

Characterization of Functionally Terminated Polybutadienes of Low Molecular Weight

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Synopsis

A difunctional hydroxyl-terminated polybutadiene (sample A) was characterized by light scattering (LS), vapor pressure osmometry (VPO), and gel permeation chromatography (GPC). Sample A was then esterified, and the product (sample B) was also characterized. Light-scattering measurements were carried out in different solvents (some were theta solvents for polybutadiene), and the results were corrected for anisotropy. Values of M_n (3100) and M_w (8000) determined respectively by VPO and LS for samples A and B were similar to those computed by GPC using two sets of columns of different resolution. The value of 2.3 found for the polydispersity index M_w/M_n is higher than the value which is usually reported by other workers (ca. 1.3 to 1.7) for functionally terminated polybutadienes.

INTRODUCTION

In order to improve quality control on propellant ingredients, better knowledge of the molecular weight (MW) and the molecular weight distribution (MWD) of the prepolymers used as propellant binders are required. These prepolymers are generally functionally terminated polybutadienes with MW lower than 10,000.

Many workers^{1,2} have applied the method of gel permeation chromatography (GPC) to study the MWD in prepolymers. Defence Research Establishment Valcartier (DREV) participated recently with other laboratories in a cooperative MWD program³ in order to study the utility of this method (precision and convenience). Gel permeation chromatography is not an absolute method of characterization but can provide information on the MWD of a polymer if a suitable calibration curve exists. As the universal calibration method⁴ does not apply to polymers of low MW,⁵ the generally used calibration curve which relates the elution volume to the logarithm of the MW was adopted. This method of calibration requires a separate curve for each type of polymer studied.

The polydispersity index (M_w/M_n) can be computed in an absolute way by using physical methods to determine both the weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of the polymer studied.

Osmometry and vapor pressure osmometry (VPO) are among the many methods used for the absolute evaluation of M_n . When the MW of the

polymer studied is lower than 10,000, osmometry becomes difficult due to the permeability of the membranes. Although some workers⁶ have recently found some membranes which enable a value as low as 1500 for M_n to be measured, these membranes are selective, and their application remains restricted to certain types of polymers. VPO is probably the most widely used method⁷ to determine M_n for a polymer of low MW.

Light scattering (LS), which yields M_w , was not applied in an extensive manner to low MW polymers. This is due to many factors such as the presence of dust particles and impurities in the solution, the possibility of formation of gels and aggregates, and intra- and intermolecular interactions. These factors, not negligible for high polymers, become even more important for a low MW polymer. The purpose of this work is to study the effect of interactions on the precision of this method and to verify experimentally the possibility of characterizing, in an absolute manner, a polymer of MW lower than 10,000.

Difunctionally terminated polybutadienes (hydroxyl and acetate terminated) of very low MW were, therefore, characterized by VPO and LS. These two methods yielded values of M_n and M_w which were then compared to those obtained from GPC.

EXPERIMENTAL

Materials

The first polymer studied (sample A) was a dihydroxyl-terminated polybutadiene, R45-M (lot 906291), which is a liquid and amorphous prepolymer manufactured by Arco Chemical Company.

The second polymer studied (sample B) was obtained from the esterification of sample A with acetyl chloride according to the two procedures described by Galin and co-workers.⁸ The first procedure with pyridine and the second procedure without pyridine yielded identical products. By comparing the IR spectra of sample B to the one of sample A, the presence of acetate groups and the disappearance of the absorption band of the hydroxyl groups were observed. IR spectra were recorded on a Perkin-Elmer instrument (Model 521); the samples were put between two sodium chloride plates.

Vapor Pressure Osmometry (VPO)

VPO measurements were carried out with a Hewlett-Packard instrument (Model 302B) in chloroform at 37°C. Benzyl was used as a calibration standard.

Light Scattering (LS)

LS measurements were carried out on a SOFICA photometer (Model 42000) using unpolarized light of wavelength 5461 Å.

Samples A and B were characterized in different solvents: *n*-hexane (at 35°C), *n*-heptane (at 25°C), chloroform (at 37°C), methyl ethyl ketone (MEK), which is a theta solvent at 26°C for hydroxyl-terminated polybutadiene,⁹ 3-pentanone, 5-methyl-2-hexanone, and isobutyl acetate, which are, respectively, theta solvents at 10.3°C, 12.6°C, and 20.5°C for *cis*-1,4-polybutadiene.^{10,11} Solutions were filtered on alpha-metricel membranes (porosity 0.2 micron) made by Gelman Instrument Company.

Scattered intensities were recorded for a number of solutions of different concentration for each solvent at an observation angle of 90°. The data for each solvent, after correction for anisotropy, were extrapolated to zero concentration. The values of M_w and A_2 , the second virial coefficient, were determined from the relations

$$\frac{c}{I(90)} = \frac{1}{M_w} + 2A_2c$$

$$I(90) = \frac{N_A \lambda^4}{2\pi^2 (dn/dc)^2} \frac{R_{st}}{n_{st}^2} \left[\frac{\Delta - \Delta^0}{\Delta_{st}} \right] \frac{1}{f}$$

where $I(90)$ is the normalized intensity of scattering, N_A is Avogadro's number, λ is the wavelength of incident light in vacuum, dn/dc is the specific refractive index increment for the solute-solvent system studied, c is the solute concentration in g/ml, R_{st} is the Rayleigh ratio for the calibrating liquid, n_{st} is the refractive index of this liquid, Δ , Δ^0 , and Δ_{st} are, respectively, the output readings of the photometer for the solution, solvent, and standard, and f is the usual Cabannes' factor $(6 + 6\rho)/(6 - 7\rho)$ with ρ the depolarization factor.

Benzene was used as the calibrating liquid, and a value of $17.2 \times 10^{-6} \text{ cm}^{-1}$ was chosen¹² for the Rayleigh ratio of this liquid at 5461 Å and 25°C. For the variation of the Rayleigh ratio with temperature T , the relation given by Ehl and co-workers¹³ was used:

$$R_T = R_{25}[1 + 0.00368(T - 25)].$$

The dn/dc measurements were carried out at 5461 Å and 4358 Å using a differential refractometer (Model BP-2000V) made by the Phoenix Precision Instrument Company.

Gel Permeation Chromatography (GPC)

The chromatograph used was the ANA-PREP Waters Associates instrument. The solvent was tetrahydrofuran (THF), and the operating temperature was 23°C. The concentrations used were between 0.1% and 0.2%, and the flow rate was 1 ml/min.

Two sets of Styragel columns were used in this study. The first set (set I) comprises four columns of medium porosity 7×10^5 , $1.5-5 \times 10^4$, 700-2000, and 80-100 Å. The second set (set II) comprises four columns of medium porosity 2000-5000, 700-2000, 700-2000, and 100-350 Å.

The chromatograph is provided with an automatic injector and a curve digital transcripter made by Waters Associates. Data were registered on a perforated tape read and analyzed with a FORTRAN program on a Sigma 7 computer.

RESULTS AND DISCUSSION

Vapor Pressure Osmometry (VPO)

The calibration was accomplished according to the method described by Muenker and Hudson.⁷ Values of M_n and A_2 for samples A and B are presented in Table I. Samples A and B have similar values for M_n ($3100 \pm 10\%$) and A_2 (2.3×10^{-3} ml mole/g² $\pm 10\%$).

TABLE I
Characterization of Samples A and B by VPO in Chloroform at 37°C

Sample	$M_n \pm 10\%$	$A_2 \times 10^3$, ml mole/g ²
A	2800	2.6
B	3400	2.1

Light Scattering (LS)

The value of dn/dc was found to be independent of concentration, and it was observed that samples A and B had identical (dn/dc) values in each solvent studied. The dn/dc values at 5461 Å and 4358 Å are listed in Table II.

TABLE II
Specific Refractive Index Increment (dn/dc) Values for Samples A and B

Solvent	Temp., °C	(dn/dc)	
		5461 Å	4358 Å
<i>n</i> -Hexane	35	0.169	0.177
Methyl ethyl ketone	26	0.159	0.165
<i>n</i> -Heptane	25	0.150	0.157
Isobutyl acetate	20.5	0.143	0.149
3-Pentanone	10.3	0.139	0.145
5-Methyl-2-hexanone	12.6	0.120	0.125
Chloroform	25	0.0868	0.0920
	37	0.0931	0.0958

It was found that ρ was not a function of the concentration and that f had a value of about 1.10 for samples A and B in all the solvents studied except chloroform (where f is equal to 1.20 for sample A and 1.40 for sample B).

The values of M_w and A_2 obtained for samples A and B in all the solvents studied are listed in Table III.

TABLE III
Characterization of Samples A and B by Light Scattering

Solvent	$M_w \pm 10\%$		$A_2 \times 10^3, \text{ ml mole/g}^2$	
	Sample A	Sample B	Sample A	Sample B
<i>n</i> -Hexane	10,600	—	0	—
Methyl ethyl ketone	12,000	7140	0	-0.6
<i>n</i> -Heptane	7950	—	-0.3	—
Isobutyl acetate	10,200	8770	0	0
3-Pentanone	9900	8900	0	0
5-Methyl-2-hexanone	10,900	8160	0	0
Chloroform	—	8200	-	2.0

Sample A. In chloroform at 37°C, it was impossible to extrapolate data to zero concentration with good precision. This difficulty was attributed to the dn/dc value which is relatively low in this solvent. In fact, it is solely this difference of refractive index between the solution and the solvent which determines the lowest MW that can be precisely measured.

Sample A was then characterized in *n*-heptane and *n*-hexane where the dn/dc values are relatively high. In *n*-heptane at 25°C (Fig. 1), a value of 7950 for M_w was obtained. At 35°C, *n*-hexane acted as a theta solvent (A_2 is zero), and a value of M_w equal to 10,600 was obtained for sample A. In order to explain the difference between the results in *n*-heptane and *n*-hexane, other theta solvents were tried where the solvent-solute interactions are equal to the solute-solute interactions.

MEK, isobutyl acetate, 5-methyl-2-hexanone, and 3-pentanone (Fig. 1) turned out to be theta solvents for sample A at 26°, 20.5°, 12.6°, and 10.3°C,

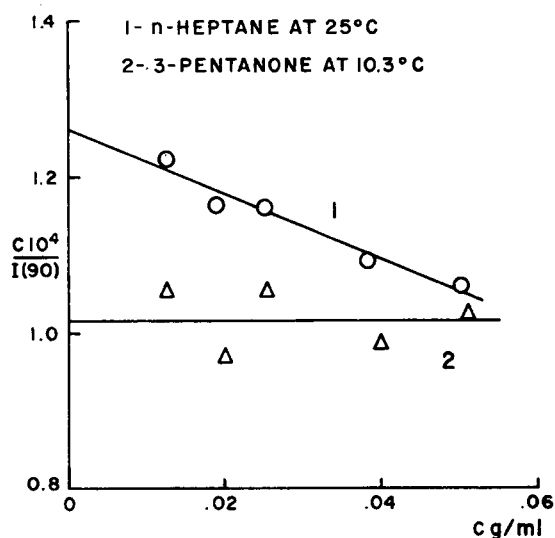


Fig. 1. Variation with concentration of $c/I(90)$ for sample A: (1) *n*-heptane at 25°C; (2) 3-pentanone at 10.3°C.

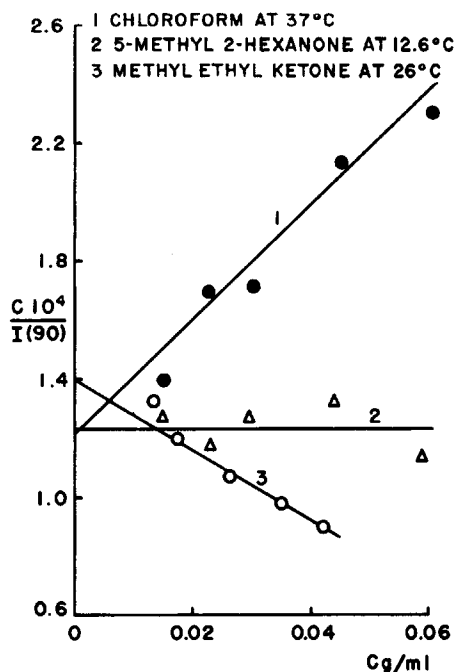


Fig. 2. Variation with concentration of $c/I(90)$ for sample B: (1) chloroform at 37°C; (2) 5-methyl-2-hexanone at 12.6°C; (3) methyl ethyl ketone at 26°C.

respectively. On the other hand, values of M_w that lie between 9900 and 12,000 were observed in these solvents.

In order to explain this large spread in the M_w values, it was then decided to prepare sample B by the esterification of sample A. This would determine whether the results were improved by replacing the hydroxyl groups by acetate groups since the interactions depend on the functional groups present on the polymer.

Sample B. Sample B was characterized in the same solvents used for sample A.

Data extrapolation to zero concentration was possible in chloroform at 37°C where a value of M_w equal to 8200 was obtained for sample B (Fig. 2). It is therefore the interactions involving the hydroxyl groups and chloroform that hindered the extrapolation of data in the case of sample A.

In *n*-heptane at 25°C and *n*-hexane at 35°C, a dissymmetry was observed. A similar phenomenon due to the formation of crystals was previously noticed by Strazielle¹⁴ on polyoxyethylene of MW 10,000 in methanol, but by heating at 40°C the dissymmetry disappeared. In our case the dissymmetry remained even by heating up to 60°C. The molecular association (or aggregate formation) for sample B in *n*-hexane and *n*-heptane could be the cause of this dissymmetry.

MEK at 26°C was not a theta solvent for sample B; a value of 7140 was obtained for M_w in this solvent (Fig. 2).

Isobutyl acetate at 20.5°C, 5-methyl-2-hexanone at 12.6°C (Fig. 2), and 3-pentanone at 10.3°C proved to be theta solvents also for sample B. Values of M_w measured in these solvents for sample B lie between 8160 and 8900, which is a remarkable improvement compared to the results obtained for sample A.

The precision on M_w for each solvent studied is about 10% for samples A and B. On the other hand, the spread in the values obtained for M_w is larger in the case of sample A than it is for sample B. In fact, if the results in all solvents are combined, an average value for M_w of $10,000 \pm 20\%$ for sample A and $8000 \pm 10\%$ for sample B is obtained.

If the spread of the results in the case of sample A is attributed to the interactions involving hydroxyl groups, it can be concluded that samples A and B have an identical value for M_w which is equal to about $8000 \pm 10\%$. It can also be noticed that the value of A_2 found by LS in chloroform at 37°C (2.0×10^{-3} ml mole/g²) is similar to the value determined by VPO (2.3×10^{-3} ml mole/g²) in the same solvent and at the same temperature.

Gel Permeation Chromatography (GPC)

The calibration curve for the set I columns (Fig. 3) was constructed with narrow polystyrene standards. The columns have a high resolution for MW of polystyrene between 5000 and 160,000. The chromatograms obtained with the set I columns for samples A and B are presented in Figure 4. The analysis of these chromatograms by the calibration curve of Figure 3 yields only apparent values for M_w and M_n (Table IV, section a) because

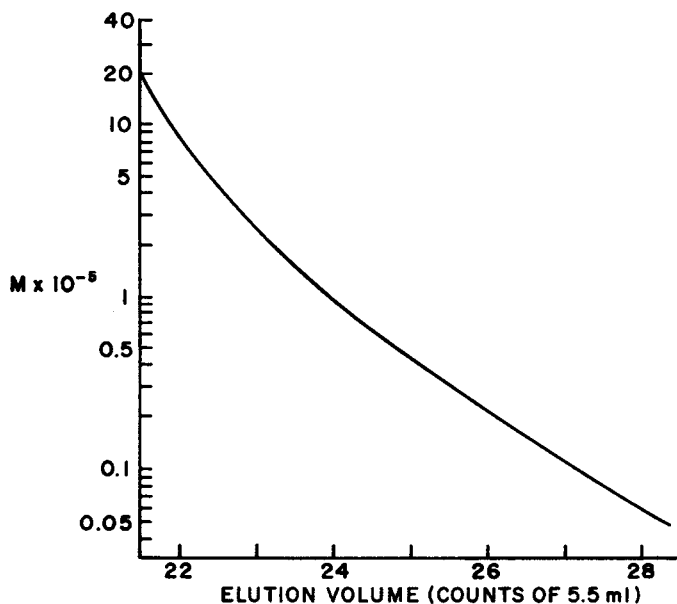


Fig. 3. Calibration curve for set I columns.

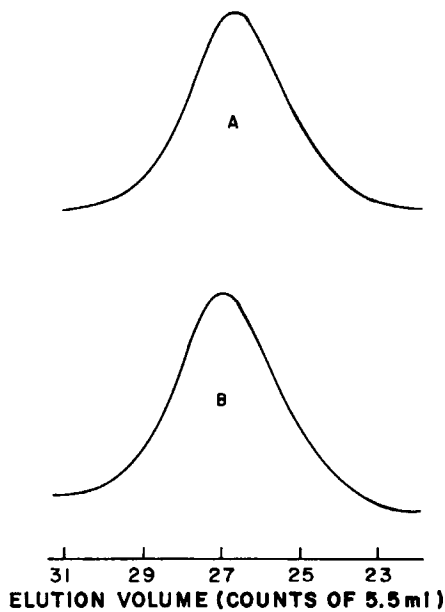


Fig. 4. Chromatograms of samples A and B in set I columns.

the set I columns were calibrated with polystyrene standards. Nevertheless, these results show clearly that samples A and B have a polydispersity index of about 2.

The set II columns were proposed by workers at the Naval Ordnance Station who suggested a cooperative program³ in which DREV participated; this program involved many laboratories adopting all the same experimental conditions and calibrating procedures. The set II columns were calibrated with polystyrene standards (PS), narrow fractions of hydroxyl- (HTPB) and carboxyl- (CTPB) terminated polybutadienes. The calibration curves (Fig. 5) are linear for MW between 2000 and 20,000 (PS), 1500 and 10,000 (HTPB), and 200–20,000 (CTPB).

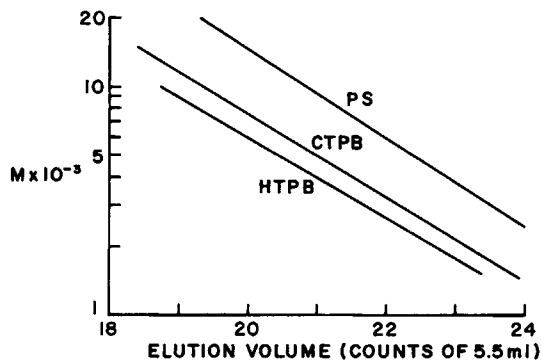


Fig. 5. Calibration curve for set II columns.

TABLE IV
Characterization of Samples A and B by GPC^a

Sample	Section a			Section b			Section c	
	M_w^b	M_n^b	M_w/M_n^b	M_w^b	M_n	M_w/M_n^b	M_w	M_w/M_n
A	18,680	9720	1.92	4980	3450	1.44	7470	2.16
B	18,860	9170	2.05	5020	3260	1.54	7540	2.31

^a Section a: set I columns with PS calibration; section b: set II columns with HTPB calibration; section c: combined results for the columns of set I and set II.

^b Apparent.

It was noticed that the set II columns had a low resolution for high MW. Moreover, the chromatograms obtained for samples A and B (Fig. 6) showed "humps" at the high end of the distribution. Consequently, the chromatograms of Figure 6 can only be used to evaluate M_n , which is sensitive to the amount of low MW polymer.

The HTPB calibration curve of Figure 5 was used to determine M_n for sample A (Table IV, section b). Since a calibration curve for an acetate-terminated polybutadiene was not available, the chromatogram obtained for sample B in the set II columns was analyzed, first with the HTPB calibration curve and then with the CTPB calibration curve. The M_n value (Table IV, section b) found for sample B with the HTPB calibration curve agrees with the one determined by VPO (Table I). On the other hand, by using the CTPB calibration curve, a relatively high value (4500) of M_n for sample B was obtained. Therefore, the CTPB calibration curve is not valid in the case of sample B whose hydrodynamic volume is similar to sample A.

The values of M_w and M_w/M_n listed for sample A and B (Table IV, section b) are meaningless because of the low resolution of the set II columns

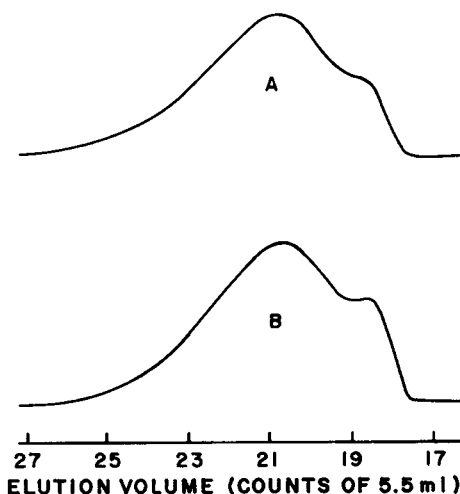


Fig. 6. Chromatograms of samples A and B in set II columns.

in the high MW region. If the apparent values of M_w (Table IV, section a) computed with the set I columns are divided by the factor 2.5, the real values of M_w for samples A and B (Table IV, section c) are obtained. This 2.5 factor is obtained from the PS and HTPB calibration curves of Figure 5 and represents the MW ratio between a PS and HTPB molecule having the same elution volume. The M_w/M_n values listed for samples A and B in section c of Table IV are calculated from the ratio between the M_w values of section c and the M_n values of section b.

The M_w value (7500) computed by GPC (Table IV, section c) agrees with the value of 8000 measured by LS. If the M_w value obtained from LS is divided by the M_n value determined by VPO, a polydispersity index of 2.44 is obtained which also agrees with the value of 2.24 computed from GPC. The value of 1.50 listed for M_w/M_n in section b of Table IV and in the cooperative program³ is consequently too low due to the wrong choice of the set II columns.

CONCLUSIONS

The solute-solvent and solute-solute interactions involving hydroxyl groups are more important than those involving the acetate groups of a difunctionally terminated polybutadiene. In fact, the absolute value of M_w measured by LS is equal to $10,000 \pm 20\%$ in the case of a dihydroxy-terminated polybutadiene and is equal to $8000 \pm 10\%$ for the same esterified polybutadiene characterized in the same solvents.

It is possible to characterize by LS, in an absolute manner, a polymer of MW at least as low as 7000. However, in order to increase the precision, one has to take great care in choosing a solvent in which the dn/dc value is high and the molecular interactions are negligible.

The hydrodynamic volume of a difunctional hydroxyl-terminated polybutadiene is identical to that of the same polybutadiene with acetate groups.

By combining the results of LS and VPO, a value of 2.3 was obtained for the polydispersity index M_w/M_n , which is similar to the one computed from GPC by using to set of columns of different resolution covering the whole MWD in samples A and B.

The values of M_w/M_n that vary from 1.3 to 1.7 and that are reported by other workers for similar prepolymers are consequently too low because of the wrong choice of the GPC columns.

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