves are now under consideration and will be decreased in later papers.

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