Molecular Weight Characterization of Polybutadiene Rubber with High Molecular Weight and Broad Molecular Weight Distribution

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Synopsis

Following the molecular weight characterization of two polybutadiene samples, it was found that $\overline{M}_w$ from gel permeation chromatography with universal calibration and light scattering were in agreement, but $\overline{M}_n$ by gel permeation chromatography was less than $\overline{M}_n$ from membrane osmometry. A more detailed analysis revealed that the high molecular weight and broad molecular weight distribution of the two samples forced two corrections to the membrane osmometry results for (a) diffusional layer effects caused by high solution viscosities, and (b) solute permeability of the membrane. In the latter effect, the high viscosities of the solutions prevented actual diffusion through the membrane, but "reflection" of these species as defined by the Staverman coefficient prevented an accurate $\overline{M}_n$ determination. After making these corrections, it was found that $\overline{M}_n$ from membrane osmometry using a very tight membrane was in very good agreement with $\overline{M}_n$ from gel permeation chromatography. A method is demonstrated for obtaining $\overline{M}_n$ from a combination of membrane osmometry and gel permeation chromatography, where membrane osmometry data from membranes of different porosities (after corrections for diffusional layers and membrane reflection) are used to verify the accuracy of the gel permeation chromatography data as representing the true molecular weight distribution, allowing the gel permeation chromatography data to be used to calculate $\overline{M}_n$.

INTRODUCTION

Polymer molecular weight characterization in industrial laboratories is quickly becoming dominated by the use of gel permeation chromatography (GPC). Despite its relative ease of operation and quickness of testing, compared to more absolute characterization tools such as membrane osmometry and light scattering, GPC suffers from its reliance on calibration. By a combination of universal calibration (UC) and appropriate Mark–Houwink coefficients, molecular weights can be calculated routinely. However, prior to establishing a GPC procedure for a specific polymer type, a certain amount of absolute molecular weight measurements must be made to verify the accuracy of GPC.

Some commercial polybutadiene polymers have a high molecular weight and a broad molecular weight distribution. In establishing GPC procedures in this laboratory for the molecular weight analysis of these rubbers, values of number–average molecular weight ($\overline{M}_n$) from membrane osmometry, weight-average molecular weight ($\overline{M}_w$) from light scattering, and these values from universally calibrated GPC (UC–GPC) did not agree, even though all the normal precautions were taken for each type of experimental measurement to ensure that accurate data were obtained and other polybutadiene and polystyrene samples of lower molecular weight and narrower molecular weight distribution had presented no problems in earlier work. In taking a more detailed look at these three charac-

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terization techniques and trying to ascertain why their results did not agree, it was found that the samples' peculiar molecular weight distribution, i.e., the high molecular weight and broad molecular weight distribution, created peculiar problems for the membrane osmometry method. The oddities of the samples' molecular weight distribution did not affect the light scattering and GPC measurements. These problems were not readily apparent in the membrane osmometry data, but after auxiliary measurements were made to correct for the deficiencies in the data caused by these peculiarities, all the molecular weight data agreed.

This article reviews the characterization of two polybutadiene rubber samples of high molecular weight and broad molecular weight distribution for $\overline{M}_n$ and $\overline{M}_w$ by membrane osmometry, light scattering, and UC–GPC which were carried out in this laboratory. These samples are now being used in our laboratory as secondary GPC standards. It is illustrative of the problems encountered when accurately characterizing commercial polymers with peculiar molecular weight and molecular weight distribution properties.

EXPERIMENTAL

All commercial rubber samples were produced by The Goodyear Tire and Rubber Co., Akron, Ohio. Two different production lots of one type (PBd-N) of commercial polybutadiene sample, PBd-N-1 and PBd-N-2, and a sample of another type of oil-extended commercial rubber (PBd-D), PBd-D-1, were studied. Both types are of high molecular weight, broad molecular weight distribution, and of almost entirely 100% cis-1,4 microstructure. Characterized polybutadiene standards were from two commercial sources: Phillips Petroleum Co., Bartlesville, Oklahoma, and The Goodyear Tire and Rubber Co. Characterized polystyrene standards came from two commercial suppliers, Waters Associates, Framingham, Massachusetts, and The Goodyear Tire and Rubber Co., and from Professor D. McIntyre, The Institute of Polymer Science, Akron University, Akron, Ohio. All standards were of very narrow molecular weight distribution and of suitable quality as molecular weight standards. Polybutadiene standards ranged from 450 to 450,000 molecular weight (Table I); polystyrene standards ranged from 600 to 10 million molecular weight.

Infrared spectroscopic measurements were made from CS_2 solutions of the sample using a Beckman IR-20 infrared spectrometer. Refractive index mea-

TABLE I
Polybutadiene Standards

	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
Phillips standards			
A	423	286	1.48
B	332	226	1.47
C	272	206	1.32
D	170	135	1.26
E	17.0	16.1	1.06
Goodyear standards			
F	—	2.350	—
G	—	0.960	—
H	0.439	0.411	1.07

surements were made on thin films of sample with a Bausch and Lomb model 3L Abbé refractometer. Light scattering measurements were made with a standard Sofica light scattering photometer. Refractive index increment measurements were made using a Brice–Phoenix No. 1993 differential refractometer. The Melabs model CSM-2 and Mecrolab model 502 membrane osmometers were used with membranes purchased from Arro Laboratories, Joliet, Illinois, and Millipore Corporation, Bedford, Massachusetts. Four gel permeation chromatographs from Waters Associates were used, with the following column sets: Column set A was operated on chloroform at 30°C, with seven 4-ft Styragel columns (10^7, 10^6, 10^5, 10^4, 10^4, 10^3, and 10^2 Å). Column set B was operated on toluene at 30°C, with nine 4-ft Styragel columns (10^7, 10^7, 10^6, 10^6, 10^5, 10^4, 10^3, 10^3, and 10^2 Å). Column set C was operated on chloroform at 30°C, with six 4-ft Styragel columns (10^2, 10^2, 10^3, 500, 10^3, and 10^2 Å). Column set D was operated on THF at 30°C, with seven 4-ft Styragel columns (10^6, 5×10^5, 10^5, 3×10^4, 10^4, 10^4, and 3×10^3 Å). In all cases, differential refractometer detectors were used. Techniques and equipment for the filtration of polymer solutions and for determining intrinsic viscosities were those employed earlier.[1,2] The three polybutadiene samples contained antioxidant at about 0.5 wt %, but this was removed before the membrane osmometry experiments were made.

DISCUSSION

Two polybutadiene samples were characterized: PBd-N-2 and PBd-D-1. In addition, sample PBd-N-1, a second production lot almost identical to PBd-N-2 in molecular weight and molecular weight distribution, was partially characterized.

Auxiliary Measurements

Before the characterization can be done, some preliminary experiments have to be done in anticipation of some problem areas that might develop during characterization and to provide standards with which to deal with them.

The distribution of microstructure with molecular weight (M) was sought. The PBd-N-2 sample was fractionated and the fractions were characterized for refractive index and microstructure by infrared spectroscopy (Table II). Results indicated a good molecular weight fractionation into 12 fractions and no change in refractive index and vinyl-1,2 content over the entire molecular weight distribution. There was only a small increase in *trans*-1,4 content in the 7% lowest molecular weight species. No auxiliary corrections are needed to reduce the observed chromatogram to units of weight fraction. The constancy of vinyl-1,2 allows the use of one set of Mark–Houwink coefficients (that for low vinyl-1,2 content polybutadiene) over the entire molecular weight distribution.

Further, the use of coefficients established with lithium-polymerized polybutadiene can be used, since it has been shown in the literature that polybutadienes of high *trans*-1,4 and high *cis*-1,4 content (but all of low vinyl-1,2 content) have the same $[\eta]$–M relationships, with only high vinyl-1,2 rubbers differing in their $[\eta]$–M relationships. These trends for both refractive index and microstructure are assumed to apply to PBd-D-1 as well, since it is polymerized in a system similar to PBd-N-2. The fact that at least 97% of the original sample

TABLE II
Composition of PBd-N-2

Fraction number	Weight, g	wt %	ml Bz	ml MeOH	% MeOH	Description	nD^{25}	% cis-1,4	% trans-1,4	% vinyl-1,2
(Total)	5.1676			0	0	(rubbery solid)	1.5217	97.9	0.6	1.6
1	1.5540	31.0	1000	202	16.8	(leathery plastic)	1.5206	98.3	0.6	1.1
2	0.5135	10.2	0	6	17.2		1.5226	—	—	—
3	0.1107	2.2	0	5	17.6	→	1.5215	—	—	—
4	0.6133	12.2	0	10	18.2		1.5216	—	—	—
5	0.1083	2.2	0	4	18.5		1.5210	—	—	—
6	0.2366	4.7	0	9	19.1	(rubbery solid)	1.5219	—	—	—
7	0.6343	12.6	0	16	20.1		1.5220	—	—	—
8	0.4792	9.6	0	26	21.8		1.5219	—	—	—
9	0.3210	6.4	0	36	23.9	→	1.5220	—	—	—
10	0.0990	2.0	0	60	27.2	(oily liquid)	1.5215	96.1	1.5	2.4
11	0.1566	3.1		residue	—		1.5206	63.2	35.6	1.2
11b	0.1858	3.7		residue	—		1.5218	71.1	27.7	1.3
	5.0123	99.9					ave. = 1.5216			
							(± 0.0006)	(IR determination, ± 1%)		

% Recovery = 97.0

was polybutadiene indicates extremely low levels of nonrubber contamination. This is critical to the GPC and membrane osmometry measurements, and it can safely be assumed that all pertinent data will result from the rubber only and no auxiliary corrections to either the GPC curve or osmotic pressure readings need be made for this effect.

After confirming all molecular weight characterization data on the standards by our own measurements, Mark–Houwink coefficients were determined or confirmed in several solvents by plotting zero-shear intrinsic viscosity versus molecular weight. These are listed in Table III. All GPC solvents were included. It was found that for polystyrene the Mark–Houwink coefficients K and α changed with molecular weight, while those for polybutadiene did not, over extended molecular weight ranges. This was important for the GPC analyses because the range of molecular weight entities in PBd-N-1, PBd-N-2, and PBd-D-1 is appreciable and extends over the different molecular weight regions listed in Table III.

A blend of polystyrene standards was made which approximated the molecular weight distribution, $\overline{M}_w$, $\overline{M}_n$, and the breadth of the molecular species (particularly the lower end of the molecular weight distribution) of PBd-N-2. The GPC curves (shown later) of this blend and PBd-N-2 were found to be similar. Average molecular weights calculated from the weight percentages and molecular weights of each standard in the blend are listed in the last column of Table X. The molecular weight distribution contained species from 2000 to 7,200,000 molecular weight, almost exactly the breadth of molecular weight species in PBd-N-2.

An error in the GPC experiment would arise if the polybutadiene sample were to adsorb onto the column packing during its travel through the column. This would create an artificial broadening of the chromatogram, a lowering of $\overline{M}_n$, and make interpretation difficult. To check for this, 50 cc of a 0.2% toluene solution of PBd-N-2 was added to 5 cc dry 10^7 Å Styragel column packing and mixed overnight. After the slurry was allowed to settle, a check of the polymer concentration in the solution above the Styragel indicated that no adsorption onto the packing had occurred. Adsorption of rubber during the GPC separation would not be suspected in toluene or the other more polar solvents, THF and chloroform. This was later supported by the actual GPC data of the polybutadiene standards.

GPC analyses based on universal calibration is complicated greatly when

TABLE III
Mark–Houwink Coefficients

	Solvent/temp., °C	$K \times 10^4$	α	Molecular weight range
Polybutadiene	THF/30	4.57	0.693	$500 < M < 10,000,000$
	Toluene/30	5.19	0.679	$500 < M < 10,000,000$
	Chloroform/30	4.51	0.704	$190 < M < 10,000,000$
Polystyrene	Chloroform/30	1.36	0.708	$24,000 < M < 10,000,000$
	Chloroform/30	11.1	0.502	$160 < M < 24,000$
	Toluene/30	1.20	0.714	$17,000 < M < 10,000,000$
	Toluene/30	9.86	0.499	$560 < M < 17,000$
	THF/30	1.05	0.731	$36,000 < M < 10,000,000$

analyzing branched polymers. In this case more information than just linear Mark–Houwink coefficients are needed to calculate molecular weights. However, earlier work[3] as well as the literature had shown that polybutadiene made with nickel-based catalysts (PBd-N type) was predominantly linear, while titanium-based catalyst (PBd-D type) made rubber only slightly branched. Corrections for branching were not made and will not be dealt with here; the consequence of this omission will be an underestimation of $\overline{M}_w$ by GPC while the true $\overline{M}_n$ will still be calculated.

Normally, neither type of polybutadiene rubber contains gel. This was found for all the samples studied here. For the light scattering and GPC studies, all solutions were filtered through 0.45-μ filters before analysis, while for membrane osmometry the solutions were analyzed without prior filtration.

All membrane osmometry work was done at temperatures above ambient. Polymer concentrations determined at room temperature were corrected for solvent expansion upon heating.

Characterization of PBd-N-1

As a preliminary study, PBd-N-1 was characterized and a comparison was made of the results from light scattering, membrane osmometry, and GPC. (1) The data from the light scattering photometer resulted in a rectilinear Zimm plot and, when coupled with dn/dc determined with the differential refractometer, provided an unambiguous value of $\overline{M}_w$.[4] No interferences such as depolarization of the scattered light were observed.[5] A 4% error in dn/dc, coupled with the error in the scattering data, resulted in an error of about ±10% for $\overline{M}_w$. (2) $\overline{M}_n$ was determined by membrane osmometry using a Mechrolab 502 membrane osmometer and an S&S-08 membrane.[4] The square root plot gave a straight-line relationship to the data. Abnormally long equilibration times were encountered but no evidence for solute permeability of the membrane was seen. An error of about ±10% in $\overline{M}_n$ was estimated. (3) Two GPCs were used on different solvents. Universal calibration[6] techniques were employed to calculate molecular weights from the chromatogram using the appropriate Mark–Houwink coefficients of Table III.

Results are shown in Table IV. $\overline{M}_w$ values from two GPCs (382,000–391,000) are in agreement and are considered to be in good agreement with that from light scattering (381,000 ± 40,000). $\overline{M}_n$ values from two GPCs are in reasonable agreement (78,800–86,200) but are much lower than that determined by membrane osmometry (114,000 ± 12,000).

TABLE IV
Characterization of PBd-N-1

		Column set A	Column set B
	Light scattering[a]		
$\overline{M}_w$	381,000 ± 40,000	382,000	391,000
	Membrane Osmometry[b]		
$\overline{M}_n$	114,000 ± 12,000	86,200	78,800

[a] Benzene, 30°C: $A_2 = (5.3 \pm 0.6) \times 10^{-4}$, $\langle S^2 \rangle_z^{1/2} = 1640 \pm 90A$.

[b] Toluene, 37°C, S&S-08 Membrane, Mechrolab 502; $A_2 = (9.6 \pm 1.7) \times 10^{-4}$.

The data indicated that no problems should be expected in determining $\overline{M}_w$ from GPC (using column sets as in Table IV) for samples like PBd-N-1; but because of the observed discrepancies in membrane osmometry and GPC results for $\overline{M}_n$, it was decided to do a more in-depth study of the characterization to find out which was in error. Two other samples, PBd-N-2 and PBd-D-1, were selected for this evaluation and all final characterizations. The literature is unclear as to where the problem lies, although it is clear that high molecular weights and broad molecular weight distributions can deleteriously affect both membrane osmometry and GPC if certain precautions are not taken. Thus, before beginning the characterization of PBd-N-2 and PBd-D-1, the necessary experiments were made for both GPC and membrane osmometry to find out where the problem was in determining $\overline{M}_n$ for PBd-N-1.

Calibration of GPC Column Sets

Errors in the GPC can arise from several areas. Studies of these factors have been made and discussed before[1,2] and only the GPC operational variables are summarized here. Column sets A and B were found to have essentially no spreading[2] when characterized narrow molecular weight distribution polystyrene standards from 10,000,000 to 2,000 molecular weight were evaluated. Calibrations were developed using ultrahigh molecular weight standards, and over the elution volume where PBd-N-1 eluted, the calibration curve was an interpolated one. Resolution was rendered adequate over the entire elution volume region of PBd-N-1 by using abnormally long column sets, special high and low molecular weight resolving columns, and a column combination specially designed for this molecular weight distribution.

Further work was performed with these column sets (Table V). Analyses of the polystyrene blend (see Table X) on column set A indicated that it generated accurate molecular weight data (8 and 3% errors in $\overline{M}_w$ and $\overline{M}_n$, respectively) for this sample of broad molecular weight distribution similar to that of PBd-N-1. For both column sets, all narrow molecular weight distribution polybutadiene standards appeared to be analyzed accurately for molecular weight and molecular weight distribution by GPC (see Table I). For comparison purposes, Table V contains molecular weight distribution data calculated from GPC experiments using a special oligomeric column set having resolution from 100 to 10,000 molecular weight.[7] All calculations were done without the aid of spreading corrections. Since spreading is expected to rapidly diminish as the molecular weight distribution of the sample increases, these data suggest that the chromatogram of PBd-N-1 represents its actual molecular weight distribution with accurate calculated $\overline{M}_w$ and $\overline{M}_n$. No preferential spreading (especially of the low molecular weight tail) of PBd-N-1 is expected to occur and reduce the calculated $\overline{M}_n$ from GPC.

These results do not indicate any problems in the GPC of PBd-N-1. Attention was next paid to the membrane osmometry of PBd-N-1. Before the evaluation of the membrane osmometry data is presented, however, some theoretical discussion needs to be made, based on previous studies done in the literature.

TABLE V
GPC Analyses of Standards[a]

	Column set A			Column set B			Column set C		
	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
Blend standard	433,000	80,600	5.37	—	—	—	—	—	—
Polystyrene									
A	387,000	302,000	1.28	444,000	401,000	1.11	—	—	—
B	325,000	238,000	1.37	350,000	321,000	1.09	—	—	—
C	263,000	199,000	1.32	272,000	249,000	1.09	—	—	—
D	—	—	—	—	—	—	—	—	—
Polybutadiene									
E	17,200	16,100	1.06	17,300	15,800	1.09	—	—	—
F	—	—	—	—	—	—	2,700	2,600	1.04
G	—	—	—	—	—	—	946	774	1.22
H	—	—	—	—	—	—	462	395	1.17

[a] Calculated using "universal calibration" and Mark–Houwink coefficients of Table III.

Aspects of Membrane Osmometry

Membrane osmometry works best when the sample is monodisperse and the membrane is semipermeable to the polymer. In this case an accurate $\overline{M}_n$ is determined. With samples with broad molecular weight distribution, $\overline{M}_n$ will generally be overestimated. Usually, membrane osmometry on unfractionated samples is not recommended and is known to not be reliable.[8] There are two unique properties of PBd-N-1 that may cause problems during membrane osmometry testing. Because of its high $\overline{M}_w$, concentrations needed to give reasonably high osmotic heights, 5–13 g/l., will be fairly viscous, 3–10 times that of the solvent. Also, owing to its broad molecular weight distribution, there is an appreciable amount of low molecular weight species that can penetrate the membrane. Because of these factors, PBd-N-1 represents the worst type of sample to be analyzed by membrane osmometry.

An osmometer cell consists of two half-cells separated by a membrane capable of allowing passage of solvent molecules in either direction. In dynamic membrane osmometry, accurate values of $\overline{M}_n$ are usually determined, but conditions can occur whereby the experiment does not measure $\overline{M}_n$ accurately.[9] If the polymer solution is viscous, osmotic equilibrium at the membrane surface will occur before equilibrium can be established throughout the sample half-cell. This is the so-called "diffusion layer" effect. Also, if the membrane pore structure is coarse enough to allow passage of not only solvent molecules but also any or all of the polymer solute molecules, the membrane is no longer "semipermeable" but is "solute permeable".

With diffusional layers, the following equations have been developed (both equations were originally derived (see ref. 94 of ref. 9) in terms of specific osmometer constants which were canceled out before expressing eqs. (1) and (2) in the form shown here):

$$(\Delta h_t)_0 - \left(\frac{60}{n}\right)\left(\frac{d\,\Delta h_t}{dt}\right) = (\Delta h_t)_{th} \tag{1}$$

where

$$n = \frac{\ln(\Delta h_{\text{start}}/\Delta h_t)}{\Delta t} \tag{2}$$

and $(\Delta h_t)_0$ = apparent osmotic height at equilibrium, (Δh_t) = osmotic height at time t, $(\Delta h_t)_{th}$ = real or expected osmotic height at equilibrium, Δh_{start} = osmotic height at start of membrane osmometry experiment, t = equilibration time, $(d\,\Delta h_t/dt)$ = instantaneous change in osmotic height with time, and n = rate of equilibration of the solvent as $t \to 0$. Equation (1) was derived from a kinetic expression describing the rate of return to equilibrium in terms of various cell constants and solution (or solvent) properties and relates the change in osmotic height with time at which any solution equilibrates to that of the equilibration rate of the solvent. If a diffusional layer is present, the cell is effectively smaller and the half-cell equilibrates faster than it should. Equation (1) provides the necessary correction for the effective thickness of the cell. Ordinarily, if the effective cell volume of the solution with $(\Delta h_t)_0$ osmotic height is the same as that cell volume for the solvent of cell constant n, the rate of equilibration will be so much less than the solvent that $(d\,\Delta h_t/dt)$ will be less than $(60/n)$ and $(\Delta h_t)_0$ will be equal to $(\Delta h_t)_{th}$. However, if a diffusional layer is established,

($d \, \Delta h_t/dt$) increases and then $(\Delta h_t)_0$ could be less than $(\Delta h_t)_{th}$ (here, n is negative). With a strip chart recording of the rate of equilibration, $(\Delta h_t)_{th}$ can be determined using eq. (1). The data at short experimental times are emphasized. First, $(60/n)(d \, \Delta h_t/dt)$ vs. $\exp(\Delta h_t)$ is plotted. The value of $\exp(\Delta h_t)$ at $(d \, \Delta h_t/dt) = 0$ corresponds to that of $(\Delta h_t)_0$. [Alternatively, $(\Delta h_t)_0$ can be determined directly by awaiting equilibrium.] Then $(\Delta h_t)_0 - (60/n) \, (d \, \Delta h_t/dt)$ vs. $\exp(\Delta h_t)$ is plotted. The value of $(\Delta h_t)_0 - (60/n)(d \, \Delta h_t/dt)$ at $\exp(\Delta h_t) = 0$ is $(\Delta h_t)_{th}$.

Solute-permeable membranes will always generate underestimated osmotic heights, Δh. Polymer molecules, if small enough, can continuously diffuse out of the sample half-cell into the solvent half-cell. Evidence for this is a slow reduction in Δh with time after a maximum value is reached. Usually, a nonreproducible Δh_0 (solvent vs. solvent) value is evidence of solute in the solvent half-cell. However, unless the diffusing particle is very low in molecular weight, around 100, its diffusion coefficient is too small to allow translation into the solvent half-cell in the time span of dynamic osmometry, 1 hr or less.[10] Diffusion will be slowed further if the viscosity of the solution is high. This is the case when the sample is broad in molecular weight distribution and high in $\overline{M}_w$. Therefore, a stable nondrifting value of Δh does not necessarily mean that the membrane is not solute permeable. Staverman has shown that these molecules, even though they are still physically in the sample cell, will not contribute properly to Δh. In this case, for monodisperse species the measured molecular weight is referred to as the "reflected average" molecular weight, M_R, related to $\overline{M}_n$ by

$$M_R = \frac{\overline{M}_n}{\sigma(M)} \tag{3}$$

where $\sigma(M)$ is the reflection coefficient of the membrane for that value of $\overline{M}_n$. The lowest molecular weight at which $\sigma(M) = 1$ is the diffusion limit of the membrane, $M_{\lim}$, and is an indication of the porosity of the membrane. For all $M < M_{lim}$, $\sigma(M)$ varies with molecular weight and goes from 1 to 0 as the molecular weight decreases linearly to zero. For $M \geq M_{\lim}$, $\sigma(M) = 1$. Equation (3) indicates that whenever the membrane "leaks" [$\sigma(M) < 1$], the measured molecular weight, M_R, will be greater than the true molecular weight, $\overline{M}_n$. It has been shown that extrapolation of Δh back to zero time will not compensate for this effect, since even at $t = 0$, solute molecules which will (or could) leak at $t = \infty$ will act almost as solvent molecules and not add to Δh. For any given membrane–osmometer–solvent cell combination, $\sigma(M)$ can be calibrated with suitable narrow molecular weight distribution standards since by definition,

$$\sigma(M) = \frac{\text{true } \overline{M}_n}{\text{apparent } \overline{M}_n} = \frac{\overline{M}_n}{M_R} \tag{4}$$

For broad molecular weight distribution samples, M_R is related to the molecular weight distribution by

$$M_R = \frac{1}{\sum [\sigma(M)_i \, W_i/M_i]} \tag{5}$$

Equation (5) reduces to the definition of $\overline{M}_n$ when $\sigma(M) = 1$. In the past, using eq. (5), membrane osmometry data have been used to determine molecular weight distribution from measurements of M_R and $\sigma(M)$.

Both diffusional layers and solute permeable membranes contribute in different ways to provide underestimated osmotic heights and thus overestimated molecular weights. The general approach in analyzing unknowns that should be used in analyzing any membrane osmometry data is to first [after calibrating the cell for $\sigma(M)$ vs. molecular weight] obtain the experimental data (Δh_t) and then correct for diffusional layer (viscosity) effects to obtain $(\Delta h_t)_{th}$. $(\Delta h_t)_{th}$ is then used to determine M_R. Repeat the calibrations for several osmometer membranes, then plot M_R vs. M_{lim} (as in Figs. 1 and 2) and extrapolate to a sufficiently low M_{lim} to obtain the asymptotic value of M_R, which is $\overline{M}_n$. If the sample is not sufficiently narrow in molecular weight distribution, however, $\overline{M}_n$ may never be determined accurately in this way by membrane osmometry. Molecular weight distribution data are needed to complete the calculation of $\overline{M}_n$.[11] Only the diffusion layer effect can be measured from the membrane osmometry data alone without auxiliary information. The reflection effect on the membrane osmometry data can be accounted for only with a description of molecular weight distribution, such as the GPC curve. Membrane osmometry alone cannot always determine $\overline{M}_n$, but with the GPC curve, $\overline{M}_n$ could be determined for a majority of these cases. The central problem in this approach is the availability of an accurate description of molecular weight distribution. Thus, for samples like PBd-N-1 the question to be answered is whether the GPC chromatogram represents its true molecular weight distribution. This can be verified by direct molecular weight calibration of the GPC, as in the previous section, followed by comparing values of M_R calculated from the chromatogram at various values of M_{lim} with M_R values from membrane osmometry experiments. Good agreement verifies that the GPC data represent the actual molecular weight distribution of the sample and can be used to calculate $\overline{M}_n$. If the correlations cannot be made, the chromatogram for some reason does not
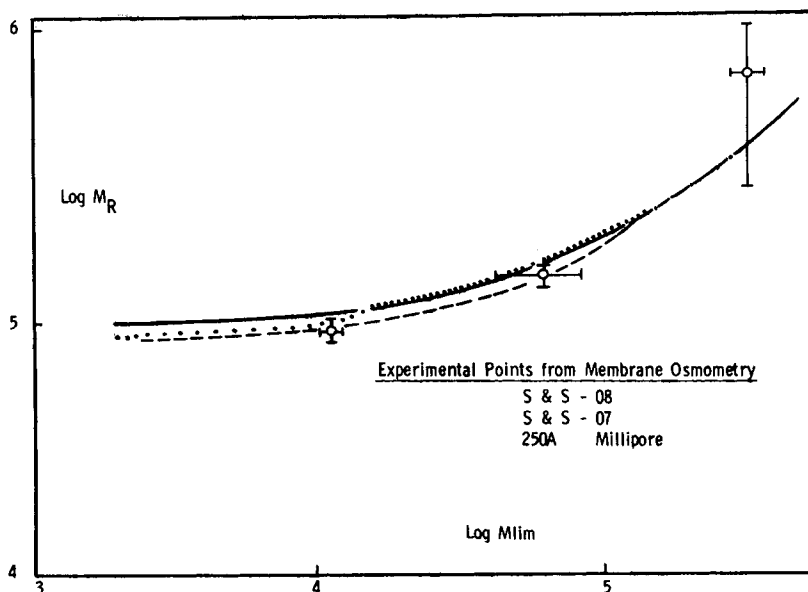

Fig. 1. PBd-N-2: Experimental and calculated reflected molecular weight M_R as functions of membrane diffusion limit M_{lim}. Calculated lines from GPC: (- - -) column set A; (—) column set B; (. . .) column set D.
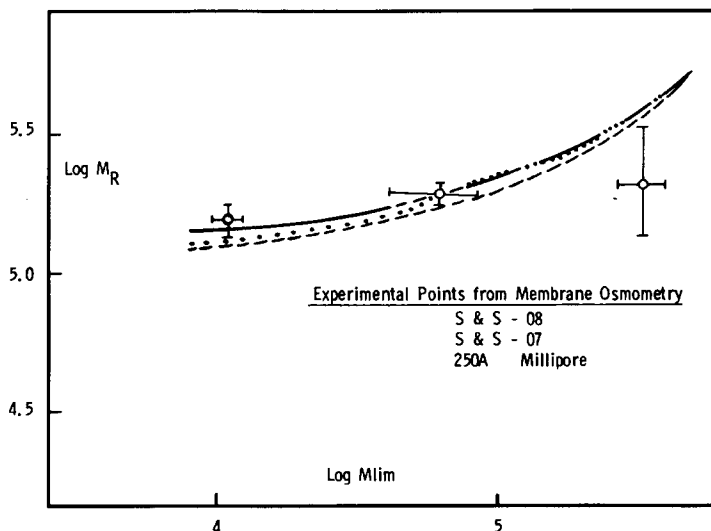
Fig. 2. PBd-D-1: Experimental and calculated reflected molecular weight M_R as functions of membrane diffusion limit M_{lim}. See Fig. 1 for legend.

represent the actual molecular weight distribution of the sample and $\overline{M}_n$ cannot be determined by GPC.

Membrane Osmometry of Narrow Molecular Weight Distribution Polystyrene Standards

Polystyrene standards which were of very narrow molecular weight distribution and ranged in molecular weight from 5,000 to 773,000 were evaluated in toluene at 34°C with the Melabs CSM-2 membrane osmometer using three different membranes. Results are listed in Tables VI–VIII. Osmotic molecular weight values are labeled as M_R, as defined earlier. Both diffusion layer and reflection effects were evaluated for each of the membranes. For the very low molecular weight samples, <10,000, actual diffusion of polymer molecules caused a slow drifting of Δh with time as well as a nonreproducible Δh_0 reading. This required flushing of the solvent half-cell, an advantage of the Melabs design. With the higher molecular weight samples, only reflection was indicated.

For the tight membrane (S&S-08), diffusional layers were absent at $\overline{M}_n =$ 94,500 and presumably at all lower molecular weights as well. For a coarser membrane (S&S-07), diffusion layers are greater, particularly at higher $\overline{M}_n$. No diffusion layer measurements were made for the very coarse (Millipore) membrane, but based on the previous data, M_R values are probably overestimated severely.

Even after diffusion layer effects are corrected, some of the values of $\sigma(M)$ are significantly less than 1, indicating possible solute permeability of, or reflection at, the membrane. This was seen for all three membranes. In each case $\sigma(M)$ increased to 1 as molecular weight increased. For each membrane, by plotting $\overline{M}_n$ vs. $\sigma(M)$, the value of $\overline{M}_n$ at $\sigma(M) = 1$ corresponds to M_{lim}. These values are listed in Table IX. Also listed are the nominal diffusion limits quoted by

TABLE VI

Membrane Osmometry Data for Narrow Molecular Weight Distribution Polystyrene Standards (Membrane S&S-08)

Standard	Reported $\bar{M}_n \times 10^{-3}$	Before diffusion layer corrections		After diffusion layer corrections		
		$\bar{M}_R \times 10^{-3}$	$A_2 \times 10^4$	$\bar{M}_R \times 10^{-3}$	$A_2 \times 10^4$	$\sigma(M)$
25169	4.6	12.0 ± 7.5	303 ± 118	—	—	0.38 ± 0.14
25171	9.7	10.9 ± 0.2	13.7 ± 6.0	—	—	0.89 ± 0.02
41995	96.2	94.5 ± 3.3	5.2 ± 0.3	94.5 ± 10.0	5.3 ± 1.0	1.02 ± 0.10
41984	196	196 ± 4	2.6 ± 0.1	—	—	1.00 ± 0.02
25166	355	—	—	—	—	—
4190038	773	—	—	—	—	—

TABLE VII
Membrane Osmometry Data for Narrow Molecular Weight Distribution Polystyrene Standards (Membrane S&S-07)

Standard	Reported $\overline{M}_n \times 10^{-3}$	Before diffusion layer corrections		After diffusion layer corrections		$\sigma(M)$
		$\overline{M}_R \times 10^{-3}$	$A_2 \times 10^4$	$\overline{M}_R \times 10^{-3}$	$A_2 \times 10^4$	
25169	**4.6**	—	—	—	—	—
25171	9.7	15.6 ± 0.7	86.2 ± 16.8	13.8 ± 0.4	78.7 ± 10.6	0.70 ± 0.02
41995	96.2	124 ± 10	6.2 ± 0.1	104 ± 7	5.7 ± 0.3	0.92 ± 0.05
41984	196	354 ± 26	5.2 ± 0.2	206 ± 8	4.7 ± 0.1	0.95 ± 0.03
25166	355	—	—	—	—	—
4190038	773	—	—	—	—	—

TABLE VIII
Membrane Osmometry Data for Narrow Molecular Weight Distribution Polystyrene Standards
(Membrane 250A Millipore Ultra-Filter)

Standard	Reported $\overline{M}_n \times 10^{-3}$	Before diffusion layer Corrections		After diffusion layer Corrections		$\sigma(M)$
		$M_R \times 10^{-3}$	$A_2 \times 10^4$	$M_R \times 10^{-3}$	$A_2 \times 10^4$	
25169	4.6	—	—	—	—	—
25171	9.7	—	—	—	—	—
41995	96.2	—	—	—	—	—
41984	196	277 ± 15	0.7 ± 0.2	—	—	0.71 ± 0.04
25166	355	334 ± 32	2.8 ± 0.2	—	—	1.06 ± 0.12
4190038	773	629 ± 93	0.3 ± 0.1	—	—	1.23 ± 0.16

the manufacturer. A general correlation is seen. The three membranes have obvious differences in porosity. A few initial experiments were made with an extremely tight commercial membrane of 2000 molecular weight diffusion limit. Extremely long solvent equilibration times were experienced. It was also observed that the membrane was asymmetric in its equilibration response. Further work with this membrane was abandoned because data with this membrane were not required to complete the characterization of the polybutadiene samples.

Errors in both M_R and A_2 were acceptable, especially for the S&S-08 membrane above 10,000 molecular weight. For all membranes, below M_{lim} where $\sigma(M) < 1$, the errors became worse, and generally the precision of the data decreased as the porosity of the membrane increased. No asymmetry problems were found with any of the membranes. For the coarsest membrane (Table VIII), M_R was less than $\overline{M}_n$ at high molecular weight, as found by other workers.[12] In general, the results for these standards are in agreement with other studies on solute-permeable membranes. These data serve as a calibration of the three membrane–osmometer cell–solvent combinations. Errors in M_R and A_2 are carried over into errors in $\sigma(M)$ and M_{lim}, but they are not felt to be abnormally high compared to other studies of this kind.[9] Although the data are sparse, plots of A_2 vs. M_R followed

$$A_2 = kM^{-b} \tag{6}$$

where A_2 is the second virial coefficient, with $b = 0.45 \pm 0.30$. This precision, although considered rather poor, is in qualitative agreement with earlier work on polystyrene in toluene, where b was found equal to 0.22, and with theory,[13] $0.05 < b < 0.25$.

TABLE IX
Diffusion Limits of Osmometer Membranes

Membrane	Diffusion limit M	
	Nominal	M_{lim}
S&S-08	20,000	$11,000 \pm 1,000$
S&S-07	80,000	$60,000 \pm 20,000$
250A Millipore	$>100,000^{\text{a}}$	$325,000 \pm 30,000$

[a] Narrow molecular weight distribution polystyrene with $\overline{M}_n$ of 100,000 has radius of gyration of 125Å in toluene.

Characterization of Broad Molecular Weight Distribution Polystyrene Standard Blend

To evaluate both diffusion layer and reflection effects on a sample of broad molecular weight distribution, particularly one similar to PBd-N-1, the standard polystyrene blend was analyzed with the S&S-08 membrane. Results are shown in Table X. No actual diffusion was sensed. Prior to diffusion layer corrections, M_R differed from the actual $\overline{M}_n$ by 11%. A diffusion layer correction for this sample provided an 8% change in M_R, although a narrow molecular weight distribution polystyrene of the same $\overline{M}_n$ did not need this correction (Table VI). With a higher $\overline{M}_w$ for this sample, higher solution viscosities are probably the cause. After diffusion layer correction, M_R was only 3% higher than the actual M, suggesting minimal reflection at the membrane. The sample's GPC chromatogram (shown later) was analyzed for $\overline{M}_w$, $\overline{M}_n$, and M_R for $M_{\lim} = 11,000$ using eq. (5). Results are listed in Table X. The calculated M_R is within $\frac{1}{2}$% of that determined experimentally by membrane osmometry. M_R was also calculated from the original weights of the standards used in preparing the blend. The GPC result was within 1% of this value and the membrane osmometry result was within 2% of this value. These molecular weight results show that the chromatogram is an accurate description of the molecular weight distribution of the blend.

These experiments, with samples of both narrow and broad molecular weight distribution, indicated that diffusion layers caused by a broad molecular weight distribution and high solution viscosity and reflection caused by a broad molecular weight distribution and low molecular weight tail make measurement of $\overline{M}_n$ by membrane osmometry alone difficult or even impossible. For the blend sample, these effects were affecting the data, but only in a small way. For PBd-N-1, they were probably more severe, since at equal molecular weight polybutadiene has a higher viscosity than polystyrene.

These results lend some insight into how osmometry is affected by molecular weight distribution. For a given membrane, all polymer species of molecular weight greater than $M_{\lim}$ contribute fully to the osmotic height, but all species less than $M_{\lim}$ will contribute to the osmotic height as if their molecular weight were $M_{\lim}$. In terms of either membrane osmometry or the GPC curve, eq. (5) can be recast in the general form, differentiating

$$M_R^{-1} = \left[M_{\lim}^{-1} 1 \sum_{M=0}^{M_{\lim}} (W_i) \right] + \left[\sum_{M=M_{\lim}}^{\infty} (W_i/M_i) \right] \qquad (7)$$

TABLE X
Characterization of Broad Molecular Weight Distribution Polystyrene Blend Membrane Osmometry (S&S-08)

	Diffusion layer correction		GPC column set A	Actual
	Before	After		
$\overline{M}_w \times 10^{-3}$	—	—	433	402
$\overline{M}_n \times 10^{-3}$	—	—	80.6	83.4
$\overline{M}_R \times 10^{-3}$	92.7 ± 2.0	86.0 ± 2.0	86.4	87.6
($M_{\lim} = 11,000$)				
$A_2 \times 10^4$	3.8 ± 0.1	3.8 ± 0.1	—	—

between the two molecular weight regions separated by $M_{\lim}$. In this case, M_R will be higher than $\overline{M}_n$. In correlating GPC to M_R, either eq. (5) or eq. (7) can be used to manipulate the GPC curve into the same "artificial" molecular weight distribution that affects the osmotic height in the osmometer cell.

It appears that in determining $\overline{M}_n$ for PBd-N-1, the error is in the membrane osmometry experiment and not the GPC experiment. The performance of the polystyrene blend standard illustrates how PBd-N-1 was affected during membrane osmometry; unfortunately the necessary data from the experiment were not taken to demonstrate this.

Characterization of PBd-N-2 and PBd-D-1

Having demonstrated that the combination of membrane osmometry and GPC can accurately calculate $\overline{M}_n$ for samples of broad molecular weight distribution, attention was turned to the characterization of PBd-N-2 and PBd-D-1. Values of M_R were determined for PBd-N-2 and PBd-D-1 (with extender oil removed) samples with all three membranes. Results are shown in Table XI. Except for one case, M_R decreased after making diffusion layer corrections. For example, with S&S-08 membrane, M_R decreased about 50% for PBd-N-2 and about 30% for PBd-D-1. These changes are much greater than those experienced earlier, a result of the greater solution viscosities. M_R decreased as $M_{\lim}$ decreased. It is noted that M_R for PBd-N-2 with S&S-08 membrane, prior to diffusion layer corrections, was similar to that determined for PBd-N-1. The two different osmometers used were susceptible to similar diffusion layer and reflection effects, indicating that these effects are caused by the sample and are not artifacts of one particular osmometer cell design. The errors in M_R using S&S-08 and S&S-07 appear to be acceptable considering the generally accepted ±10% error in M_n,[11] while the error with the coarsest membrane was not as good. Considering the earlier discussion relating M_R and $\overline{M}_n$, the value of M_R listed for S&S-08 with diffusion layer corrections would appear to be the closest approximation to $\overline{M}_n$, but since the same values of M_R were not obtained at two or more different levels of $M_{\lim}$,[11] it is felt $\overline{M}_n$ is not known unequivocally from membrane osmometry alone. Thus, the membrane osmometry data must be combined with the GPC curve to determine $\overline{M}_n$.

Molecular weight results calculated from GPC data are listed in Table XII. Column set D has also been demonstrated to exhibit negligible spreading[1,14] and to generate accurate molecular weight data for linear and branched polystyrene

TABLE XI
Membrane Osmometry Results for Polybutadiene Samples

Sample	Membrane	Before diffusion layer corrections		After diffusion layer corrections	
		$M_R \times 10^{-3}$	$A_2 \times 10^4$	$M_R \times 10^{-3}$	$A_2 \times 10^4$
PBd-N-2	S&S-08	115 ± 7	9.8 ± 0.3	86.5 ± 5.1	9.4 ± 0.4
	S&S-07	126 ± 4	9.0 ± 0.1	126 ± 6	9.2 ± 0.1
	Millipore	629 ± 386	3.4 ± 0.6	—	—
PBd-D-1	S&S-08	235 ± 53	8.2 ± 0.1	154 ± 23	8.0 ± 0.3
	S&S-07	157 ± 11	6.6 ± 0.1	184 ± 0	7.9 ± 0
	Millipore	248 ± 69	5.4 ± 0.2	—	—

TABLE XII
GPC Characterization of Polybutadiene Samples

Sample	Molecular weight	Column sets			Average
		A	B	D	
PBd-N-2	$\overline{M}_w \times 10^{-3}$	413	352	378	381 $\pm$ 31
	$\overline{M}_n \times 10^{-3}$	84.9	88.5	81.9	85.1 $\pm$ 3.3
	$\overline{M}_R \times 10^{-3}$ ($M_{\lim} = 11{,}000$)	87.0	94.0	88.0	89.7 $\pm$ 3.8
	$\overline{M}_R \times 10^{-3}$ ($M_{\lim} = 60{,}000$)	136	143	150	143 $\pm$ 7
PBd-D-1	$\overline{M}_w \times 10^{-3}$	324	331	—	327 $\pm$ 4
	$\overline{M}_n \times 10^{-3}$	132	137	—	134 $\pm$ 3
	$\overline{M}_R \times 10^{-3}$ ($M_{\lim} = 11{,}000$)	132	140	—	136 $\pm$ 4
	$\overline{M}_R \times 10^{-3}$ ($M_{\lim} = 60{,}000$)	177	186	—	182 $\pm$ 4

samples of both narrow and broad molecular weight distribution.[15] All column sets gave approximately equal values of $\overline{M}_w$ and $\overline{M}_n$. Earlier, it was shown that for PBd-N-1, $\overline{M}_w$ from GPC was found to be the same as from light scattering, and it is presumed that $\overline{M}_w$ values from GPC for these two rubbers are also accurate. For PBd-N-2, as found for PBd-N-1, $\overline{M}_n$ from GPC was lower than M_R from membrane osmometry prior to diffusion layer correction. However, after this correction was made, M_R was approximately equal to $\overline{M}_n$. The same was true for PBd-D-1. M_R at two levels of $M_{\lim}$ was calculated from the GPC curves. In Figures 1 and 2, M_R vs. $M_{\lim}$ is plotted. The data points are the experimental membrane osmometry data; the data lines are calculated from the GPC curves using eq. (7). In both cases, the GPC data for the three column sets, in different solvents, all generated quite similar molecular weight distributions, as expected when using universal calibration techniques. Here the GPC is used to define that relationship with the available membrane osmometry data used to support the relationship. The agreement in M_R from GPC and membrane osmometry was good. This suggests that for both rubbers, the GPC data from all three column sets represented accurate descriptions of the molecular weight distribution and thus provided accurate determinations of $\overline{M}_n$. The chromatograms and calibration curve for column set A, shown in Figure 3, are representative of all three column sets. Also shown is the chromatogram of the polystyrene standard blend. Most of the advantages of this column set were discussed earlier. The extending oil is completely separated from the rubber portion of PBd-D-1.

It appears from the GPC and membrane osmometry data that diffusion layer effects are the major cause of the overestimation of $\overline{M}_n$ from membrane osmometry. Reflection or solute permeability is minimal with the S&S-08 membrane. Average values of $\overline{M}_w$ and $\overline{M}_n$ calculated from all the GPC data are listed in Table XII. Error in the GPC results was less than 10% of the average values. It has been shown that the GPCs used here can generate an accurate molecular weight distribution for both PBd-N-2 and PBd-D-1. In order to accomplish this, some limits must be placed on the GPC operating conditions, these limits being the performance characteristics of the GPC sets used here. The extent to which other GPC column sets will work must be established on an individual basis.
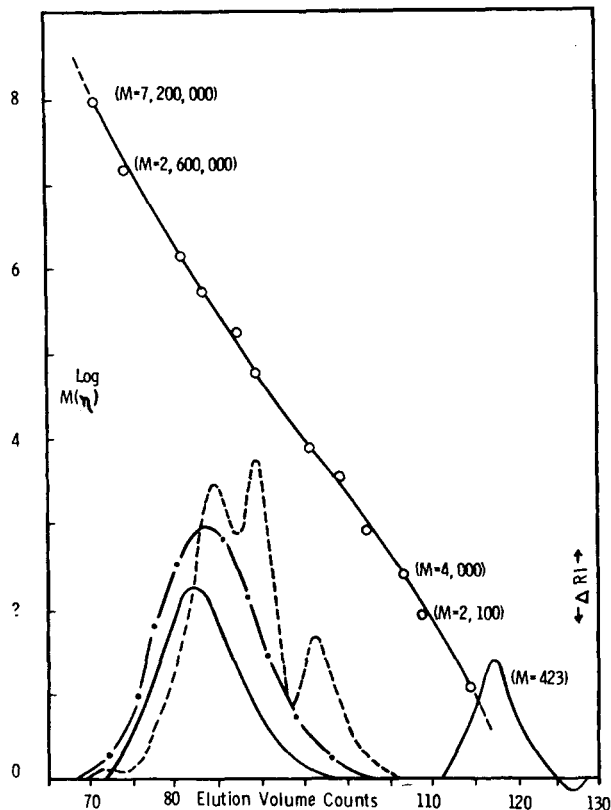
Fig. 3. GPC Column set A: separation characteristics: (- - -) polystyrene standard blend; (—·—) PBd-N-2; (—) PBd-D-1.

Final Molecular Weight Results

Following characterization by membrane osmometry, light scattering, and GPC, these two samples were found to have the following molecular weights: (1) PBd-N-2, $\overline{M}_w$ = 381,000 ± 31,000; $\overline{M}_n$ = 85,100 ± 3,300; (2) PBd-D-1, $\overline{M}_w$ = 327,000 ± 4,000; $\overline{M}_n$ = 134,000 ± 3,000. Precision for PBd-N-2 was an average ±8% relative standard deviation (RSD) in $\overline{M}_w$ and ±4% RSD in $\overline{M}_n$, found from three GPCs on different solvents. Precision for PBd-D-1 was an average ±1% RSD in $\overline{M}_w$ and ±2% RSD in $\overline{M}_n$, found for two GPCs on different solvents. For PBd-N-2, the accuracy of $\overline{M}_w$ from GPC was within ±2% of that from light scattering. Regarding the accuracy of $\overline{M}_n$, GPC values were estimated to be within approximately ±11% and ±7% of their actual values for PBd-N-2 and PBd-N-1, respectively.

CONCLUSIONS

The molecular weight characterization of two samples of polybutadiene rubber of broad molecular weight distribution and high molecular weight by membrane osmometry, light scattering, and universal calibration of GPC has been completed. Correlation of molecular weight results for the two samples were possible only after (1) correction of membrane osmometry data for "diffusion layer" and "solute permeability" or "reflection" effects were made, and (2) GPC column

sets were established with no band-spreading effects and with a wide molecular weight range of resolution. The two characterized rubber samples are now in use as secondary standards when universal calibration of GPC is used for molecular weight distribution analyses of polybutadiene and other samples.

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