Distributions of Functionality and of Molecular Weights in an Hydroxyl-Terminated Polybutadiene by Dual-Detection Size Exclusion Chromatography

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SYNOPSIS

The article deals with data treatment problems associated with the estimation (via dual-detection size exclusion chromatography) of the independent distributions of molecular weight and functionality in a derivatized hydroxyl-terminated polybutadiene. Calculations are based on an approach originally developed for linear copolymers and include corrections for (a) effect of functional groups on instantaneous mass and molecular weights, (b) dependence of refractive index with molecular weight, and (c) instrumental broadening. Compared to other more laborious analytical methods, the proposed technique is simple and provides accurate results. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Hydroxyl-terminated polybutadienes (HTPBs) are low-molecular-weight liquid prepolymers with considerable importance as adhesives, sealants, or binders for solid propellants. Industrially, they are produced through anionic or free-radical polymerizations. In the anionic process, an essentially linear and narrow-distributed "living" PB is first obtained that is capable of reacting with various electrophyllic agents for the insertion of OH groups.[1,2] In spite of the fact that only bifunctional molecules are expected, mono- and nonfunctional species are also generated, due to the inevitable deactivation of "living ends".[3,4] In the free-radical process, 1,3-butadiene is polymerized in an organic solution with hydrogen peroxide as initiator. The solvent (an alcohol) also acts as a transfer agent, lowering molecular weights. Termination is mainly by combination, and branching reactions with the polymerized material are responsible for functionalities higher than 2 in the high-molecular-weight fractions.[4,5] This is because the rate of branching is proportional to the mass of polymerized material; and therefore the number of branches (with OH substituents) increases with molecular weight. Some works on molecular microstructure[6-10] have proven useful for establishing the detailed kinetics of HTPB synthesis.

When HTPB is cured with a bifunctional agent such as toluene diisocyanate, then (a) nonfunctional polymer species do not contribute to networking, (b) species with functionality 3 and above can be classified as crosslinkers, and (c) species with functionality 2 are considered chain extenders. For this reason, number-average functionality ($\bar{f}_n$), defined as the average number of reactive functional groups (OH in this case) per molecule, is possibly the most important single parameter for predicting network properties at the curing stage. It may be estimated through:[11]

$$\bar{f}_n = \frac{\bar{M}_n}{Z} \tag{1}$$

where $\bar{M}_n$ is the number-average molecular weight that is measurable by vapor pressure osmometry (VPO), and Z is the average equivalent weight (in grams of HTPB/equivalent OH), that can be chemically determined.[12]

Apart from the global functionality, the distributions of molecular weight and functionality are

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important in relation to end-product properties. Let us classify each of the different molecular species in an HTPB sample according to their molecular weight (M) and functionality (f). Calling n the number of butadiene (B) repeating units in a molecule, then

$$M = nM_B + fM_{OH} \tag{2}$$

where M_B and M_{OH} are the molecular weights of B and OH, respectively. Calling G the mass of species with a given (f, M) combination, then the bivariate distribution $G(f, M)$ is representative of the detailed molecular macrostructure. The measurement of $G(f, M)$ requires of independent fractionations, according to molecular weight and functionality. From $G(f, M)$, the univariate molecular weight distribution $G(M)$ and the univariate functionality distribution $G(f)$ can be obtained:

$$G(M) = \sum_f G(f,M) \tag{3}$$

$$G(f) = \sum_M G(f,M) \tag{4}$$

Since only low integers of f are observed, $G(f)$ and $G(f, M)$ are, strictly speaking, highly discrete functions. From $G(M)$ and $G(f)$, the following averages can be calculated:

$$\bar{M}_w = \frac{\sum_M G(M)M}{\sum_M G(M)} \tag{5}$$

$$\bar{M}_n = \frac{\sum_M G(M)}{\sum_M \left[\frac{G(M)}{M}\right]} \tag{6}$$

$$\bar{f}_w = \frac{\sum_f G(f)f}{\sum_f G(f)} \tag{7}$$

$$\bar{f}_n = \frac{\sum_f \left[\frac{G(f)}{M}\right]f}{\sum_f \left[\frac{G(f)}{M}\right]} \tag{8}$$

where $\bar{f}_w$ is the weight-average functionality. It has been proven[11] that if f increases monotonically with M, then $\bar{f}_w/\bar{f}_n > 1$; and if f decreases with M, $\bar{f}_w/\bar{f}_n < 1$.

In ideal size exclusion chromatography (SEC), fractionation is according to hydrodynamic volume; and a one-to-one relationship between elution volume and molecular weight can be established only in the case of linear homopolymers.[13] This makes it difficult to accurately evaluate molecular weights in a (branched and functionalized) material like a free-radical HTPB. In spite of this and other problems such as degradation of very high molecular weight material and instrumental broadening (IB) in the columns, SEC is presently the best technique for estimating $G(M)$. In standard dual-detection SEC, a differential refractometer (DR) and an ultraviolet (UV) spectrophotometer at a fixed wavelength are used. In a first approximation, the DR signal can be assumed proportional to the total elution mass, while the UV sensor may respond to one specific component only. In this case, the DR to UV signal ratio is approximately equal to the instantaneous mass fraction of the detected component. Dual-detection SEC was applied on anionic and free-radical HTPBs[5,11] for estimating $G(M)$ and $f(M)$. To make the OH groups detectable by the UV sensor, a complete derivatization (with phenyl isocyanate) of the hydroxyls into phenyl urethane groups is required,[5] according to:

$$ROH + C_6H_5NCO \rightarrow C_6H_5NHCOOR$$

In the more recent work by Ninan et al.,[4] preparative and analytical SEC were employed on anionic and free-radical HTPBs, for the estimation of $G(M)$, $f(M)$, correlations with mechanical properties, and sol contents of the cured resin. Each of the samples obtained by preparative SEC were analyzed by VPO, dual-detection analytical SEC (to estimate distributions of molecular weight and functionality), and mechanical testing (to estimate the stress–strain properties of the cured resin). The molecular weight distributions (MWDs) of the fractions proved relatively wide, and the functionality distributions showed similar tendencies as in Baczek et al.[5]

Several works have attempted to fractionate HTPB according to functionality. For example, a technique based on the adsorption of the prepolymer on activated silica gel with subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power was proposed by Muenker and Hudson.[3] The objective was the determination of the weight fractions of the non-, mono-, and difunctional components in an anionic HTPB. For each fraction, the equivalent weight was determined by infrared (IR) spectroscopy, and $\bar{M}_n$ by VPO.[3] In a later study by Law,[14] separation by stepwise elution from silica gel was reattempted, but on free-radical HTPBs. Each of the fractions were later analyzed by SEC. The problems associated with

this laborious two-dimensional separation were more recently investigated by Amato and Marot,[15] concluding that high-pressure liquid chromatography instead of preparative fractionation would be required to render the technique more practical. In two interesting studies, Min et al.[16] and Inagaki et al.[17] also attempted a fractionation on the basis of functionality, but with thin-layer chromatography (TLC) in the case of an anionic HTPB, and preparative SEC followed by TLC in that of a free-radical HTPB. The two techniques were applied in the latter case because TLC separates according to molecular weight as well as functionality,[14] and therefore TLC alone is strictly applicable when narrow-distributed (anionic) HTPB is analyzed. In the case of free-radical HTPBs, another difficulty is that TLC seems incapable of adequately separating molecules of similar (but high) functionalities. In general, two-dimensional fractionation is experimentally tedious and has as yet proven incapable of yielding acceptable estimations of $G(f, M)$.

In all of the cited works dealing with SEC, the IB correction has been neglected. Such broadening is mainly caused by axial dispersion in the fractionation columns; and its correction may be important in the case of narrow-distributed polymers, or when fine details of the molecular weight distribution are of interest. For linear copolymers and dual-detection SEC, the IB correction associated with the determination of the univariate molecular weight and chemical composition distributions has been recently investigated.[18,19] In Meira and García-Rubio,[19] it was concluded that (a) the IB correction involves independent deconvolutions on each of the distorted signals and (b) for such operations, the standard broadening function determined for linear homopolymers and mass detectors can be applied. Two possible correction paths were proposed.[18,19] In the so-called Correction 1, the original chromatograms are corrected for IB before calculating the mass and composition retention time distributions. In Correction 2, these last distributions are directly calculated from the raw measurements, and then such functions are independently deconvoluted. In Bielsa and Meira,[18] it was found that the molecular weight distributions are always reasonably well recuperated, independently of the calculation path. In contrast, the composition distributions are much noisier (especially at the molecular weight tails), and are more path-dependent.[18] A derivatized HTPB can be regarded as a special copolymer built up of butadiene and phenyl urethane repeating units. For this reason, a treatment similar to that of Refs. 18 and 19 can be applied.

In this work, standard dual-detection SEC is employed for the analysis of a commercial free-radical HTPB. But unlike publications 4, 5, and 11, the data treatment here presented includes the following: (a) a new derivation of the main equations that is based on absolute detector calibrations; (b) a correction for the dependence of refractive index increment with molecular weight; and (c) a correction for IB that is based on the approach of Refs. 18 and 19. The effect of molecular branching is neglected in all that follows.

THEORETICAL CONSIDERATIONS

Detector Equations

Consider the analysis of a fully derivatized HTPB, in the sense that the original hydroxyls have been replaced by phenyl urethane groups. Call $i = 1, 2, 3, \cdots$ the discrete retention time; $A(i)$ the UV chromatogram; and $n(i)$ the DR chromatogram. We shall assume that (a) $A(i)$ is proportional to the instantaneous mass of OH substituents; (b) $n(i)$ is proportional to the mass of PB and of chromophore groups, but in the case of PB the slight dependence of the proportionality constant with molecular weight is also considered; and (c) both chromatograms $A(i)$ and $n(i)$ are distorted by IB. The following detector responses may be written:

$$A(i) = kG_\phi(i) \tag{9}$$

$$n(i) = \nu_{PB}(i)G_{PB}(i) + \nu_\phi G_\phi(i) \tag{10}$$

where G_ϕ and G_{PB} represent the instantaneous mass of derivatized OH groups and of bound B units, respectively. While k and ν_ϕ are constant, ν_{PB} is a function of retention time, to include the dependence of n with molecular weight. To estimate k and ν_ϕ, any well-characterized component with chromophores identical to those in the derivatized HTPB can be used. The calibration involves the representation of the sum of chromatogram heights (a dimensionless integer) vs. the total injected mass (in milligrams). The slopes of the resulting (linear) calibrations are the sought constants. Consider now the estimation of $\nu_{PB}(i)$.

Correction for Variations of the Refractive Index Increment

The coefficient $\nu_{PB}(i)$ in Eq. (10) is proportional to the refractive index increment $(\partial n(i)/\partial c)$ of the PB portion of the polymer:

$$\nu_{PB}(i) = \kappa \frac{\partial n(i)}{\partial c} \tag{11}$$

where κ is a constant. The refractive index increment in turn presents the following weak dependence with molecular weight:

$$\frac{\partial n(i)}{\partial c} = a - \frac{b}{M_{PB}(i)} \tag{12}$$

where a and b are positive constants that may be determined from two narrow-distributed PB samples of known $[M(i), \partial n(i)/\partial c]$. A technique that has been proposed to correct for variations in $(\partial n/\partial c)$ consists of multiplying each of the DR heights by the ratio.[13,20]

$$\frac{(\partial n/\partial c)_{max}}{\partial n(i)/\partial c}$$

where $(\partial n/\partial c)_{max}$ and $\partial n(i)/\partial c$, respectively, represent the refractive index increments of the highest molecular weight in the sample and of any generic species of (a longer) elution time i. All of these values can be determined through Eq. (12). Since $(\partial n/\partial c)_{max} > \partial n(i)/\partial c$, the correction tends to raise the low-molecular-weight tail of the DR chromatogram.

An alternative procedure that involves the direct calculation of $\nu_{PB}(i)$, will be here applied. Replacing Eq. (11) into Eq. (12), one obtains

$$\nu_{PB}(i) = a' - \frac{b'}{M_{PB}(i)} \tag{13}$$

where constants a' and b' may be found from two narrow-distributed PB samples of known average values of M_{PB} and $\bar{\nu}_{PB}$. The (constant) calibrations $\bar{\nu}_{PB}$ may be obtained as in the case of k and ν_ϕ; i.e., from the plot sum of chromatogram heights vs. injected mass.

Main Equations

From Eqs. (9) and (10), the following is found:

$$G_{PB}(i) = \frac{n(i)}{\nu_{PB}(i)} - \frac{\nu_\phi}{k\nu_{PB}(i)} A(i) \tag{14}$$

Instead of G_{PB}, one is really interested in the total instantaneous mass of original (underivatized) HTPB. This variable, which we shall call G, can be obtained from

$$G(i) = G_{PB}(i) + G_{OH}(i) \tag{15}$$

where G_{OH} is the (theoretical) instantaneous mass of original OH groups. Calling M_ϕ the molar mass of a phenyl urethane group, one can write: $G_{OH}(i)/M_{OH} = G_\phi(i)/M_\phi$; with $M_{OH} = 17$ and $M_\phi = 136$. Therefore:

$$G(i) = G_{PB}(i) + \frac{M_{OH}}{M_\phi} G_\phi(i) \tag{16}$$

Inserting Eqs. (9) and (14) into Eq. (16), we finally obtain

$$G(i) = \frac{1}{\nu_{PB}(i)} n(i) + \left[\frac{M_{OH}}{\kappa M_\phi} - \frac{\nu_\phi}{k\nu_{PB}(i)}\right] A(i) \tag{17}$$

Note that Eq. (17) is numerically well-behaved because all of its terms are linear in the measurements $n(i)$ and $A(i)$.

At each retention time, the instantaneous molar functionality $\bar{f}(i)$ is

$$\bar{f}(i) = \frac{\text{OH mol}}{\text{polymer mol}} = \frac{G_\phi(i)/M_\phi}{G(i)/M(i)} = \frac{G_\phi(i)/M_\phi}{G_{PB}(i)/M_{PB}(i)} \tag{18}$$

where M and M_{PB} are the instantaneous molecular weights of the original HTPB and of the PB portion of the same polymer, respectively. $M(i)$ and $M_{PB}(i)$ are representative of the molecular weight calibrations of the original HTPB and of a PB homopolymer. This last calibration is easier to obtain than $M(i)$, and for this reason will be here preferred. Even in the absence of IB, the molar functionality is an instantaneous average because fractionation occurs by molecular size, and therefore a whole distribution of discrete functionalities f coexists in the detector cell at any retention time. If the instantaneous molar functionality $\bar{f}(i)$ increases monotonically with molecular size, then a fractionation according to functionality is simultaneously produced. However, the statistical nature of polymerization determines that such fractionation must be relatively poor, in the sense that the true discrete functionality distribution is irrecuperable. Introducing Eqs. (9) and (13) into Eq. (18), one obtains

$$\bar{f}(i) = \frac{M_{PB}(i)}{M_\phi} \frac{A(i)/k}{\frac{n(i)}{\nu_{PB}(i)} - \frac{\nu_\phi}{k\nu_{PB}(i)} A(i)} = \frac{\nu_{PB}(i) M_{PB}(i) [A(i)/n(i)]}{M_\phi \{k - \nu_\phi [A(i)/n(i)]\}} \tag{19}$$

Equation (19) indicates that $\bar{f}(i)$ is strictly proportional to the signals ratio only when $k \gg \nu_\phi[A(i)/n(i)]$. Unlike the case of $G(i)$, numerical problems with the estimation of $\bar{f}(i)$ at the chromatogram tails are to be expected because large relative errors in the signals ratio are feasible at those ends.

From the measurements $[A(i), n(i)]$, and the calibrations $[k, \nu_\phi$, and $\nu_{PB}(i)]$, Eqs. (17) and (19) allow to find the (IB-distorted) solutions $G(i)$ and $\bar{f}(i)$. The calculation of $\bar{f}(i)$ with Eq. (19) requires a molecular weight calibration involving PB standards. From $\bar{f}(i)$ and such calibration, the molecular weights of the original HTPB can be estimated as follows:

$$M(i) = M_{PB}(i) + \bar{f}(i)M_{OH} \tag{20}$$

Equation (20) avoids the difficulty of an independent calibration with HTPB standards. From $G(i)$ and $M(i)$, the (IB-distorted) molecular weight distribution $G(M)$ for the original HTPB can be finally represented. If a linear horizontal axis is required in this representation, then an appropriate "continuization" procedure must be applied that consists in dividing each $G(i)$ ordinate by its corresponding molecular weight increment.[13] From $G(i)$ and $\bar{f}(i)$, the (IB-distorted) average functionality distribution $G(\bar{f})$ can be obtained. This transformation again involves a modification of the heights due to the unequally spaced points along $\bar{f}$. With $G(M)$ and $G(\bar{f})$, then Eqs. (5)-(8) (with f replaced by $\bar{f}$) could be applied to estimate the molecular weight and functionality averages. However, it is numerically preferable to directly calculate such averages from the elution time distributions, as follows:

$$\bar{M}_w = \frac{\sum_i G(i)M(i)}{\sum_i G(i)} \tag{21}$$

$$\bar{M}_n = \frac{\sum_i G(i)}{\sum_i \left[\frac{G(i)}{M(i)}\right]} \tag{22}$$

$$\bar{f}_w = \frac{\sum_i G(i)\bar{f}(i)}{\sum_i G(i)} \tag{23}$$

$$\bar{f}_n = \frac{\sum_i \left[\frac{G(i)}{M(i)}\right]\bar{f}(i)}{\sum_i \left[\frac{G(i)}{M(i)}\right]} \tag{24}$$

To prove that Eq. (24) is equivalent to Eq. (1), first replace Eq. (18) into Eq. (24); to obtain:

$$\bar{f}_n = \frac{\sum_i [G_\phi(i)/M_\phi]}{\sum_i [G(i)/M(i)]} = \frac{\sum_i \bar{f}(i)}{\sum_i [G(i)/M(i)]} \tag{25}$$

where $\sum_i \bar{f}(i)$ represents the total moles of OH substituents. Multiplying and dividing by the total sample mass $\sum_i G(i)$, one finds

$$\bar{f}_n = \frac{\frac{\sum_i G(i)}{\sum_i [G](i)/M(i)]}}{\frac{\sum_i G(i)}{\sum_i \bar{f}(i)}} = \frac{\bar{M}_n}{Z} \tag{26}$$

Instrumental Broadening Correction

Assume the following: (a) an ideal standard consisting of identical species from the point of view of molecular weight and functionality and (b) an ideal chromatograph, in the sense that steric exclusion is the only fractionation mechanism, and IB is absent. If the ideal standard were injected into the ideal chromatograph, then impulsive DR and UV chromatograms (i.e., "delta" functions) appearing at a characteristic retention time i_0, would be expected. Assume now a real chromatograph, in the sense that IB is present. The spreading function depends on the mean retention time i_0 only, and is independent of functionality. If the ideal standard were injected into the real chromatograph, then the normalized DR and UV chromatograms would coincide; and such chromatograms would be representative of the (common) broadening function $h(i)$. Thus, the following Tung's models can be written:[21-23]

$$A(i) = \sum_{i_0} h(i, i_0)A^c(i) \tag{27}$$

$$n(i) = \sum_{i_0} h(i, i_0)n^c(i) \tag{28}$$

where superscript c will in general indicate that a variable has been corrected for IB (while its absence is indicative of IB distortion), and $h(i, i_0)$ is the spreading function or normalized set of chromatograms of hypothetical monodisperse homopolymers with different mean elution times i_0. Equation (27) permits the calculation of $A^c(i)$ from $A(i)$ and $h(i, i_0)$; and Eq. (28) allows to find $n^c(i)$ from $n(i)$ and $h(i, i_0)$.

It is easy to show that Eqs. (17) and (19) are also valid when $G(i)$, $n(i)$, $A(i)$, and $\bar{f}(i)$ are replaced by $G^c(i)$, $n^c(i)$, $A^c(i)$, and $\bar{f}^c(i)$. This is a

consequence of the linearity observed in Eqs. (9), (10), (27), and (28). Thus, $A^c(i)$ and $n^c(i)$ can be first determined with Eqs. (27) and (28), and then $G^c(i)$ and $\bar{f}^c(i)$ can be obtained through the IB-corrected versions of Eqs. (17) and (19). This numerical procedure we shall call Correction 1.

The linearity of Eqs. (9), (10), and (17) also determines that the broadening function associated to $G(i)$ must coincide with $h(i, i_0)$ of Eqs. (27) and (28). Therefore, one can write

$$G(i) = \sum_{i_0} h(i, i_0) G^c(i) \qquad (29)$$

Equation (29) suggests an alternative way of determining $G^c(i)$, which we shall call Correction 2. It consists in first calculating $G(i)$ with Eq. (17), to then obtaining $G^c(i)$ with Eq. (29). This procedure seems preferable to Correction 1 because only one deconvolution operation is involved. The obtainment of $\bar{f}^c(i)$ through an expression equivalent to Eq. (29) is not easily justified and will be not considered in this work.

EVALUATION EXAMPLE

Consider the analysis of a Liquiflex H (Petroflex, Brazil) HTPB prepolymer. For the SEC analysis, a derivatization as in Refs. 5 and 11 was applied. The sample was first dried during 4 h at 80°C and 11 mmHg. Then, a 100% excess of phenyl isocyanate (Aldrich), together with 0.03% in weight of dibutyl tin laurate (a catalyst) were added. The reaction was carried out during 4 h under a nitrogen blanket, and finally vacuum was applied to eliminate the isocyanate excess.

Global Analyses

The microstructure of butadiene units in HTPB was determined by ^{1}H-NMR, as described in Vilar and Akcelrud,[10] yielding the following molar fractions: 1,2-vinyl, 21%; trans-1,4, 58%; and cis-1,4, 21%.

To estimate $\bar{M}_n$, a Wescan 232A (Santa Clara, CA) VPO was utilized as in Tinoco and Akcelrud.[24] A calibration with polystyrene (PS) standards was applied; and a correction for the presence of antioxydant (2,6 di-tert-butyl-, 4 methyl phenol) was included. The analysis provided $\bar{M}_n$ = 2990.

The global equivalent weight (Z) was determined following Collins et al.[12] First, the OH groups were acetylized during 3 h at 100°C with an excess of acetic anhydride (Riedel de Häen) in pyridine (Merck). The anhydride excess was then hydrolized with water during one hour at 100°C; and finally the solution was titrated in reflux with an KOH alcohol solution and phenolphtalein. The analysis yielded Z = 1248 g/eq OH.

From Eq. (1) and the mentioned measurements, the number-average functionality resulted: $\bar{f}_n$ = 2.40 eq OH/mol.

Chromatographic System and its Calibration

A Waters Assoc. (Milford, MA) ALC/GPC 244 was employed, fitted with four thermostatted (30°C) μ-Styragel columns of nominal pores: 100, 500, 10^3 and 10^4 Å; a Waters 440 UV absorbance detector at 254 nm; and a thermostatted (30°C) Waters R-401 differential refractometer. The solvent was tetrahydrofuran (THF) at 1 mL/min. The chromatograms were digitalized by means of a Minc 11 process computer, and the data treatment programs were written in FORTRAN 77 for a Digital VAX 11/780 computer. All samples were dissolved in THF (0.1% weight/volume); and toluene was utilized as internal standard to correct for variations in the carrier flow rate. In Figure 1(a), the raw chromatograms are represented. The DR chromatogram is shown shifted, to correct for the volume lag between sensors. The curves consist of 75 and 76 nonzero points, taken at approximately 0.142 mL intervals. Thus, the following relationship between the discrete time i and the discrete retention volume v_r can be established: $v_r(i) \cong 0.142i$. In what follows, i and v_r will be indistinctly employed.

For the *molecular weight calibration,* reliable PB standards were not available, but acceptable Mark-Houwink constants of this homopolymer were known.[25] For this reason, a universal calibration[26]

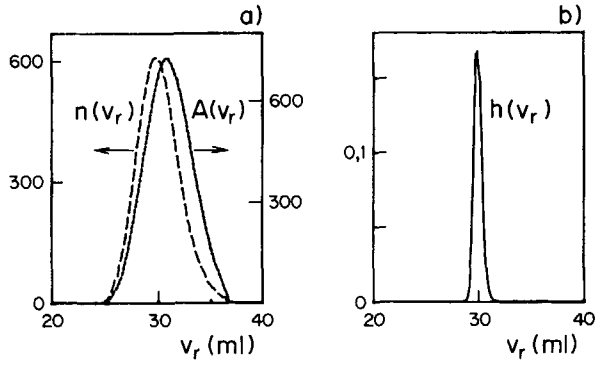

Figure 1 (a) UV and DR chromatograms [$A(v_r)$ and $n(v_r)$, respectively], for the analyzed free-radical HTPB sample. (b) IB calibration.

involving the representation of $\log\{M(v_r)[\eta(v_r)]\}$ vs. v_r was implemented, with $[\eta]$ being intrinsic viscosity. A set of narrow PS standards (Waters Assoc.) of known molecular weight averages was employed; and the intrinsic viscosities were measured with a Cannon Feske N 50 capillary viscometer at 30°C, according to standard ASTM D 2857-70. The calibration resulted:

$$\log J(v_r) = \log\{[M(v_r)\eta(v_r)]\} = 11.7026 - 0.1960v_r \quad (30)$$

Replacing the Mark–Houwink equation for the PB:

$$[\eta]_{PB} = K_{PB}(M_{PB})^{a_{PB}} \quad (31)$$

into Eq. (30), one obtains

$$\log M_{PB}(v_r) = \frac{\log J(v_r) - \log K_{PB}}{a_{PB} + 1} \quad (32)$$

The following constants were adopted:[25] $K_{PB} = 4.57 \times 10^{-4}$ and $a_{PB} = 0.693$. These values correspond to a THF solution, at 30°C, of a linear PB with a microstructure (cis-1,4; 30%; trans-1,4; 42%; and 1,2-vinyl, 28%) similar to that of the analyzed polymer.

Consider the *detectors calibration.* To determine the response of both sensors to the phenyl urethane groups 120, 250, 400, and 500 μL of a phenyl isocyanate solution were injected, and the functions: cumulative chromatograms vs. injected mass were represented. For the calibrations, it proved convenient to change operating conditions (such as detector attenuations, computer sampling rate, or carrier flow rate) with respect to nominal conditions. In such cases, care must be taken to adequately rescale the obtained calibration slopes in order to compensate for such readjustments. The molecular weights of phenyl isocyanate and of the derivatized group are 119 and 136 g/mol, respectively. For this reason, the calibration slopes obtained with phenyl isocyanate must be multiplied by the ratio 119/136. The following was finally obtained:

$$k = 527522 \text{ mg}^{-1} \quad v_\phi = 96661 \text{ mg}^{-1} \quad (33)$$

To find a' and b' in Eq. (13), two PB standards (Polysciences Inc., Warrington, PA) of nominal molecular weight averages ($\bar{M}$) were employed. Assuming that each standard presented a constant calibration $\bar{v}_{PB}$, the following values were found:

$$\bar{v}_{PB} = 27{,}711 \text{ mg}^{-1} \quad (\bar{M} \cong 439)$$

$$\bar{v}_{PB} = 29{,}405 \text{ mg}^{-1} \quad (\bar{M} \cong 22{,}000)$$

Therefore, the sought coefficients result: $a' = 29439$; $b' = 758522$; and finally Eq. (13) may be written:

$$v_{PB}(i) = 29439 - \frac{758522}{M_{PB}(i)} \quad (34)$$

From Eq. (34), the v_{PB} values corresponding to the highest and lowest molecular weight in the sample are 29,402 and 26,626, respectively. As expected, a small variation is observed.

For the *instrumental broadening correction,* the spreading function was considered uniform in the observed chromatogram range, and identical to the normalized chromatogram obtained from the injection of 1 μL of toluene. This function $h(v_r)$ is represented in Figure 1(b). It is considerably narrower than the measured chromatograms in Figure 1(a); and therefore only moderate corrections for IB are to be expected. The deconvolution operations were carried out with a technique based on the Kalman filter.[22] The algorithm gain can be iteratively adjusted from observing the resulting solution and the corresponding "innovations" sequence. This normally implies a compromise between nonnegative values in the corrected tails and adequate recuperations of the measured chromatogram.[22]

Results

Measurements $A(v_r)$ and $n(v_r)$ of Figure 1(a) were processed as suggested above. In Figure 2, the retention volume distributions are presented. $G(v_r)$ and $\bar{f}(v_r)$ of Figures 2(a,b) were obtained by direct application of Eqs. (17) and (19), and do not include corrections for IB. Figures 2(c,d) show the deconvoluted chromatograms (first step of Correction 1); with the original measurements included for comparison. Figure 2(e) represents the instantaneous corrected functionality $\bar{f}^c(i)$, obtained from processing $A^c(i)$ and $n^c(i)$ with the IB-corrected version of Eq. (19) (second step of Correction 1). In Figure 2(f), two practically coincident solutions for $G^c(i)$ are observed that correspond to the two ways of finding such a function.

The final distributions are presented in Figure 3, while global averages are indicated in Table I. In Figure 3(a), the IB-uncorrected molecular weight distribution $G(M)$ is very similar to the other two (superimposed) $G^c(M)$ curves. Figure 3(b) shows the functionality distributions obtained with and without IB correction. In Figure 3(c), the IB-corrected and uncorrected functionality vs. molecular weight functions are presented. Linear molecular weight axes are employed in Figures 3(a) and 3(c).

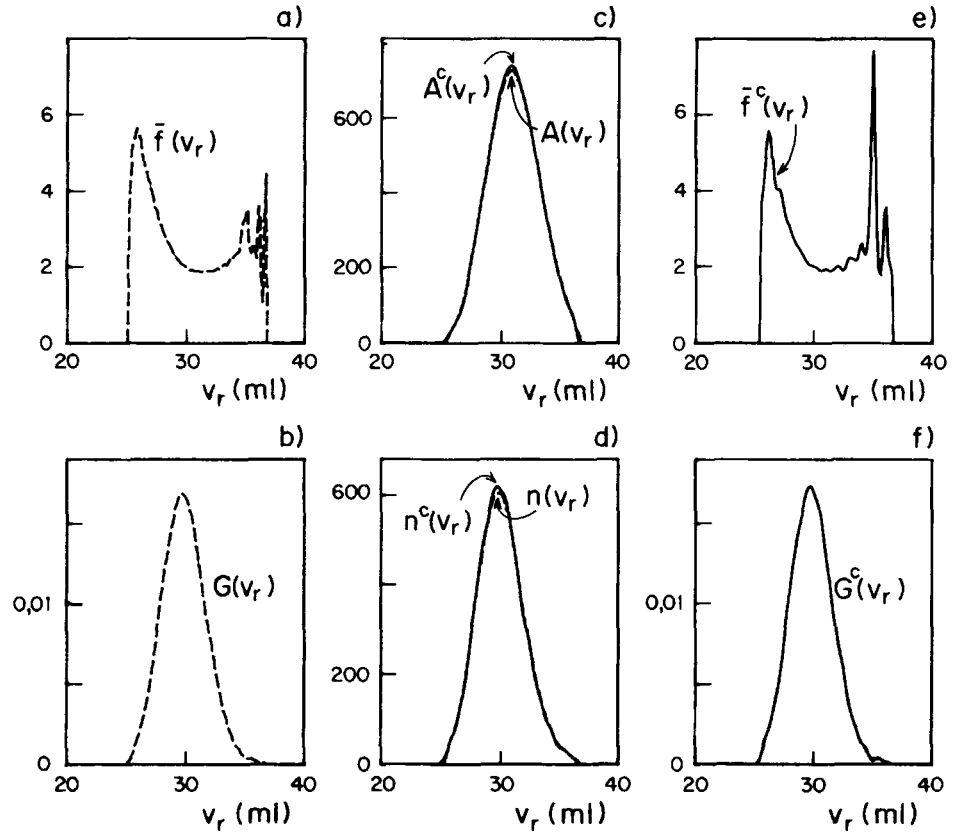

Figure 2 Intermediate retention volume distributions.

The following comments can be made:

1. For the analyzed polymer, IB correction has been shown unimportant, and polydispersity $\bar{M}_w/\bar{M}_n$ is only reduced from 1.64 (without correction) to 1.61 (with correction). These values are characteristic of a free-radical polymerization with termination by chain transfer and by recombination.
2. Except for the oscillations observed at the low-molecular-weight end, $\bar{f}(M)$ grows more or less monotonically with molecular weight. The oscillations are evidence of the large errors in the signals ratio at the chromatogram

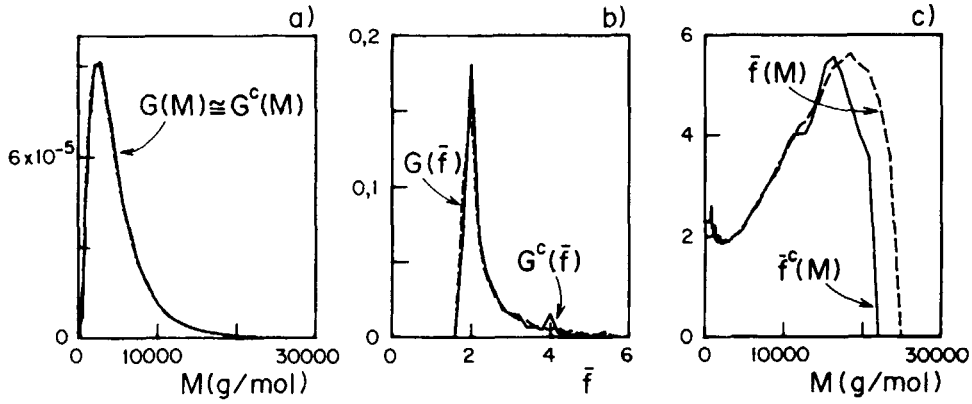

Figure 3 Final distributions: (a) of molecular weights, (b) of functionality, and (c) functionality vs. molecular weight.

Table I Estimated Averages

	By Size Exclusion Chromatography			
	Without IB Correction	With Correction 1	With Correction 2	Independent Method
$\bar{M}_n$	2896	2953	2951	2990[b]
$\bar{M}_w$	4760	4753	4749	—
$\bar{M}_w/\bar{M}_n$	1.64	1.61	1.61	—
$\bar{f}_n$	2.12	2.14	—	2.40[d]
$\bar{f}_w$	2.38	2.37	—	—
Z	1366[a]	1380[a]	—	1248[c]

[a] $(= \bar{M}_n/\bar{f}_n)$.
[b] VPO.
[c] Titration measurement.
[d] [= (b)/(c)].

tails. The increase of $f(M)$ with molecular weight is an indication that many OH groups are introduced through branching reactions. The negative skewness in $\bar{f}(M)$ is reflected by the fact that $\bar{f}_w > \bar{f}_n$.[11] The reduced number of points of $\bar{f}^c(M)$ with respect to $\bar{f}(M)$ at the high-molecular-weight end is a consequence of the deconvolution operations. The difference between such curves has a small effect on functionality averages, because negligible mass fractions are present at that end.

3. The $\bar{M}_n$ values obtained via SEC are notably close to the independent VPO measurement. A difference of around 11% is observed between the two independent estimations of $\bar{f}_n$.

DISCUSSION

With an adequate calibration and data treatment, double-detection SEC is a simple and rapid technique to estimate the univariate distributions of molecular weight and chemical composition in commercial HTPBs. The main assumptions of this work were that butadiene repeating units negligibly contribute toward the UV signal, and that branching has a negligible effect on hydrodynamic volume. Based on these assumptions and on the use of simple standards for the calibration of detectors and molecular weights, accurate expressions for the estimation of the instantaneous values of mass, average functionality $(\bar{f})$, and molecular weights for the original HTPB were developed. Such expressions compensate for the fact that a derivatized HTPB (instead of the original HTPB) is in reality chromatographed.

Replacing the detector calibrations [Eqs. (33) and (34)] into Eq. (17), it results that the instantaneous original (underivatized) HTPB mass is basically proportional to the DR signal, with a minor contribution from the UV signal. Equation (17) is numerically well-behaved since both terms are linear in the measurements. In contrast, the instantaneous average functionality [Eq. (19)] is essentially proportional to the signals ratio, and therefore large errors are to be expected at the chromatogram tails. In Eqs. (19) and (17), the relatively minor dependance of refractive index with molecular weight is directly taken into consideration through a variable DR calibration coefficient. The linearity of Eq. (17) also determines that for obtaining the IB-corrected MWD, a single deconvolution of $G(i)$ is required. In contrast, the nonlinearity of Eq. (19) determines that independent deconvolutions of the two raw chromatograms are necessary to obtain the IB-corrected $\bar{f}(i)$ function. The IB correction has proven to be little important for the analyzed free-radical HTPB sample; but this may not be the case of a narrow-distributed anionic HTPB. In summary, accurate estimations of the MWD are feasible; while the calculation of the chemical composition distribution is considerably more complicated and subject to errors.

Instead of the mass vs. instantaneous functionality distribution $G(\bar{f})$, one would really like to determine the true discrete functionality distribution $G(f)$, or mass fractions with $f = 1, 2, 3$, etc. The insurmountable difficulty for obtaining this discrete function stems from the fact that fractionation in SEC is by hydrodynamic volume rather than by OH

composition. However, since functionality increases monotonically with molar mass in free-radical HTPB, a simultaneous (crude) functionality fractionation is produced along with steric exclusion. A gross estimation of the discrete masses corresponding to $f = 1, 2, 3$, etc. could be obtained from Figure 3(b), by finding the areas under $G(\bar{f})$ between 0.5 and 1.5, 1.5 and 2.5, 2.5 and 3.5, etc. These concepts need to be further investigated and represent the limits of the present data treatment.

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