Polymer Bulletin 38, 455–460 (1997)

Polymer Bulletin

Molecular weight determination of HTPB resins by vapor pressure osmometry (VPO) and gel permeation chromatography (GPC): The effect of calibration standards

Marta Ferreira Koyama Takahashi[1,*], **Mauro de Lima**[1], **Wagner Luiz Polito**[2]

[1] Instituto de Aeronáutica e Espaço, CTA, CEP, 12228-904 São José dos Campos, SP, Brasil
[2] Instituto de Química de São Carlos, USP/SC, CEP, 13560-250 São Carlos, SP, Brasil

Received: 7 October 1996/Revised version: 12 December 1996/Accepted: 23 December 1996

SUMMARY: **GPC** and **VPO** behaviours of **HTPB** samples have been examined in toluene employing polystyrene and polybutadiene standards. The results show that the molecular weights obtained depend on the nature of the calibration standards , particularly in the **GPC** analysis.

INTRODUCTION

Hydroxyl-terminated polybutadiene (**HTPB**) is extensively used as a propellant fuel binder in modern solid propellants. **HTPB** dominates in the propellant industry because of its superior mechanical and ballistic properties. Differences in the manufacture of these polymers result in batch to batch variability and gives polymers that vary in molecular weight, molecular weight distribution (**MWD**) and functionality distribution. These differences greatly affect propellant processability, pot life, cure behavior, mechanical properties, and aging characteristics (1).

VPO and **GPC** are the most employed techniques for determining molecular weight. These techniques need calibration.

Many authors (2-5) have demonstrated that a calibration function must every time be determined for **VPO** measurements. This calibration may also affect molecular weight, although Kamide (6) assumed that it is possible to suppress the molecular weight dependence by using a specially constructed **VPO** apparatus. Brzezinski, et al. (3) and others authors (4,5) recommended that to obtain correct results, the calibration should be done with pure substances having molecular weights in the vicinity of the measured molecular weight, or the dependence $K=f(\overline{Mn})$ should be found by calibrating with several substances over the molecular range. It has not been proved, however, that these calibration dependences are universal, i.e., independent of the primary structure of the polymer standard.

Most **GPC** users work with a single detector, generally a differential refractometer. From the chromatogram, they wish to obtain number and weight average molecular

---

* Corresponding author

weights ($\overline{Mn}$ and $\overline{Mw}$). Thus it is necessary to establish a calibration curve relating retention volume to molecular weight.

Several methods have been suggested (7-9) and used to obtain absolute molecular weights from the **GPC** trace, i.e., "**Q**" factor, hydrodynamic volume, molecular volume, wide molecular weight distribution standards; however a calibration curve (i,e., one determined by injecting a series of narrow-distribution polymer standards) is still preferred for routine analysis. The conventional calibration is usually superior for making sample-to-sample comparisons, specially for long-term use (10). Its disadvantage is the need of standards with very narrow molecular weight distributions and of the same composition as that of the samples (ideal calibration).

It is common practice to use a polystyrene calibration curve for all purposes. When using the polystyrene calibration curve one obtains $\overline{Mn}_{PS}$ and $\overline{Mw}_{PS}$, number and weight average molecular weights of the sample in polystyrene equivalent, i.e., the $\overline{Mn}$ and $\overline{Mw}$ values of a polystyrene sample which have the same chromatogram. It is necessary to keep in mind that these results are not true values but they can be useful for comparative tests or for qualitative discussion.

In this work, the effect of the nature of **PS** and **PB** standards on the molecular weight determination of **HTPB** liquids was investigated. This was done by means of **VPO** and **GPC** techniques and by using conventional equipment.

EXPERIMENTAL

The narrow mol.wt. standards were supplied by Water Associates (**PS**) and Polymer Laboratories (**PB**). Toluene (spectroscopic grade) was supplied by Nuclear. The **HTPB** samples were supplied by Petroflex (Liquiflex resins) and ARCO (R45M resin).

VPO measurements were obtained with a Wescan Osmometer - Model 233 operated at 50°C, with toluene. Calibration was carried out using **PS** ($\overline{Mn}$ = **1800**) and **PB** ($\overline{Mn}$ = **3000**) solutions in the 0.1-0.8g/L concentration range. Four polymer solutions for each standard were used to generate (**ΔV/C**) versus **C** plots, where ΔV is the voltage imbalance for the solution minus the voltage imbalance for the solvent, and **C** is concentration in gL^{-1}. The best fit straight line was extrapolated to zero concentration and used to calculate the calibration constant, **K**. The values for K_{PS} and K_{PB} were obtained, respectively, for **PS** and **PB** standards. The molecular weights of the samples were determined using sample solutions in the same concentration range and the K_{PS} and K_{PB} previously determined.

GPC measurements were performed with a HP1084B gel permeation chromatograph. The data were obtained with a column set of three Waters Associates Ultrastyragel columns, 10^4, 10^3 and 500Å, calibrated with **PS** and **PB** standards. The eluent was toluene at 1mL/min. The concentration of **PS**, **PB** standards and **HTPB** samples were 0.1, 0.1, and 0.4% (w/v) respectively. The injection volume of standards and samples was 150µL. Triplicate analyses were carried out at 30°C.

RESULTS AND DISCUSSION

Table 1 shows the **VPO** calibration constants obtained with **PS** and **PB** standards. These calibration constants were used to determine the $\overline{Mn}$ of the **HTPB** samples shown in Table 2.

Table 1 - **VPO** calibration constants using **PS 1800** and **PB 3000** standards

STANDARD	**$(\Delta V/C)_{c\to 0}$ (mVL/g)**	**K**
PS 1800	1.48	2657
PB 3000	0.94	2823

Table 2 - **$\overline{\text{Mn}}$** values of **HTPB** obtained by **VPO** using **PS** and **PB** standards

HTPB RESINS	**$\overline{\text{Mn}}$**	
	PS 1800 (K_{PS}=2657)	**PB 3000 (K_{PB}=2823)**
Liquiflex P	2371	2519
Liquiflex H	2070	2199
Liquiflex 33	2865	2769
Liquiflex 36	2607	3044
Liquiflex 42	2772	2945
R45M	2599	2761

The **$\overline{\text{Mn}}$** values obtained by **VPO** using **PB** standards are 6% greater than those obtained by using **PS** standards. This difference is small and is in the error range of 10% reported for **VPO** measurements (6,11). **$\overline{\text{Mn}}$** values obtained with **PB** standards agree better with the **$\overline{\text{Mn}}$** = 2800 value reported by **HTPB** resins suppliers(12,13). This behavior cannot be attributed only to the difference in standards. It is possible that these results include a small dependence of **$\overline{\text{Mn}}$** with the molecular weight of the calibration compounds.

Figure 1 shows the **GPC** calibration curves obtained with **PS** and **PB** standards.

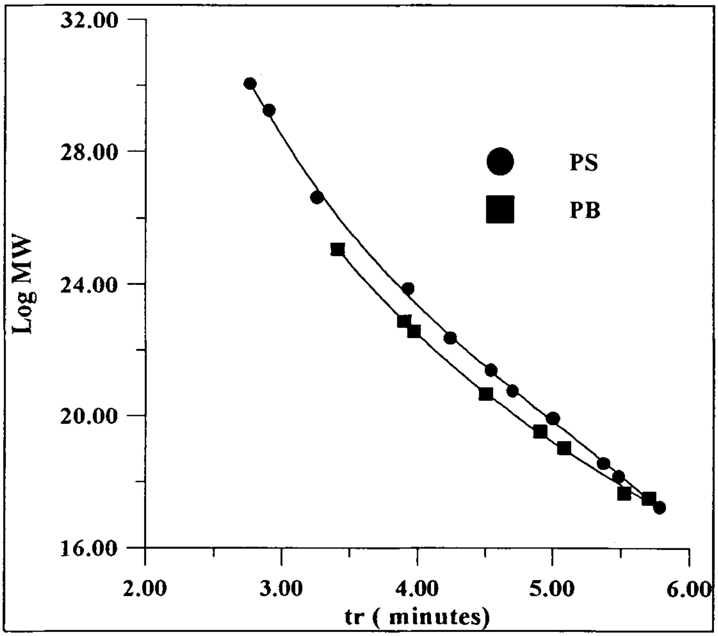

Figure 1 - **GPC** calibration curves with **PS** and **PB** standards

The values of **$\overline{Mn}$** and **$\overline{Mw}$** and polydispersity (**D**) for **HTPB** are shown in Table 3. These values were determined from the chromatograms obtained for each sample (Figure 2) and the calibration curves shown in Figure 1.

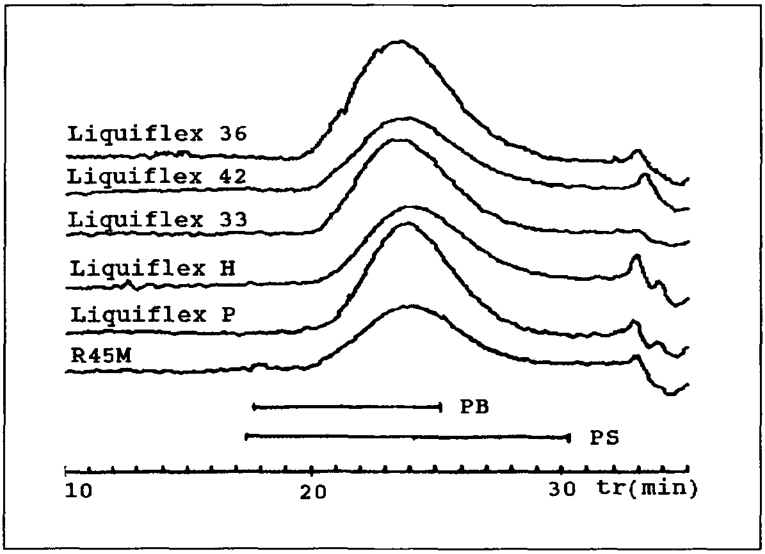

Figure 2 - Representative chromatograms of **HTPB** resins

Table 3 - **$\overline{Mn}$**, **$\overline{Mw}$** and **D** of **HTPB** by using **PS** and **PB** standards*

RESINS	**PS**			**PB**		
	$\overline{Mw}$	$\overline{Mn}$	D	$\overline{Mw}$	$\overline{Mn}$	D
Liquiflex P	10886±97 (1%)	4975±90 (1.8%)	2.19±0.03 (1.4%)	6288±54 (0.9%)	3024±34 (1.1%)	2.09± 003 (1.4%)
Liquiflex H	9582±50 (0.5%)	4392±132 (2.4%)	2.18±0.01 (0.6%)	5517±28 (0,6%)	2670±30 (1.1%)	2.07±0.01 (0.6%)
Liquiflex 33	12294± 125 (1%)	5472±125 (1%)	2.24±0.04 (2%)	7073±88 (1.2%)	3297±74 (2.3%)	2.14±0.6 (2.8%)
Liquiflex 36	13323±88 (0.6%)	5481±39 (0.7%)	2.43±0.02 (1%)	7690±56 (0.7%)	3308±22 (0.7%)	2.31±0.02 (1.3%)
Liquiflex 42	11863±59 (0.5%)	4925±58 (1.2%)	2.41±0.03 (1.1%)	6849±41 (0.6%)	2985±38 (1.3%)	2.29±0.03 (1.3%)
R45M	10932±73 (0.7%)	4848±65 (1.3%)	2.25±0.02 (0.7%)	6278±36 (0.5%)	2936±38 (1.3%)	2.13±0.02 (0.9%)

*Values in brackets represent relative error.

The **$\overline{Mn}$** and **$\overline{Mw}$** values obtained from the **PS** calibration curve are almost two times those obtained from the **PB** calibration curve. All these values show small average deviations. The **PS** calibration curve covers better the **MWD** range of **HTPB** resins (Figure 2). Despite this fact the results obtained from the **PB** calibration curve are in better agreement with those obtained by **VPO**, especially with those determined by using **PB**

3000 standard. This suggests that the nature of the standard can affect the determination of molecular weights of **HTPB** by **GPC**.

PS, **PB** and **HTPB** have different structures. The difference between the structures of **PS** and **HTPB** is greater than the difference between the structures of **PB** and **HTPB**. The last pair of compounds differs only by the terminal hydroxyl groups in **HTPB**. The difference between standards and samples causes different behaviours during **GPC** separation. This probably occurs due to differences in the sample-gel-solvent interactions.

Solvent, temperature, flow rate and gel (Ultrastyragel columns) were kept constant during the chromatographic process. The only variable was the nature of the solute (standard and sample). The samples were always **HTPB** but the standards changed, **PS** was replaced by **PB** standards.

When **PS** calibration is employed, it is assumed that the **PS** and **HTPB** solute-gel-solvent interactions are the same, which is not true.

A similar approach is done with the **PB** calibration. **HTPBs** differ from the **PB** standard by their terminal hydroxyl groups. Despite this, it is assumed that **PB** and **HTPB** have the same solute-gel-solvent interaction during **GPC** separation . Here, despite the possibility of presence of hydrogen bonds, the assumption of similar interactions is more acceptable because of the small number of hydroxyl groups , i.e., two per macromolecule. The $\overline{\mathbf{Mn}}$ and $\overline{\mathbf{Mw}}$, determined by **GPC** by using **PB** calibration, are $\overline{\mathbf{Mn}}$ and $\overline{\mathbf{Mw}}$ in equivalent polybutadiene.

These $\overline{\mathbf{Mn}}$ values agree with those determined by **VPO** (Table 4), specially the **VPO** results obtained by using the **PB** standard. The small difference observed in these results occurs because **VPO** measures the global variation of a property, in this case the $\overline{\mathbf{Mn}}$. **VPO** considers the entire sample, while **GPC** fractionates the sample and correlates the fractions with a molecular size (weight). The interaction, in the **VPO** process is a solvent-solute interaction, while in the **GPC** process more complex, solute-gel-solvent interactions prevail.

Table 4 - $\overline{Mn}$ of **HTPB** obtained by **VPO** and **GPC**

RESINS	**VPO**		**GPC**		η	**Ih**
	PS 1800	**PB 3000**	**PS**	**PB**	**25°C (cps)**	**(meqOH.g^{-1})**
Liquiflex P	2520	2370	4975	3025	6350	0.70
Liquiflex H	2200	2070	4390	2670	5700	0.82
Liquiflex 33	2770	2600	5470	3300	8440	0.66
Liquiflex 36	3040	2865	5480	3310	9060	0.67
Liquiflex 42	2950	2770	4925	2985	8540	0.69
R45M	2760	2600	4850	2935	7680	0.77

Table 4 shows that the **VPO** values agree better with experimental viscosity(η) and hydroxyl number (**Ih**) data, i.e., the higher $\overline{\mathbf{Mn}}$ values correspond to the higher viscosity values and to the smallest hydroxyl numbers.

The ideal calibration for both techniques would be one with **HTPB** standards. These standards are not available and an attempt to obtain them by fractionation resulted in some **PBLH** fractions with reasonable polydispersity but they could not be used as standards because only a small quantity was available .

CONCLUSION

The different structures of standards and samples in **GPC** process cause different solute-gel-solvent interactions that affect molecular weight determination by this technique. For determining molecular weight of **HTPBs** by **GPC**, **PB** standards are better. On the other hand, in **VPO** measurements both standards, **PS** and **PB** give good results.

ACKNOWLEDGMENTS

The authors would like to thank Mr. João Alves Costa for assistance with the **VPO** experimental work. This research was supported by the CNPq.

REFERENCES

1. **RAMARAO, M.; SCARIAH, K. J.; RAVIDRAN, P. V.; CHANDRASEKHARAN, G.; ALWAN, S.; SASTRI, K. S.** - (1993) J. Appl. Polym. Sci. 49: 435.
2. **MORRIS, C. E. M.** - (1976) J. Polym. Sci. Symposium nº 55, 11.
3. **BREZINSKI, J.; GLOWALA, H.; KORNAS-CALKA, A.** - (1973) Europ. Polym. J. 9, 1251.
4. **BERSTED. B. H.** - (1973) J. Appl. Polym. Sci. 17, 1415.
5. **MARX-FIGINI, M.; FIGINI, R. V.** - (1980) Makromol. Chem. 181, 2401-2407.
6. **KAMIDE, K.; TERAKAWA, T.; UCHIKI, H.** - (1976) Makromol. Chem. 177, 1447-.
7. **QUANO, A C.** - (1973) J, Macromol. Sci. - Revs. Macromol. Chem. 9(11), 123.
8. **FLORY, P.J.** - (1978) “Principles of Polymers Chemistry”, 10th ed., Cornell University Press, pp 399-43.
9. **NWANKWO, E.; ABBOTT, S.D.** - (1995) J. Appl. Polym. Sci. 58, 191.
10. **MOUREY, T.H.; BALKE, S.T.** - (1994) J. Appl. Polym. Sci. 54, 1455.
11. **MAYS, J. W.; GREGORY, E. G.** - (1987) J. Appl. Polym. Sci. 34, 2619.
12. **PETROFLEX** - (1990) Technical Report - "Liquiflex P".
13. **ARCO CHEMICAL COMPANY** - (1974).Poly bd liquid resins Product Bulletin BD-1.