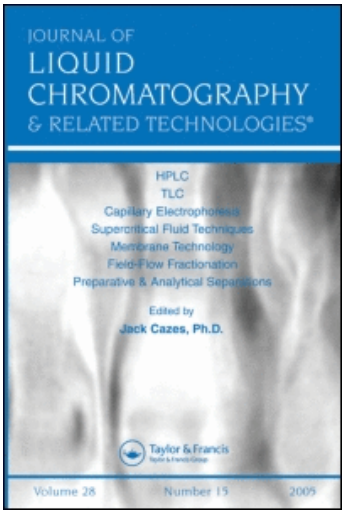

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Cyclic Oligomer Considerations in the Size Exclusion Chromatography of Poly(Ethylene Terephthalate)

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CYCLIC OLIGOMER CONSIDERATIONS IN THE SIZE EXCLUSION CHROMATOGRAPHY OF POLY(ETHYLENE TEREPHTHALATE)

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ABSTRACT

Room temperature Size Exclusion Chromatography (SEC) for poly(ethylene terephthalate) (PET) was developed using a mobile phase mixture of 5% hexafluoroisopropanol (HFIP) in methylene chloride ($MeCl_2$). Calibration was carried out with three different approaches, each time with and without considering the presence of cyclic oligomer in PET samples and standards. At typical concentrations of cyclic oligomer a calibration curve generated from a chromatogram truncated to eliminate the oligomer peak had its slope distorted such that it gave molecular weight average values inaccurate by up to 8%, whereas correcting for the oligomer explicitly resulted in average errors of about 1%. Although the effect of this small peak may be negligible for typical SEC applications involving repeated analysis of similar samples, it may alter the calibration curve significantly if not corrected.

INTRODUCTION

HFIP is an excellent room temperature solvent for PET but is very costly and somewhat hazardous. Its use has been reported as pure mobile phase [1], mixed with other solvents [2], and as a 2% mixture with chloroform [3], but most commonly as a 30% (or azeotropic) mixture with methylene chloride [4,5]. This paper reports the use of 5% HFIP with methylene chloride, a composition which lowers cost and health risk yet is still suitable for higher molecular weight and crystalline PET samples.

SEC chromatograms of PET often show a distinct low molecular weight peak which corresponds to cyclic oligomers, mainly trimer [3,4]. Although the true molecular weight of trimer represented by this peak is 576, the peak retention volume corresponds to molecular weights ranging from about 275 [4] to 2500 [6,7] on extrapolated PET calibration curves, depending upon the mobile phase used.

Interpretation of PET chromatograms containing the "trimer" peak requires consideration of three main aspects: (i) definition of the chromatogram to be interpreted, (ii) assignment of molecular weight averages corresponding to the defined chromatogram, and (iii) use of the chromatogram and molecular weight averages to obtain calibration curves. These three aspects are discussed in turn in the next section.

THEORY

Definition of the Chromatogram to be Interpreted

Figure 1 shows a typical PET chromatogram containing a "trimer" peak. This peak originates from the presence of 0.5-1.5% of cyclic oligomers which are mainly trimer [3,4],

$$(-CO-C_6H_4-CO-O-CH_2-CH_2-O-)_n\ ,\quad n = 2\text{-}9 \qquad (1)$$

where n = 3 for trimer. As mentioned above, these species may not obey molecular weight calibration curves obtained for linear PET molecules. In this solvent system, the trimer peak elutes at a retention volume corresponding to a molecular weight of about 1000 to 2000.

The most common method of dealing with this problem is to avoid using the trimer peak in the interpretation. This is conventionally done by drawing the baseline to intersect the PET chromatogram in front of the trimer peak (Figure 2). In this work this "Truncation" approach is compared with two alternatives: allowing the trimer peak to remain in the interpreted chromatogram and mathematically subtracting the trimer peak. The latter alternative involved fitting the trimer peak with a spline fit.

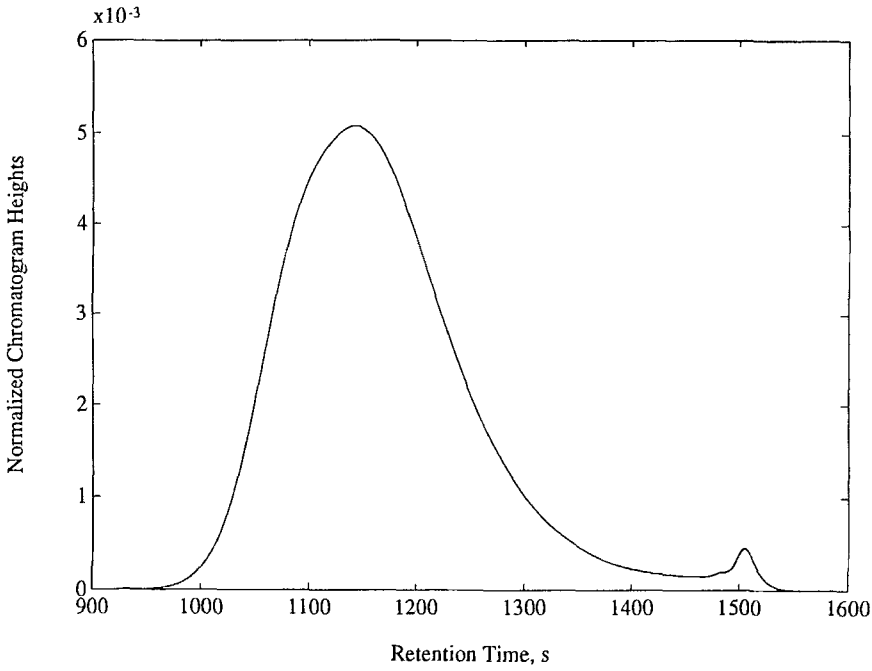

FIGURE 1 Typical chromatogram of PET showing "trimer" peak.

Assignment of Molecular Weight Averages to the Defined Chromatogram

Vendor values of M_n and M_w are generally based upon absolute methods such as light scattering, viscometry, and osmometry which reflect the presence of all molecules actually present in the sample. Thus, when the trimer peak is not included in the SEC interpretation, these values must be corrected for the absence of these species so that the averages correspond to the molecules represented by the defined chromatogram. Assuming the UV detector response factor is the same for all species, the fraction of the total area under the trimer peak and the fraction under the remainder of the chromatogram (the "linear PET" peak) provide an estimate of the weight fractions of cyclic oligomers (w_{trimer}) and polymer ($w_{polymer}$) respectively. Then, the vendor value of M_w, $M_{w,vendor}$ is:

$$M_{W,vendor} = w_{polymer} M_{W,polymer} + w_{trimer} M_{W,trimer} \quad (2)$$

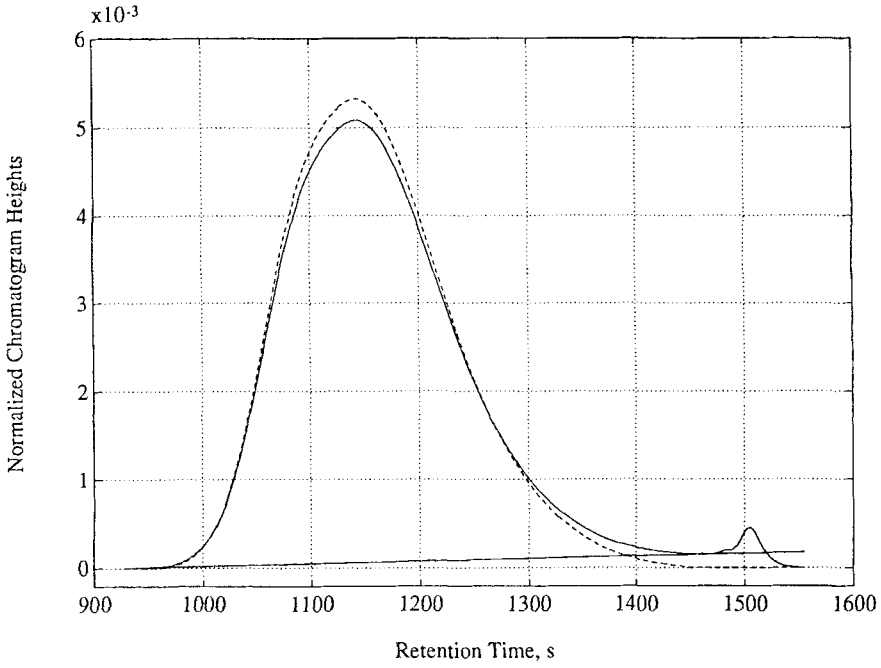

FIGURE 2 Example of truncation of "trimer" peak from chromatogram: original chromatogram and baseline (solid lines), truncated chromatogram (dashed line).

where $M_{w,polymer}$ is the weight average molecular weight of the molecules constituting the linear PET peak and $M_{w,trimer}$ is the weight average molecular weight of the cyclic oligomers responsible for the trimer peak.

Now, solving for $M_{w,polymer}$ and setting $M_{w,trimer}$ equal to three times the monomer molecular weight ($3 \cdot M_0$) we obtain:

$$M_{W,polymer} = \frac{M_{W,vendor} - w_{trimer} \cdot 3 \cdot M_0}{1 - w_{trimer}} \quad (3)$$

Calibration Curve Determination

Narrow standards of PET are generally not available for calibration. Thus, broad molecular weight distributions displaying the usual trimer peak are used in calibration curve search methods. Three such methods are examined here: (i) search for a linear

calibration curve which, when applied to the chromatogram of the standard, yields the "true" M_n and M_w (the "Linear" calibration curve search method) [8]; (ii) using a polystyrene calibration curve in a search for two groups of Mark Houwink constants to derive a PET calibration curve which, when applied to the chromatogram of the standard, yields the "true" M_n and M_w (the "Mark Houwink Constants" search method) [9]; and (iii) calculation of a calibration curve from the chromatogram of a PET standard of known molecular weight distribution (the "MWD" calibration method). These methods are well known in the published literature [10].

With respect to the MWD calibration method, the molecular weight distribution used for standards was obtained from two sources [11,12]: vendor supplied molecular weight distributions obtained via SEC; and by use of the theoretically based "Flory distribution" for linear condensation polymers [13]. The Flory distribution is described by the following equation:

$$W_n = np^{n-1}(1-p)^2 \tag{4}$$

where W_n is the weight fraction of n-mers and p is the degree of polymerization, which may be calculated from molecular weight averages with the companion equations for these averages:

$$M_n = \frac{M_0}{(1-p)} \qquad M_w = M_0\frac{(1+p)}{(1-p)} \tag{5}$$

In this work the effect of all three of the above factors was of interest: definition of the chromatogram used, assignment of the molecular weight averages to the defined chromatogram, and calibration curve determination method. Table I shows the specific combinations of these factors examined.

EXPERIMENTAL

PET samples were dissolved in 30% HFIP/70% $MeCl_2$ at room temperature in less than one hour. Highly crystalline PET is more soluble in 30% HFIP than in pure HFIP [4]. The solutions were then diluted down to 5% HFIP, 1-2 mg polymer/mL, before injection into the 5% HFIP mobile phase. The addition of 1.0 g/L of tetraethylammonium chloride to the mobile phase and sample was used to eliminate the "polyelectrolyte effect", or agglomeration of polymer molecules [14] (apparent as a

Table 1
Information Used in Calibrations

Method	Standards	Chromatogram oligomer peak	Molecular Weight Information
Linear, Truncated	Std 1	Truncated	Vendor MW Averages
Linear, Included	Std 1	Included	Vendor MW Averages
Linear, Subtracted	Std 1	Subtracted	Corrected MW Averages
Mark Houwink Constants, Included	Std 1,3	Included	Vendor MW Averages
Mark Houwink Constants, Subtracted	Std 1,3	Subtracted	Corrected MW Averages
MWD, Truncated	Std 1	Truncated	Vendor MW Distribution
MWD, Subtracted	Std 1,3	Subtracted	Synthetic MW Distribution

high molecular weight prepeak). An internal standard was required for flowrate adjustment as the low boiling point of the solvent mixture tended to cause a non-reproducible flowrate [15]. In PET samples the cyclic oligomer served as an internal standard for correcting flowrate changes from run to run. Trichlorobenzene was used for polystyrene samples.

Detection by UV absorption at 254 nm with a Perkin-Elmer Tri-Det detector provided excellent chromatogram signal-to-noise ratio and baseline resolution. Jordi Gel Linear columns (Jordi Associates, Inc.) were stable in this solvent mixture for at least seven months. A Waters 510 pump and a Hewlett Packard Series 1050 autosampler completed the SEC equipment. Data was collected with an ADALab A/D conversion card, a PC-compatible computer, and in-house software.

To evaluate the sensitivity of the system to changes in the sample preparation and analysis technique, factorial design was used to plan experiments and analysis of variance was applied to the resulting molecular weight averages, peak area, and oligomer fraction w_{trimer}. Analysis of samples aged four days showed no significant differences, indicating that the polymer was stable in the solvent. High sample concentration combined with larger injection volume (ie. 2 mg/mL and 100 µL) affected the chromatograms, indicating a limit above which a concentration effect existed in the size exclusion separation. All experiments were performed with small enough total polymer injection to eliminate this effect.

Chromatograms of broad PET standards were defined three different ways with respect to cyclic oligomer peaks, as described earlier. With respect to the method of subtraction of the trimer peak, a spline fit of the peak shape was obtained from the highest molecular weight PET standard.

RESULTS AND DISCUSSION

Oligomer Content in PET Standards

Table 2 shows that the weight fraction of cyclic oligomer in the PET samples used ranged from 1.4% for Standard 1 to 0.5% for Standard 4. With this amount of trimer removed mathematically from the polymer, scarcely any effect on the vendor values of M_n or M_w was evident. Calculated values of degree of polymerization, p, obtained from Equation (5) using the $M_{w,polymer}$ values are also shown in Table 2, and are all above 0.99.

There appears to be a strong relationship between w_{trimer} and p. The weight fraction of cyclic oligomer decreased as the degree of polymerization of the sample increased. Figure 3 illustrates that equally good fits were obtained with linear, quadratic, or logarithmic equations.

In the published literature there are diverse results with respect to the correlation of w_{trimer} and p. Well-established theory predicts a positive correlation [16], though this has not been systematically confirmed for PET. There are numerous reports [4,17,18,19] that maintaining PET at a temperature between the glass transition and the melting point results in a decrease in w_{trimer}. If the conditions of the heat treatment permit solid-state polycondensation [20], large increases in molecular weight may arise, indicating a negative correlation between w_{trimer} and p. Keeping in mind that the PET standards of different molecular weight are prepared by solid-stating, and that an equilibrium distribution of cyclic oligomers may not be present without lengthy treatment [19], the negative correlation obtained in this work and elsewhere may be a non-equilibrium trend.

Table 2
PET Standards

Name	M_w, Vendor	w_{trimer} (mean, std.dev)	$M_{w,adj}$	p_{adj}	Comments
Std 1	M_n 21,000 M_w 39,000	1.427% ± .097	M_n 21,836 M_w 39,556	0.99033	American Polymer Standards 39K
Std 2	47,240	0.957% ± .035	47,691	0.99198	Eastman 7352, solid stated
Std 3	58,000	0.838%	58,485	0.99345	Eastman 9902, solid stated
Std 4	71,560	0.529%	71,937	0.99467	Eastman 10388, solid stated

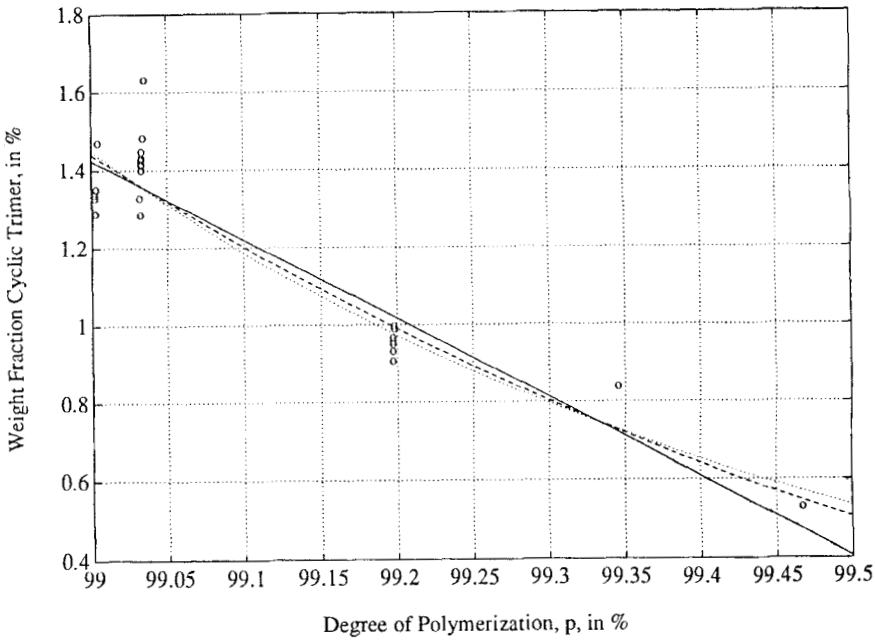

FIGURE 3 Correlation between w_{trimer} and p: linear fit (solid line), quadratic fit (dashed line), logarithmic fit (dotted line).

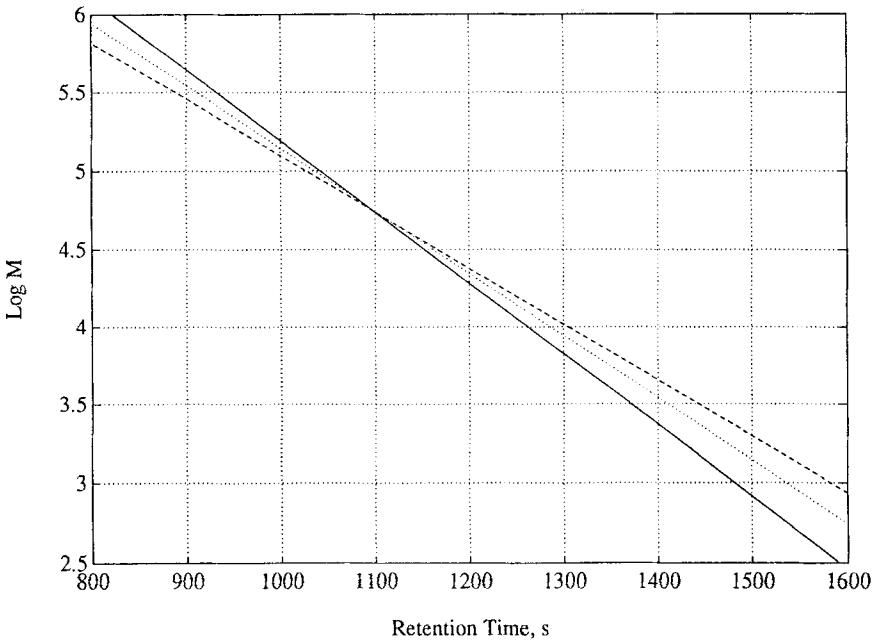

FIGURE 4 Calibration curves using Linear method: truncated trimer peak (solid line), included trimer peak (dashed line), subtracted trimer peak (dotted).

A possible reason for this trend involves annealing, which also occurs under heat-treatment conditions. If cyclic oligomers are not incorporated into the growing crystalline regions, they will be forced towards an equilibrium concentration with respect to amorphous fraction only [4]. The weighted average of w_{trimer} in the semi-crystalline sample will then decrease as crystallinity increases. Further thermal treatment can completely change the crystalline content much more quickly than the cyclic oligomer content, so this theory cannot be easily tested without preparing the samples from a common starting material.

Comparison of Calibration Curves and Molecular Weight Averages

The PET calibration curves obtained from the information summarized in Table 1 are plotted in Figures 4 to 6. Molecular weight averages calculated using each calibration curve are given in Table 3. For each method, the test chromatograms were defined in

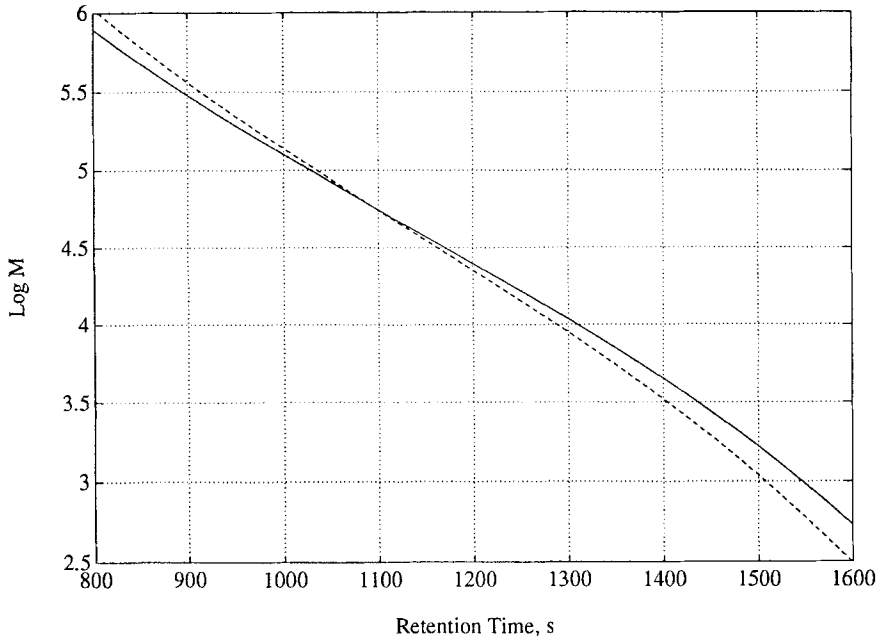

FIGURE 5 Calibration curves using Mark Houwink Constants method: included trimer peak (solid line), subtracted trimer peak (dashed line).

the same way as the calibration chromatograms: for instance, to test the Linear Truncated calibration curve, the chromatograms for Standards 2, 3 and 4 were also truncated. The main points evident in making these comparisons are:

i) The slopes of calibration curves increased with respect to trimer peak in the chromatogram in the order Included, Subtracted, and Truncated. As a result, the Linear Truncation calibration overestimated the M_w of the highest molecular weight test standard by over 8%, whereas the calibrations using Included chromatograms underestimated M_w. The calibrations using the Subtracted chromatograms were most accurate across the entire molecular weight range.

ii) Linear and Mark Houwink Constants methods gave very similar calibration curves when used with the same chromatograms and averages. The errors in calculated molecular weight averages likewise was very close, though the use of an

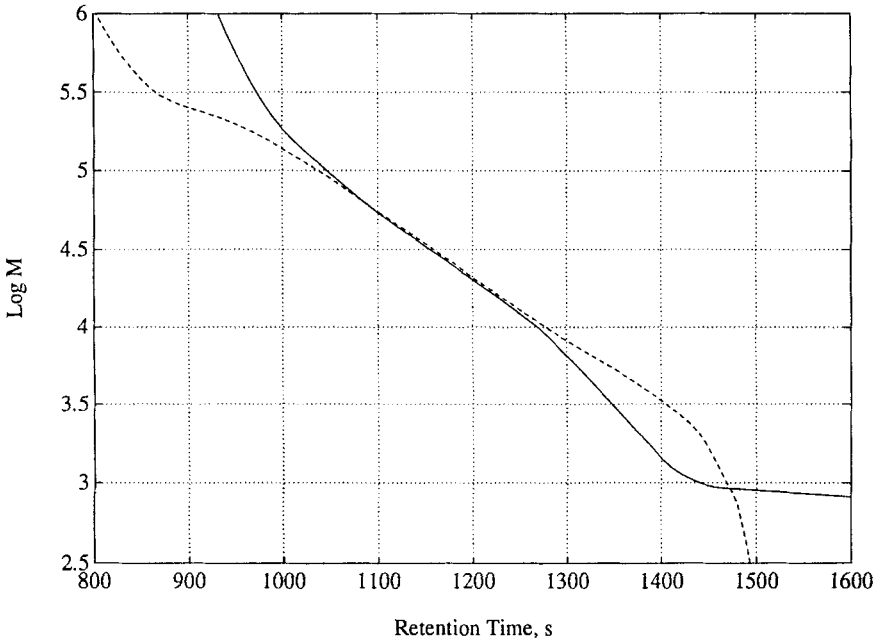

FIGURE 6 Calibration curves using Molecular Weight Distribution method: truncated trimer peak with vendor molecular weight distribution (solid line), subtracted trimer peak with Flory distribution (dashed line).

additional higher molecular weight standard for the Mark Houwink Constants method resulted in slightly smaller errors in high molecular weight test samples.

iii) The MWD method gave calibration curves which overlapped the others in the center, but deviated erratically at the tails. This is due to the intrinsic sensitivity of this method to the tails of both the chromatograms and the "true" molecular weight distributions. In addition, since the calibration data points were fitted with splines, extrapolation beyond the molecular weight range of the calibration standard(s) was very unreliable, and gave molecular weight averages in very large error.

iv) The molecular weight predicted for trimer, which is listed in the last column of Table 3, is higher than the true value with almost all calibration methods. It is highest for calibrations using Included trimer peaks and lowest for Truncated trimer peaks, in accordance with the trend of calibration slopes. For calibrations using Subtracted

Table 3
Comparison of Calibration Methods
Errors in Calculated Molecular Weight Averages [a]

Whole Polymer Sample

Standard and MW averages	Std 1		Std 2		Std 3		Std 4		MW predicted for trimer
Calibration	21000	39000	23737[b]	47240	29098[b]	58000	35866[b]	71560	576
Linear Truncated	***0.1%***	***0.2%***	4.8%	4.4%	-2.0%	1.6%	-0.7%	8.2%	782
Linear A	***0.0%***	***0.0%***	9.8%	0.2%	1.0%	-4.6%	-0.5%	-5.4%	1899
Mark Houwink A	***-0.6%***	***2.8%***	9.5%	2.4%	1.1%	***-2.4%***	-0.4%	-3.6%	1575
MWD A	***-2.5%***	***3.6%***	0.8%	11.2%	-5.2%	17.4%	-4.0%	86.2%	891

Linear Fraction

Standard and MW averages	Std 1		Std 2		Std 3		Std 4		MW predicted for trimer
Calibration	21836	39556	23961[c]	47691	29339[c]	58485	36054[c]	71937	576
Linear B	***0.0%***	***0.0%***	12.4%	2.5%	4.5%	-0.5%	1.3%	0.9%	1327
Mark Houwink B	***-0.1%***	***0.5%***	12.3%	2.3%	4.8%	***-0.4%***	0.7%	0.6%	1031
MWD B	***-12.6%***	***-1.2%***	-1.4%	1.6%	***-0.8%***	***-2.1%***	-17.0%	-1.5%	120

Notes: [a] Values in ***bold italics*** were used in obtaining calibration: represent goodness-of-fit of search
[b] Calculated from p and w_{trimer} in Table 2 using Equations (3) and (5)
[c] Calculated from p in Table 2 using Equation (5)

trimer peaks and corrected molecular weight averages, which would represent linear PET molecules only, the trimer peak elutes at a retention time corresponding to a molecular weight of about 1000 to 1300.

In contrast to the small effect of correcting the molecular weight averages for w_{trimer}, definition of the chromatogram used had a very significant effect on the SEC calibration curve obtained. The reasons are evident in the moment analysis plots [10] for M_n shown in Figure 7. In a moment analysis plot, the areas under the plot across a specific retention time range reflects the importance of chromatogram heights in that range to the calculation of a molecular weight average. The small changes in the extreme low molecular weight tail were magnified in the moment W/M(t) which is used in the calculation of M_n. The portion of the chromatogram after 1450 s contributed less than 0.05% to the calculation of M_n for the Truncated chromatogram, 4% with trimer subtracted, and an inflated 18% with trimer included. The calibration searches "found" calibration curves which were pivoted as required to obtain the same

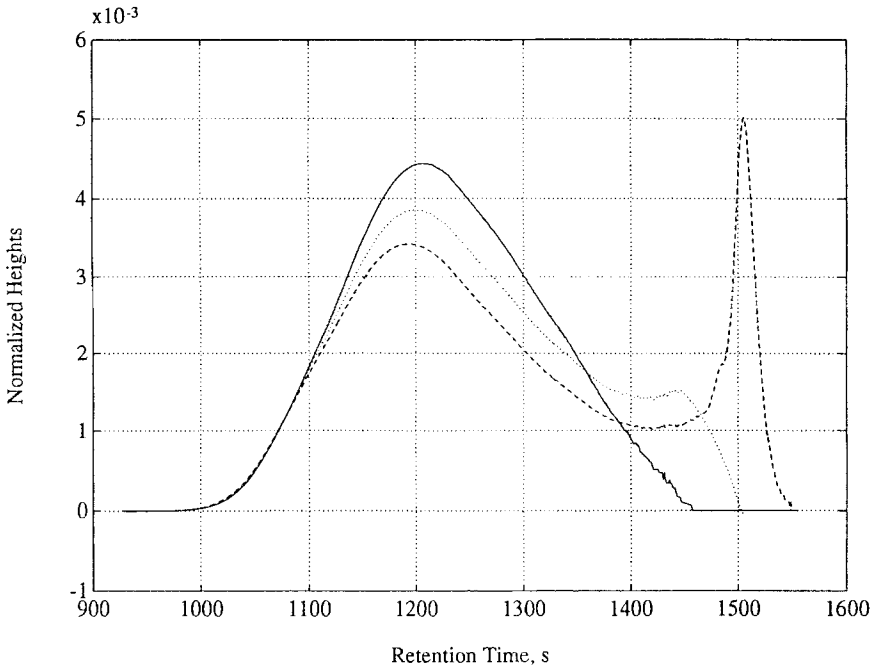

FIGURE 7 Moment analysis plots for M_n: trimer peak truncated (solid), trimer peak included (dashed), trimer peak subtracted (dotted).

molecular weight average with these differing moment distributions. Moment analysis plots for M_w were almost identical for all three chromatograms.

Note that "known" M_n values for Standards 2, 3, and 4 were estimated using the Flory distribution and the oligomer weight fraction. This would appear to be a poor estimate for Standard 2, since all calibrations except the two Direct methods gave M_n about 10% to 12% higher. Standard 2 was the lowest molecular weight standard obtained from Eastman, and had been solid-stated [20] the least: perhaps it was not at an equilibrium distribution as described by Flory.

CONCLUSIONS

A solvent system consisting of 5% hexafluoroisopropanol in methylene chloride was demonstrated for the room temperature size exclusion chromatography of

poly(ethylene terephthalate). It is a suitable alternative to much more expensive and/or hazardous solvent systems, and samples dissolve at room temperature. Experiments in a factorial design showed that the effect of sample preparation on the chromatograms was not significant, indicating that the polymer is stable in the solvent system, though care must be taken to avoid concentration effects.

The practice of truncating PET chromatograms to eliminate the cyclic oligomer peak led to calibration curves which give M_w values too high by up to 8%. Since the cyclic oligomers do not elute at retention times corresponding to their true molecular weights on a linear polymer calibration, they must be properly removed from both the chromatograms and molecular weight averages used to construct calibration curves.

Of the methods used in this work, a Universal Calibration type of method using oligomer-corrected data from multiple PET standards of differing molecular weights gave the most accurate calibration curve. A Linear Calibration using one corrected standard was almost as good. In order to avoid using both the Universal Calibration assumption and narrow PS standards, the Linear Calibration may be preferred, especially if it is modified to use more than one standard. The method of Direct Calibration, using a known molecular weight distribution for the standard, was unreliable beyond the range of molecular weight in the calibration standards as well as being too dependent on accurate tails of the chromatograms, which are difficult to obtain.

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