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A METHOD OF SELF CALIBRATION FOR MOLECULAR WEIGHT DISTRIBUTION DETERMINATIONS FOR LIQUID CRYSTALLINE POLYMERS

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ABSTRACT

A method of molecular weight calibration was devised for various substituted liquid crystalline polymers with substantial molecular weight repeat units. With the use of gel permeation chromatography, oligomer peak separation was achieved offering a method for self calibration for molecular weight distribution determinations. Employing an overlay of a low molecular weight polystyrene standard, a retention time marker was utilized as a source from which to mark an oligomer peak. The calibration plot produced using this technique showed much better correlation coefficients than that of the polystyrene calibration plot. In addition, molecular weight determinations made from the two techniques yielded two distinct molecular weight averages and distributions, indicating polystyrene to be a poor relative calibration method for the liquid crystalline polymers tested. The technique illustrates the utility of alternative calibration methods when samples show certain physical characteristics.

INTRODUCTION

This paper describes a technique for calibrating size exclusion chromatographic columns when the molecular weight of the repeat units is large enough to allow individual peak resolution on the columns used. The important class of compounds which readily fit such criteria are liquid crystalline polymers where the use of such calibration methods may prevent erroneous molecular weight averages.

The materials used in this analysis are from a group of thermotropic aromatic polyesters designed around a triad ester mesogenic unit containing an arylsulfonyl substituted hydroquinone group and a decamethylene spacer, Figure 1 (1). The substitution on the X position allowed comparison of a series of the polymers and their respective calibration plots.

MATERIALS

The chromatograph included a Water's 510 HPLC pump, 401 Differential Refractometer and three Ultrastyrigel^T columns (500A, 10³A, 10⁴A porosity), with methylene chloride as the mobile phase, in series with an on-line computer data reduction system (Water's 840 Chromatography Station, Version 4.0). Polystyrene standards of molecular weight 110,000, 50,000, 35,000, 10,300, and 2350 were run and a third-order polynomial fit was calculated for the peak calibration plot. Solutions of 0.1% were made, filtered and injections of 110-120 microliters were used for all runs.

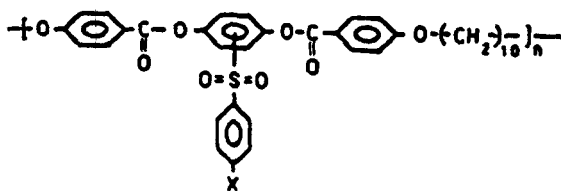


Figure 1 - Repeat unit structure
 $x = \text{-F, -Cl, -Br}$

METHODS

The method of calibration utilized peak retention times for the polymer standard or oligomer peak of interest and third-order polynomial fit using the chromatography software package 4.0 to obtain both the coefficients for the fit as well as the correlation coefficient for the polynomial fit achieved. The lowest polystyrene standard MW 2350 was used as a reference for marking the oligomer peak on the liquid crystalline polymers, which had a molecular weight closest to the standard. The liquid crystalline polymers had repeat unit molecular weights in the range of 646-707 daltons, thus indicating the tetramer would serve as the best marker for comparison with the polystyrene standard weighing 2350 daltons. As can be seen from Figure 2, comparison of the chlorine substituent group tetramer and the polystyrene standard correspond closely in the overlay plot. While it is known that the polystyrene standards and the liquid crystalline polymers are not going to elute at the same hydrodynamic volumes, it is hypothesized that at low mole-

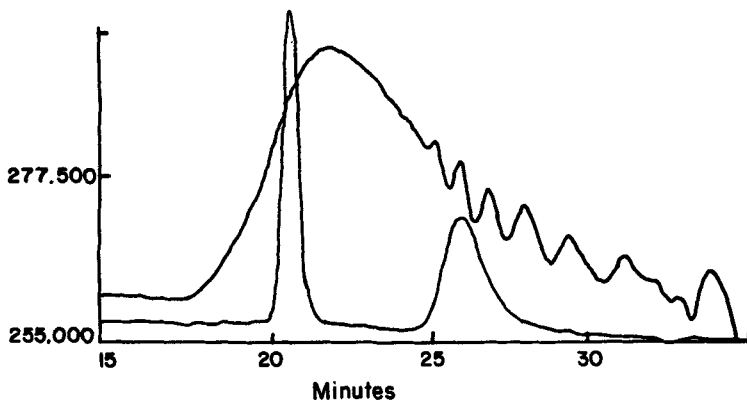


Figure 2 - Overlay plot of liquid crystalline sample (chlorine substituent) and polystyrene (35,000 and 2350) standards.

cular weight ranges they may more closely correlate in hydrodynamic volume and thus elute at approximately the same volume. It is of interest to note that the liquid crystalline polymers are not of the type exhibiting rigid rod like behavior thus giving vastly different solution or separation properties.

All comparisons are based on the results of the calibrations achieved from the peak retention times of the polystyrene standards and the oligomer peaks of the liquid crystalline polymer samples for which accurate molecular weight averages were desired.

RESULTS

The most important result of this analysis is that the molecular weight average determinations from the two methods

outlined, (i.e. the polystyrene and oligomer peak calibration), give significantly different values for the averages determined. Figure 3 shows a sample chromatogram of the liquid crystalline polymer and the beginning and ending analysis points used in the molecular weight average determination. Figure 4 demonstrates the closeness in molecular weight values determined by the oligomer calibration plot versus those calculated from knowledge of the repeat unit structure. In Table 1, a comparison of the molecular weight averages for the two methods as well as the polydispersities obtained from these averages allows one to compare the differences in the averages obtained. Three different substituent groups are also shown to allow comparison of the difference between the samples themselves.

In addition to the calculation of significantly different molecular weight averages for the samples in question, the calibration's correlation coefficients for the goodness of fit are found to be much better for the oligomer calibration than for the polystyrene calibration plots made. While the polystyrene calibration is believed to be an accurate calibration for polymers similar in structure to polystyrene, the difference in the averages obtained dramatize the difference in the structures for the two different starting materials. In Table 2, a comparison of the coefficients and their standard deviations, along with the correlation and the standard error of the estimate for the correlation is shown. This shows the excellent correlation and the small error of the estimate for the oligomer cali-

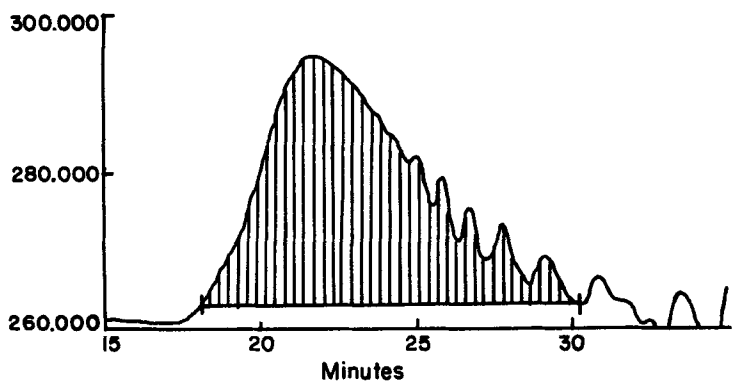


Figure 3 - Liquid crystalline sample, chlorine substituent group

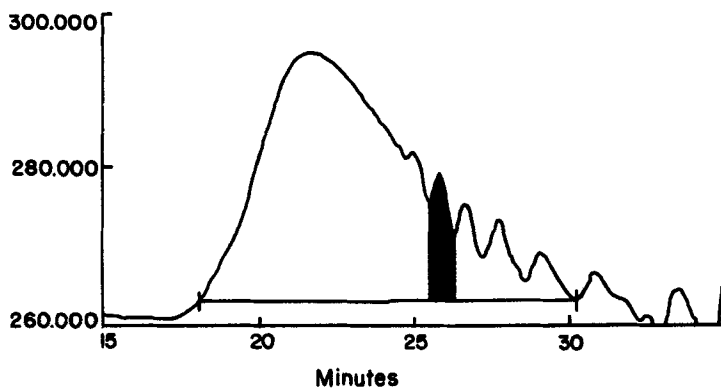


Figure 4 - Liquid crystalline sample (chlorine substituent) with tetramer peak shaded (tetramer = 2646 daltons; self calibration = 2614 daltons).

TABLE 1

Substituent	Polystyrene Calibration			Oligmer Calibration		
	M_w	M_n	dp	M_w	M_n	dp
-F	16,604	3978	4.17	4365	2682	1.62
-Cl	16,740	3944	4.24	8152	3829	2.13
-Br	16,643	3930	4.24	5565	3852	1.45

TABLE 2

	Polystyrene Calibration	Oligomer Calibration ¹
Coefficient	16.951	37.763
+/-Std. Dev. (degree zero)	+/-13.254	+/-2.960
Coefficient	-0.013	-0.066
+/-Std. Dev. (degree one)	+/-0.030	+/-0.005
Correlation	0.9998274	0.9999994
Std. Error of Estimate	0.20307	0.033252

1)Chlorine Substituent Calibration used for comparison;
other substituent calibrations were similiar.

bration plots. While the polystyrene calibration gave a correlation for the calibration, the standard error for the estimate gives an indication of the reliability of this correlation.

Since the standard error of the estimate is large enough to accommodate the difference in the molecular weight

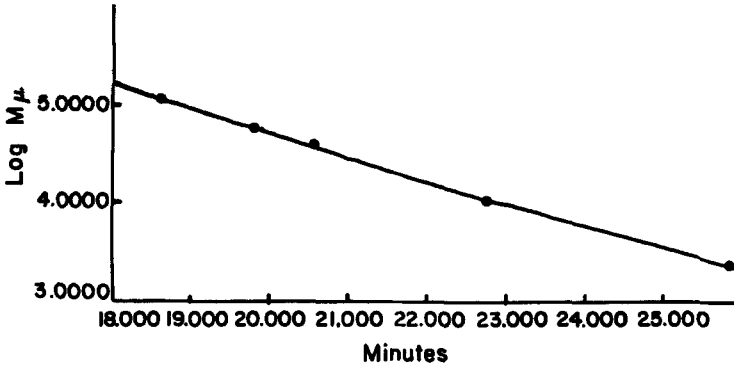


Figure 5 - Polystyrene Calibration

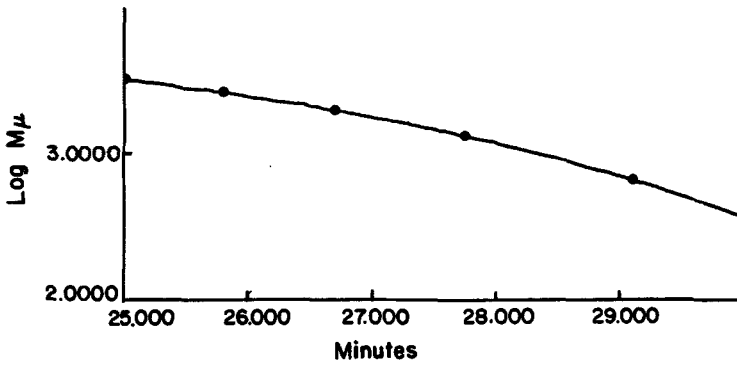


Figure 6 - Self-calibration (chlorine substituent)

of the standard and the tetramer used as a marker (2350 PS Std. versus 2646 for the tetramer) comparison of the two is acceptable from the fit offered by the polystyrene standard calibration plot produced. Figures 5 and 6 pictorially demonstrate the better fit offered by the oligomer cali-

bration plot versus the polystyrene calibration plot produced from the liquid crystalline samples.

DISCUSSION

The above comparison of calibration plots demonstrates the need for more accurate methods of determining molecular weight averages and the dangers inherent in trusting the polystyrene calibration technique to yield reliable relative average molecular weights, without major corrections based on phenomena other than peak spreading and peak skewing possible with any size separation technique.

The potential of oligomer calibration plots may become more and more evident as the use of higher molecular weight repeat units becomes more commonplace in the characterization of polymers. The continued increase in resolution obtained through the development of smaller particle size packing materials is also contributing to the development of oligomer calibration techniques and should be explored whenever possible in the characterization of polymeric materials.

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