Number-Average Molecular Weight and Functionality of Poly(tetramethylene glycol) by Multidetector SEC

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SYNOPSIS

Multidetector size exclusion chromatography (SEC) is used to simultaneously determine molecular weight and number of reactive end groups per chain (functionality) of poly(tetramethylene glycol)s. Hydroxyl groups are first quantitatively derivatized with phenyl isocyanate, providing an end-group-selective UV-absorbing tag. The number of end groups per chain is then determined from the SEC chromatogram using a UV detector. Molecular weight at each retention volume and the number-average molecular weight of the whole polymer are calculated by four methods involving (1) a concentration detector and a narrow standard log M calibration curve, (2) the UV detector and a narrow standard log M calibration, (3) a viscometry detector and a universal calibration curve, and (4) combined differential viscometry and concentration detectors using a universal calibration curve. The multidetector experiment provides a unique opportunity to assess the accuracy and limitations of each approach on low-molecular-weight polymers. In particular, the effect of end groups on the concentration detector response and the application of universal calibration principles at small molecular sizes are important factors. It is shown that the concentration response can be corrected by a simple relationship between detector response and reciprocal molecular weight. Also, the quality of calibration curves is critical to the calculation of accurate molecular weights. In general, log M calibration curves provide superior results to universal calibration methods. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Low-molecular-weight (< 10,000 g/mol) poly(tetramethylene glycol) (PTMG) is a common hydroxyl-terminated prepolymer used in the synthesis of polymers made by step-growth polymerization. It is incorporated into the polymer structure by reaction of hydroxyl end groups with diisocyanates to form polyurethanes or by reaction with diesters or diacid chlorides to form polyesters. Polymer properties are affected by the length of the PTMG segment, and the degree of polymerization is dependent on functionality, or the number of reactive hydroxyl groups per chain. Ideally, PTMG is difunctional, i.e., terminated with hydroxyl groups on both ends.

PTMG prepolymers are a mixture of oligomers with different molecular weights. The number-average molecular weight $\bar{M}_n$ is normally used to determine stoichiometry for step-growth polymerization. $\bar{M}_n$ is determined from colligative properties using vapor-phase osmometry, ebulliometry, or cryoscopy. Also, end-group analysis by spectroscopy, direct titration, or chemical derivatization is used to determine $\bar{M}_n$ provided functionality is already known. Alternatively, spectroscopic and titrimetric methods are used to measure functionality provided $\bar{M}_n$ is known. In some instances, normal or reversed-phase high-performance liquid chromatography (HPLC) can provide functional group distribution independent of molecular mass. A few methods, notably mass spectrometry and size exclusion chromatography (SEC), can measure *both* $\bar{M}_n$ and functionality simultaneously. With SEC, there may be a variety of approaches, each possibly with limitations. This is particularly true with multidetector

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SEC systems, since the same information can, in theory, be obtained independently from different detectors. Using PTMG as an example, the interrelationship between functionality, $\bar{M}_n$, and various SEC detector responses is as follows.

Functionality

Measurement of functionality requires a detector that is sensitive to polymer end groups. Often, it is difficult to measure common end groups such as hydroxyl, amino, or carboxyl groups directly with HPLC spectrophotometric detectors. However, many methods have been developed that derivatize the end groups with an ultraviolet-absorbing molecule.[1-7] This allows selective measurement of end groups by ultraviolet (UV) spectrophotometric detection, provided the polymer repeat units do not absorb light appreciably at the absorption maxima of the aromatic label.

Anderson et al.[1] described a method for hydroxyl-terminated polymers that is applicable to PTMG prepolymers. In the method, a UV detector is used to selectively measure end groups derivatized with an aromatic group, and a differential refractive index (DRI) detector is used to measure polymer concentration. The method has been successfully used on hydroxyl-terminated polybutadienes[2] and poly(caprolactones).[3] The total equivalents of end groups, E, is determined from the peak area of the UV chromatogram and a peak area calibration curve constructed at various concentrations for a molecule that is a suitable model for the aromatic end group. Total polymer equivalent weight, Z, is

$$Z = \frac{m}{E} \tag{1}$$

where m is the mass of derivatized polymer injected. The normalized chromatogram height for the DRI is

$$W_{N,i} = \frac{W_i}{\sum W_i \, \Delta v_i} \tag{2}$$

where W_i is the baseline-corrected, concentration chromatogram height at retention volume v_i and Δv_i is the volume increment between data points. An analogous expression can be written for the response of the end-group-selective (UV) detector,

$$F_{N,i} = \frac{F_i}{\sum F_i \, \Delta v_i} \tag{3}$$

where F_i is the height of the UV chromatogram at retention volume i, assuming no UV absorbance contribution from the polymer repeat units. The equivalent weight of polymer at each retention volume is then

$$Z_i = Z \frac{W_{N,i}}{F_{N,i}} \tag{4}$$

and the functionality at each retention volume, f_i, is given by

$$f_i = \frac{M_i}{Z_i} \tag{5}$$

The molecular weight at each retention volume, M_i, is obtained from one of several calibration methods. These are discussed in more detail below.

Number-Average Molecular Weight

A multidetector SEC system consisting of a concentration detector (DRI), an end-group-selective detector (UV), and a molecular mass-sensitive detector (differential viscometry or DV) provides several options for the measurement of number-average molecular weight. These options are determined by the combination of detector signals utilized.

Concentration Detection

This method uses only the concentration detector, in this case the DRI. Number-average molecular weight is calculated from

$$\bar{M}_n = \frac{\sum W_i \, \Delta v_i}{\sum (W_i/M_i) \Delta v_i} \tag{6}$$

where W_i is the height of the baseline-corrected concentration chromatogram at retention volume v_i and M_i is the molecular weight at each retention volume. The molecular weight at each retention volume, M_i, is obtained from a conventional log M–retention volume calibration curve made from narrow standards. These standards must have the same chemical composition as the samples to be analyzed.

Underlying Eq. (6) is the assumption that the baseline-corrected height of the chromatogram is directly proportional to polymer concentration at each retention volume. Equation (6) is commonly written in terms of concentration,

$$\bar{M}_n = \frac{\sum c_i}{\sum (c_i/M_i)} \tag{7}$$

However, the DRI response is sensitive to end groups at low molecular weights and response may not be uniformly proportional to concentration for all polymer molecules. Here, a correction must be applied to the baseline-corrected heights of the DRI chromatogram for Eq. (6) to be accurate. The importance of this correction increases with decreasing molecular weight and with increasing differences between the specific refractivity of the end groups and the polymer repeat units. A simple correction to the uncorrected DRI chromatogram heights, $W_{i,\mathrm{uc}}$, is based on the inverse relationship between molecular weight and corrected DRI response, $W_{i,c}$

$$W_{i,c} = \frac{W_{i,\mathrm{uc}}}{(\alpha/M_i) + 1} \tag{8}$$

where α is a constant obtained from measuring the response, at constant concentration, of a series of oligomers of known molecular weight and composition.

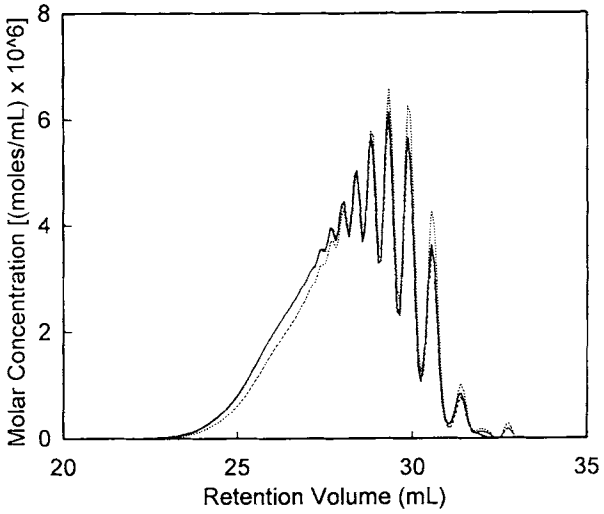

Figure 1 PTMG 650: (——) normalized UV chromatogram, (– – – – –) c_i/M_i calculated from corrected DRI response, (· · · ·) c_i/M_i calculated from uncorrected DRI response.

End-Group-Selective Detection

This method uses a detector that is insensitive to the polymer repeat units and responds only to end groups. In our case, the terminal hydroxyl groups of PTMG are derivatized with phenyl isocyanate, and absorbance is measured at a wavelength specific for aromatic groups with the UV detector. The response of the UV detector is proportional to molar concentration (c_i/M_i), which in the instance of two UV absorbing end groups per chain is given by

$$F_i\,\Delta v_i = 2k\,\frac{c_i}{M_i}\,\Delta v_i \tag{9}$$

where k is an instrument constant. The normalized UV response superimposes on the molar concentration calculated from the concentration detector (DRI), c_i/M_i, provided the DRI response is corrected using Eq. 8 (Fig. 1). Combining Eqs. (9) and (7) gives

$$\bar{M}_n = \frac{\sum F_i M_i\,\Delta v_i}{\sum F_i\,\Delta v_i} \tag{10}$$

The molecular weight at each retention volume is obtained from a log M–retention volume calibration curve made from *derivatized* PTMG oligomers. If the normalized height at each retention volume, $F_{N,i}$, is used, then the denominator of Eq. 10 is equal to 1.

Viscometry Detection

A method first proposed by Goldwasser[8,9] uses the DV detector alone, the mass of sample injected, m, and a universal calibration curve. The whole polymer $\bar{M}_n$ is as follows:

$$\bar{M}_n = \frac{m}{\sum (\eta_{\mathrm{sp},i}/J_i)\Delta v_i} \tag{11}$$

The specific viscosity $\eta_{\mathrm{sp},i}$ is obtained from the DV response and the hydrodynamic volume, $J_i = [\eta]_i M_i$ is retrieved from the universal calibration plot where $[\eta]_i$ is intrinsic viscosity. This method circumvents the complication of a molecular weight dependence on the DRI response. It also eliminates the need for narrow fractions of the same chemical composition as the polymer to be analyzed since readily available standards such as polystyrene can be used to construct the universal calibration curve. However, since the peak retention volumes of these narrow standards are measured using the DRI detector response, the interdetector volume between the DRI and DV detectors must be determined. The effect of interdetector volume on the calculation of $\bar{M}_n$ has been discussed previously.[10] Other complications of this method are that the insensitivity of the DV detector to low-molecular-weight species can bias the values of $\bar{M}_n$ high, and that axial dispersion can be important.[10]

Viscometry and Concentration Detection

This method uses a molecular mass-sensitive detector and a concentration detector. The intrinsic viscosity at each point along the chromatogram is calculated from the specific viscosity, $\eta_{sp,i}$, obtained by the DV detector, and concentration is measured by the DRI,

$$[\eta]_i = \frac{\eta_{sp,i}}{c_i} \tag{12}$$

The molecular weight at each retention volume is then calculated from $[\eta]_i$ and a universal calibration curve. Number-average molecular weight is then calculated using Eq. (7). As with the viscosity detection method, interdetector volume will affect the calculation of $\bar{M}_n$. Because the method uses a concentration detector (it actually uses this response twice), the DRI response may need to be corrected for end-group effects as a function of molecular weight [e.g., via Eq. (8)].

EXPERIMENTAL

Chemicals

All PTMG samples were obtained from Scientific Polymer Products (Ontario, NY), except PTMG, $\bar{M}_n$ = 250, which was from Aldrich (Milwaukee, WI). PTMG samples were reported by the vendors to be hydroxyl-terminated on both ends, with $\bar{M}_n$ ranging from 250 to 2900. Phenyl isocyanate (PhNCO), dibutylamine (DBA), *n*-hexanol, methanol, and 1,4-butanediol, all reagent grade, were from Fisher Scientific (Pittsburgh, PA), and dibutyltin dilaurate (DBTDL) was from Aldrich. All were used without further purification. Polystyrene and poly(tetrahydrofuran) (pTHF) narrow molecular weight standards were obtained from Polymer Laboratories (Amherst, MA).

Nonaqueous Titrimetry

Potentiometric titration curves were recorded with a Metrohm model E670 potentiograph equipped with a model E665 dosimat and a 10-mL buret. Solution potentials were monitored with a combination glass–calomel electrode (Metrohm) containing 0.1*N* tetramethylammonium chloride in methanol in the reference cell.

Size Exclusion Chromatography

Three Ultrastyragel 500-Å pore diameter and one Ultrasyragel 100-Å pore diameter columns, all 7.8 mm i.d. × 300 mm (Waters Corp., Milford, MA) were coupled in series. The outlet of the column set was connected to a Spectroflow 757 UV detector. The effluent was divided nearly equally between a Waters model 410 DRI and a model H502A differential viscometer (Viscotek Corporation, Houston, TX). The eluent, 1% by volume acetic acid in uninhibited HPLC-grade tetrahydrofuran (THF) (J. T. Baker, Phillipsburg, NJ), was continuously sparged with helium. The nominal flow rate was 1 mL/min. Flow rates were corrected using acetone as an internal flow marker. Samples were injected in a volume of 100 μL.

Preparation and Analysis of Derivatized Hydroxyl Groups by Potentiometric Titration

Primary hydroxyl groups were derivatized with PhNCO to form a urethane according to reaction I, using a modification of the procedure developed by Reed et al.[11]:

$$\mathrm{R{-}OH + Ph{-}N{=}C{=}O \rightarrow R{-}O{-}CO{-}NH{-}Ph} \quad \text{(I)}$$

Samples, containing about 0.5 meq hydroxyl, were dissolved in dry THF in the presence of the catalyst DBTDL [THF was dried for 24 h over molecular sieves, types 3A and 4A (Fisher Scientific)]. The H_2O content of THF must be minimized, since H_2O competes with ROH for PhNCO to form aniline as shown in reaction II:

$$\mathrm{H_2O + Ph{-}N{=}C{=}O \rightarrow Ph{-}NH_2 + CO_2} \quad \text{(II)}$$

Aniline can further react with PhNCO to form diphenylurea (reaction III):

$$\mathrm{Ph{-}NH_2 + Ph{-}N{=}C{=}O \rightarrow (Ph{-}NH)_2C{=}O} \quad \text{(III)}$$

A 2× molar excess of PhNCO was added, and the solution was stirred for 10 min at room temperature. The extent of reaction was monitored by quantifying the unreacted PhNCO in reactions I–III. This is accomplished by reaction of the phenyl isocyanate with dibutylamine that is in turn back-titrated:

$$Ph—N=C=O + HN((CH_2)_3CH_3)_2 \rightarrow Ph—NHCON((CH_2)_3CH_3)_2 \quad (IV)$$

$$HN((CH_2)_3)_2 + HClO_4 \rightarrow H_2^+N((CH_2)_3)_2 + ClO_4^- \quad (V)$$

Reaction IV is rapid and quantitative. The unreacted DBA from reaction IV is titrated potentiometrically with $HClO_4$ (reaction V). A representative titration curve is provided in Figure 2. The first inflection is attributed to unreacted DBA from reaction IV. The identity of the second titratable base in Figure 2 was not determined; however, it is probably aniline because (1) the amount of this base increases if H_2O is added to the reaction mixture, and (2) this base titrates at the same potential as aniline. Our calculations assume that for each milliequivalent of unknown base formed, one millimole of PhNCO was consumed.

Analysis of Derivatized Hydroxyl Groups by SEC-UV

Samples were derivatized as described above (reaction I). Subsequently a 10× excess of methanol was added to quench unreacted PhNCO. Samples were evaporated to dryness, and the derivatized material was dissolved to a final concentration of 2.5 mg/mL, based on underivatized sample weight, in THF. Both derivatized and underivatized samples were analyzed by multidetector SEC as described above. Alternatively, samples were derivatized at concentrations of hydroxyl groups that were 10–20× less than that required for potentiometric titration; equivalent results were obtained.

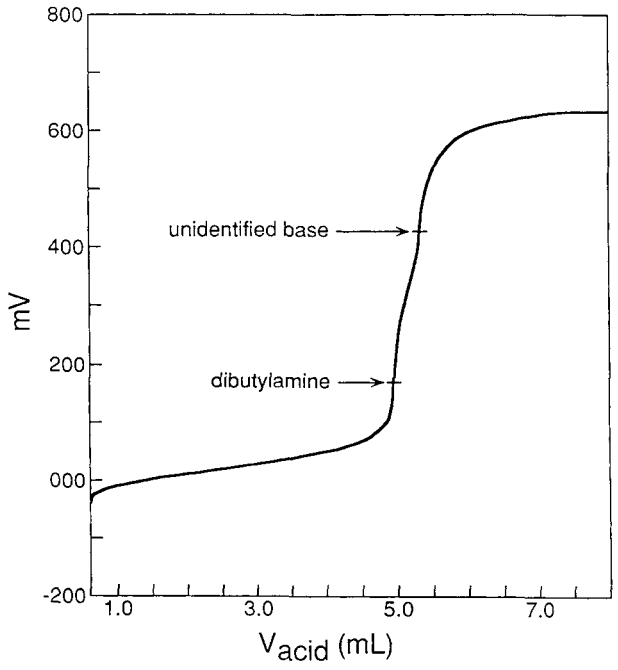

Figure 2 Typical titration curve for determining the extent of labeling of hydroxyl groups with phenyl isocyanate.

Calibration of UV Detector

The UV detector was calibrated with PhNCO-derivatized 1,4-butanediol (1,4-butanediol is the monomer unit in PTMG). Several dilutions of a 0.2-mg/mL solution of derivatized butanediol were prepared, and the UV signal was monitored at 265 nm. UV areas were plotted vs. meq ROH. The UV response was linear in the range of interest; therefore, the slope of the line, 5.369×10^5 area units/meq ROH, was taken as the UV response factor.

Correction of DRI Response

The correction first requires DRI area responses for derivatized material at a low molecular weight where the end-group effect is most significant, and at a high molecular weight where the end-group effect is negligible. PhNCO-derivatized 1,4-butanediol with a molecular weight of 328 has a DRI area response that is 2.30 times higher than that of an underivatized pTHF (pTHF is high-molecular-weight PTMG) standard with a SEC peak molecular weight, M_p = 26,600. It is assumed the DRI areas of derivatized and underivatized standards at this molecular weight are equal (high-molecular-weight standards with hydroxyl end groups are not readily available for derivatization) and the DRI correction factor is assumed to be 1.0. A pTHF standard with hydroxyl end groups and M_p = 8000 is available and was derivatized with PhNCO. These three points yield a linear plot of DRI correction factor vs. $1/M$ with a slope α = 427.1 for derivatized PTMGs. In a similar manner, α for underivatized PTMG was calculated to be −25.861.

RESULTS AND DISCUSSION

Functionality

The effectiveness of the derivatization procedure was determined by potentiometric titration of the re-

action products of a sample of *n*-hexanol derivatized with phenyl isocyanate. This analysis measured a functionality of 0.97 ± 0.01 (average of six determinations), which agrees with the manufacturer's result of 0.98, within experimental error.

Using the UV response factor determined as described in the discussion of calibration of a UV detector above and the nominal $\bar{M}_n$ values provided by the manufacturers, the average functionality of each sample can be determined from SEC-UV. These values are compared to those obtained by titration in Table I. The titration results have an error of about ±1% as determined from replicate measurements on *n*-hexanol, while the SEC-UV results have an error of about ±0.5%, as estimated from eight determinations for PTMG 2000. The methods agree within experimental error. However, to its advantage, the SEC results are obtained on samples sizes that are 25–50× smaller than those used for potentiometric titration. Since the SEC-UV method directly measures the derivatized material, analysis of these results is not affected by interfering reactions, such as the PhNCO reaction with H_2O. If smaller sample sizes were used in the titration method, however, the significance of any side reactions would increase, and the accuracy of the analysis could be compromised.

Correction of DRI Response

The effect of the change in end group on the DRI response is shown in Figure 3. The increase in size caused by derivatization shifts peaks to earlier elution times. Also, derivatization increases the DRI response because (1) there is a total increase in mass injected due to the derivatized end groups (all samples, derivatized and underivatized, were injected at a concentration of 2.5 mg/mL based on underivatized sample weight), and (2) the DRI detector is responding to the concentration of polymer repeat units and to the concentration of end groups.

Table I Whole Polymer Functionality Determined by SEC-UV and Potentiometric Titration

	Functionality[a]	
$\bar{M}_n$[b]	Titration	SEC-UV
250	1.97	2.10
650	1.93	1.98
1000	1.97	2.00
2000	1.93	1.97
2900	1.96	1.96

[a] Functionality is expected to be 2 for each sample.
[b] Vendor-supplied $\bar{M}_n$.

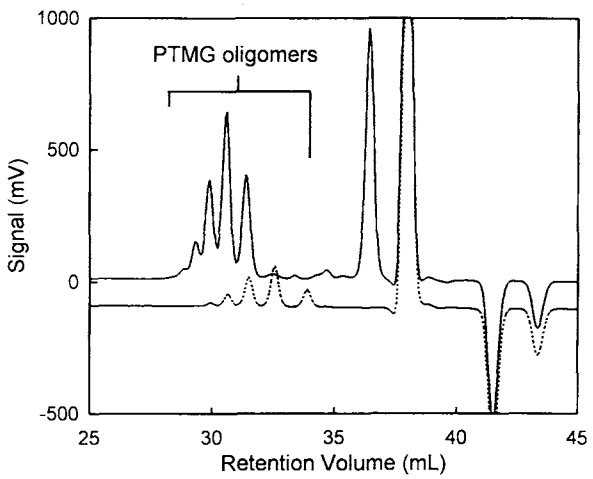

Figure 3 DRI chromatogram of PTMG 250, (- - - - -) underivatized and (——) derivatized with PhNCO.

The refractive index of an aromatic end group is greater than that of the PTMG repeat units; thus low-molecular-weight derivatized oligomers have greater response than an equivalent concentration of high-molecular-weight oligomer. In comparison, the specific refractive index of an underivatized terminal hydroxyl group is slightly *less* than oligomer repeat units. Hence, the correction factors for derivatized and underivatized DRI responses are of opposite sign.

Variation of Functionality with Molecular Weight

Functionality at each molecular weight was determined as described above, using both uncorrected and corrected DRI chromatograms. The effect of the DRI response correction on the distribution of functionality for a derivatized PTMG 1000 is shown in Figure 4. Although both the uncorrected and corrected plots have almost identical average functionalities (f = 2.10, uncorrected, and f = 2.15, corrected), the corrected plot indicates that f is nearly constant with retention volume except at the extreme high and low ends of the distribution. These are regions of low signal for the DRI and UV detectors, and the effect of noise is significant on the ratio of signals calculated using Eq. (4). Polymer functionality of 2.0 is most consistent with the vendor's description of the samples as linear, difunctional polymers, although the true distribution has not been verified

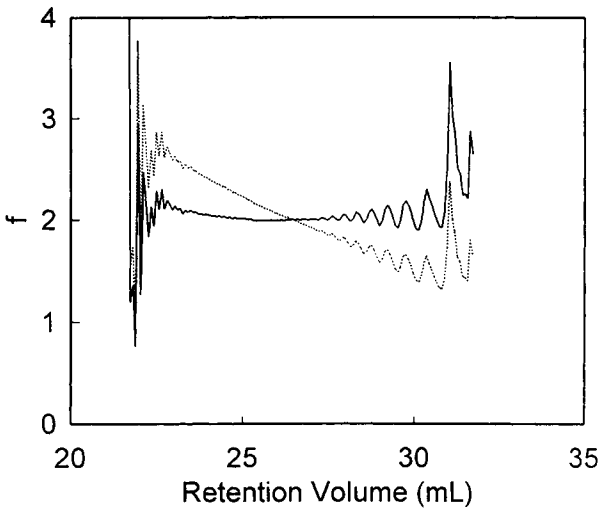

Figure 4 Functionality distribution of derivatized PTMG 1000, calculated using (- - - - -) uncorrected and (——) corrected DRI response.

by other means. The general observations made here for PTMG 1000 apply to all of the analyzed derivatized samples.

Whole Polymer Number-Average Molecular Weight

Whole polymer $\bar{M}_n$ determined by each of the four methods described above, using both uncorrected and corrected DRI responses if applicable are given in Table II.

Concentration Detection

The results obtained for concentration (DRI) detection using conventional calibration will be affected significantly by (1) the quality of the calibration curve and (2) the effect of the end groups on the DRI response. The conventional calibration plot for underivatized PTMGs shown in Figure 5 was prepared by measuring the retention volumes of butanediol, the resolved oligomers of PTMG 250 and PTMG 650, and from pTHF 8000. A fourth-order polynomial was used to fit the data. While there are several standards that elute at high (> 27 mL) retention volumes (the low-molecular-weight end of the plot), there are no standards available for retention volumes between 22 and 27 mL. This demonstrates one limitation of conventional log M calibration—the availability of suitable standards. In this instance, all samples except PTMG 250 have appreciable portions that elute in this region. Despite this limitation of the log M calibration curve, $\bar{M}_n$ results for underivatized PTMG samples, without correction of the DRI chromatograms for the effect of end groups on response, agree with the expected values within experimental error (the coefficient of variation for $\bar{M}_n$ values obtained by this method is ±2.8%, based on long-term data from this

Table II PTMG Number-Average Molecular Weights

	Concentration[a]		Visc. Conc.[b]		UV[c] Viscometry[d]	
Expected	$(\bar{M}_n)_{c,uc}$	$(\bar{M}_n)_{c,c}$	$(\bar{M}_n)_{vc,uc}$	$(\bar{M}_n)_{vc,c}$	$(\bar{M}_n)_{uv}$	$(\bar{M}_n)_v$
250[e]	241	238	278	314		282
650[e]	632	622	791	827		781
1000[e]	1010	991	1259	1281		1275
2000[e]	1865	1827	1982	2013		2330
2900[e]	2902	2859	3126	3160		3490
488[f]	470	476	423	350	488	424
888[f]	840	890	1011	1010	890	973
1238[f]	1154	1258	1422	1421	1258	1395
2238[f]	2070	2296	2508	2507	2257	2470
3138[f]	2840	3135	3470	3468	3097	3415

[a] Concentration detection (DRI) and narrow standard log M calibration. DRI response uncorrected and corrected using Eq. (8).
[b] Concentration (DRI): viscometry detection and universal calibration for uncorrected and corrected DRI response.
[c] UV detection and log M narrow standard calibration of derivatized PTMG.
[d] Viscometry detection alone and universal calibration curve.
[e] Underivatized PTMG vendor values.
[f] Derivatized PTMG, from vendor values assuming 100% derivatization.

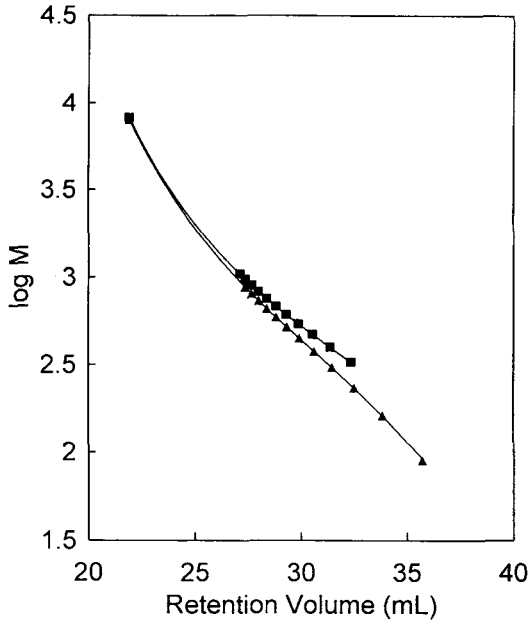

Figure 5 Conventional calibration curves for (▲) underivatized PTMG and (■) derivatized PTMG.

laboratory[12]). Correction of the DRI response for end-group effects is small for these hydroxyl-terminated oligomers, as shown in Figure 6. Correcting the DRI chromatogram does not significantly affect $\bar{M}_n$ values. This implies that the quality of results is most affected by the accuracy of the calibration data rather than the effects of end groups on the DRI response.

The calibration curve for derivatized PTMGs is also shown in Figure 5. The plot was prepared by measuring the retention volumes of derivatized butanediol, the resolved derivatized oligomers of PTMG 250 and PTMG 650, and derivatized pTHF 8000. Again, there is a lack of calibration standards in the middle of the calibration curve. For derivatized PTMG samples, $\bar{M}_n$ values calculated using the uncorrected DRI response are all lower (in the worst case, 9.5%) than expected. The correction for end-group effects on the derivatized, phenyl-terminated oligomers *is* significant, as shown in Figure 7. The correction reduces the DRI signal at high retention volumes (low-molecular-weight end) and raises the response at low retention volumes (high molecular weights). The result is an increase in the calculated values of $\bar{M}_n$.

End-Group-Selective Detection

This method is applicable only to derivatized PTMG samples with the UV-absorbing end group. The molecular weights obtained by this method are in excellent agreement with expected values (the reproducibility of this log M calibration curve method is comparable to the concentration detection method above, i.e., ±2.8%). This agreement between experimental and expected results is due to (1) the selectivity of the detector to end groups, with no interfering response from the bulk polymer, and (2) the apparent validity of the conventional calibration curve for the derivatized PTMGs over the range investigated, despite the lack of calibration standards between 22 and 27 mL.

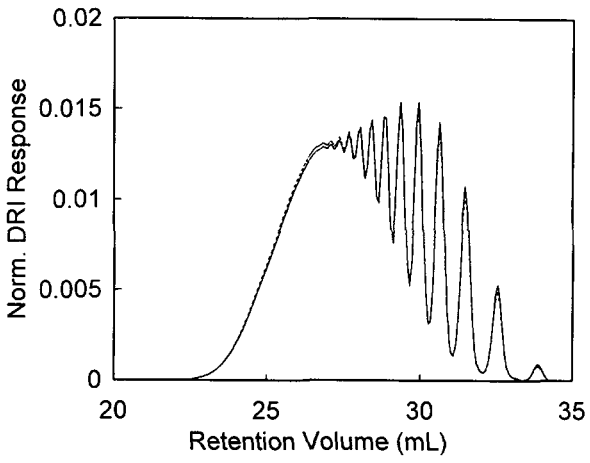

Figure 6 Normalized chromatograms of underivatized PTMG 650, (- - - -) uncorrected DRI response and (——) corrected DRI response.

Viscometry Detection

This method uses only the DV detector response and the universal calibration plot(s) shown in Figure 8, which were constructed using narrow polystyrene standards and either derivatized or underivatized

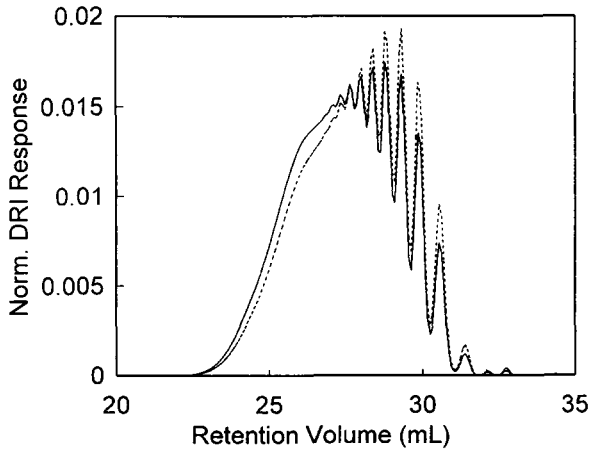

Figure 7 Normalized chromatograms of derivatized PTMG 650: (- - - -) uncorrected DRI response and (——) corrected DRI response.

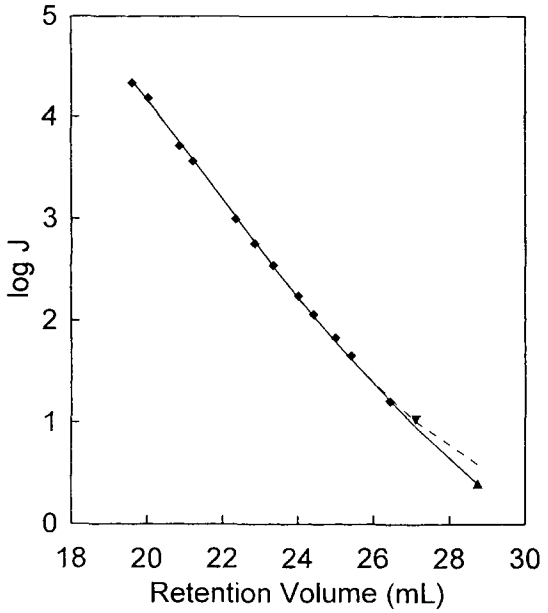

Figure 8 Universal calibration curves. (■) Polystyrene, (▲) butanediol, and (▼) derivatized butanediol.

1,4-butanediol as the lowest molecular weight standard. $\bar{M}_n$ values for both underivatized and derivatized samples are higher (in the worst case 20%) than expected (the reproducibility of $\bar{M}_n$ values by this method is ±12%[10]). Because this method is not as precise as the others, it is more difficult to distinguish differences between expected and measured values; however, a bias toward high values of $\bar{M}_n$ is consistent with a previous study on this method.[10] In the former case, the bias was attributed primarily to the insensitivity of the viscometer to the low-molecular-weight region of the chromatogram. The low-molecular-weight molecules in the sample are therefore ignored in the determination of $\bar{M}_n$. However, the $\bar{M}_n$ value for derivatized PTMG 250 is *lower* than expected, suggesting that other factors are complicating the determination of $\bar{M}_n$ at very small sizes, although others have reported the usefulness of universal calibration for certain polymers at molecular weights as low as 300.[13]

Viscometry and Concentration Detection

Unlike the preceeding methods that use responses from a single detector, this method uses both the DRI and DV detectors. Concentration at each retention volume, c_i, measured by the DRI, is used to calculate $[\eta]_i$ [Eq. (12)], which is subsequently used to calculate M_i from the universal calibration curve. Then, c_i is used to calculate $\bar{M}_n$ via Eq. (7). The effect of end groups on the DRI response thus affects the calculation of $\bar{M}_n$ twice, although the effects are partially counterbalancing. For example, if the DRI response of a low-molecular-weight oligomer is incorrectly high because of an end-group effect, the calculated intrinsic viscosity would be low and the value of M_i obtained from the universal calibration plot would be high. However, this high value of M_i is then divided into the incorrectly high value of c_i in the denominator of Eq. (7), partially compensating for the problem.

Our results show that, in general, the uncorrected values are higher than expected for both underivatized and derivatized samples and agreement with the expected values is worse than obtained by methods using conventional log M calibration curves. Differences between expected and measured values are again difficult to distinguish because the long-term reproducibility is ±8% for $\bar{M}_n$ values measured by this method.[12] Correction of the concentration detector response has little effect on the calculated values of $\bar{M}_n$. As with the method utilizing the DV detector alone, the generally poor agreement of the data with expected values implies that the universal calibration curve and the assumptions underlying its use are suspect in this application to PTMG.

CONCLUSIONS

Functionality of PTMGs can be accurately measured using multidetector SEC with sample sizes that are 25–50× less than those needed for potentiometric titration. Variation of functionality with molecular weight can also be determined; however, correction of the DRI response is required, in addition to an accurate SEC calibration plot.

Four methods have been used to calculate $\bar{M}_n$. The most accurate method uses end-group-selective (UV) detection. This is followed by the concentration detection method. Both methods use conventional log M calibration plots. The disadvantage of these methods is the availability of suitable standards over the entire elution range of samples.

The least accurate results are provided by the viscometry detection and by the viscometry and concentration detection methods that utilize universal calibration curves. Both of these methods utilize the DV detector, which can be insensitive to low-molecular-weight species; thus, results are generally biased high. To their advantage, these methods use readily available standards such as polystyrene for calibration. With these methods, the effects of axial dispersion and interdetector volume need to be considered.

Correction of the DRI response for end-group effects can be important in any method that utilizes

this detector if the specific refractivity of the end groups is significantly different from the polymer repeat units. Fortunately, a simple correction based on the reciprocal relationship between DRI response and molecular weight can be applied.

It should be emphasized that all of the SEC methods examined for determining $\bar{M}_n$ of PTMG oligomers have limitations, and these limitations are expected to affect results for other polymers of similar molecular weight. Accurate results for $\bar{M}_n$ and functionality of low-molecular-weight polymers may be obtained by multidetector SEC, but not without careful comparison and evaluation of the available detection and calibration options.

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