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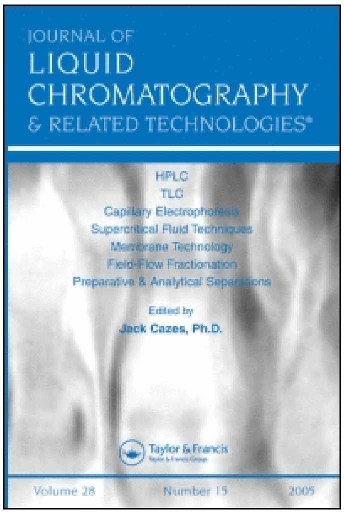

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DETERMINATION OF THE MOLECULAR WEIGHT DISTRIBUTION OF POLYETHYLENE TEREPHTHALATE BY GEL PERMEATION CHROMATOGRAPHY *

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ABSTRACT

The determination of the molecular weight distribution of polyethylene terephthalate by GPC at room temperature is described. The solvent used is o-chlorophenol-chloroform (1:9) and pure chloroform is used as eluent. K and alpha of the Mark-Houwink equation of polyethylene terephthalate and of polystyrene in this solvent system were obtained. It was shown that the universal calibration can be applied.

INTRODUCTION

The determination of the molecular weight distribution of polyethylene terephthalate (PET) is a very important problem. m-Cresol was formerly used as the

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GPC solvent. Since m-cresol has a very high viscosity, the GPC experiment must be performed at a rather high temperature. This is not only inconvenient but it is also very difficult to avoid partial degradation of the sample during the experiment (1). Recently, Paschke (2) developed a solvent system for GPC determination at room temperature, in which degradation of PET was eliminated. The procedure was troublesome, since high temperature filtration had to be used for sample preparation. Jiang (3) reported the use of o-chlorophenol - chloroform as a solvent for GPC.

This paper describes the use of o-chlorophenol - chloroform as a solvent and chloroform as eluent at room temperature for the determination of molecular weight distribution of PET. It was shown that, in this system, the universal calibration method can be applied. The intrinsic viscosity and molecular weight relationship for PET and for PS were obtained, providing the values of K and alpha that must be used in the universal calibration.

MATERIALS AND METHODS

A standard sample of PET was prepared in our laboratory. Several PET samples were dissolved in phenol - tetrachloroethane (1:1) and were fractionated by adding petroleum ether (90-120 deg. C.). Intrinsic viscosities of fractions thus obtained were determined in phenol - tetrachloroethane (1:1). The molecular weights were calculated according to the following equation (4):

$$[\eta] = 2.1 \times 10^{-2} M^{0.82}$$

The range of molecular weights of fractions was from 4000 to 30,000.

Standard samples of polystyrene were supplied mostly by Knauer, Inc., West Germany and by Waters Associates, Milford, Mass., USA.

Chloroform, A.R., was dried over anhydrous sodium sulfate or by passage through a silica gel column.

Two gel permeation chromatographic systems were used for GPC measurements. The first system was a Knauer device. Experimental parameters were as follows: Two columns in series (0.75 X 60 cm P-100) packed with Spheron gel of 20-40 microns; detector, UV, at 254 nm; flow rate 0.6 ml/min; temperature approx. 25 deg. C.; injection volume, 20 microliters (0.25%).

The second system was a Waters Model 244 GPC. Three columns of Microstyragel of 10,000, 10,000, and

1,000 Angstroms were selected. The total number of theoretical plates was 17,000. Detector, UV, at 254 nm; flow rate 1.0 ml/min; temperature approx. 25 deg. C.; injection volume, 20-40 microliters (0.1-0.2%).

The sample solutions were prepared as follows: PET samples were weighed into 10 ml volumetric flasks and 1 ml o-chlorophenol was added to each. The flask was warmed to 80 deg. C. until they were dissolved. They were then diluted with chloroform to 10 ml.

RESULTS AND DISCUSSION

Selection of Eluent and Solvent

From the thermodynamic point of view, a polymer will dissolve in a solvent only if the free energy of mixing is negative. Since

$$\Delta G_M = \Delta H_M - T\Delta S_M, \text{ and } \Delta H_M$$

usually adopts a positive value, a dissolution process will be favored when ΔH_M is very small or approaches zero. The value of ΔH_M can be related to the difference between the solubility parameters of the polymer and solvent. When the solubility parameter of a solvent is similar to that of the polymer, dissolution will be favored. The solubility parameter of PET was reported in the literature as approximately 9.7 to 10.7. We expect that chloroform, with a solubility parameter of 9.3, should be a potential solvent. Due to the high crystallinity of PET, it was found to be insoluble in pure chloroform. The sample was, therefore, first dissolved in a small amount of o-chlorophenol. Following complete solution, chloroform was added and a rather stable clear solution was obtained which would remain clear long enough for GPC measurements.

To select a suitable proportion for the mixed solvent, PET and PS sample solutions in a variety of different proportions of mixed solvent were prepared and their retention volumes were measured under identical conditions. The data obtained are given in Table 1 and

TABLE 1

The Influence of Different Proportions of Solvent for PET and PS on Their Retention Volumes

PET ($\bar{M}_\eta = 2.99 \times 10^4$)			PS ($\bar{M}_n = 3.5 \times 10^5$)		
o-Chlorophenol:Chloroform		V_e,ml	o-Chlorophenol:Chloroform		V_e,ml
1	4	18.2	1	4	15.2
1	9	18.2	1	9	15.2
1	19	18.3	1	13	15.1
			0	100	15.2

TABLE 2

The Retention Volumes of PS of Different Molecular Weight in Mixed Solvent and Chloroform

$\bar{M}_n$	o-Chlorophenol:Chloroform(1:9) V_e,ml	Chloroform V_e,ml
3.5×10^5	15.2	15.1
2.18×10^5	16.0	16.0
1.11×10^5	17.7	17.7
3.6×10^4	19.8	19.8
9.05×10^3	23.8	23.9
3.57×10^3	25.1	25.0
1.79×10^3	25.9	25.9
8.11×10^2	27.6	27.4
6.0×10^2	28.1	28.2

Table 2, which show that a proportion of one volume of o-chlorophenol to nine volumes of chloroform is good, since around this proportion, any variation of the ratio of the components changes the retention volumes of PET and PS within 1%. This will ensure the reliability of the experimental result. The presence of the o-chlorophenol in the mixed solvent does not interfere with the GPC chromatogram of the PET sample, because

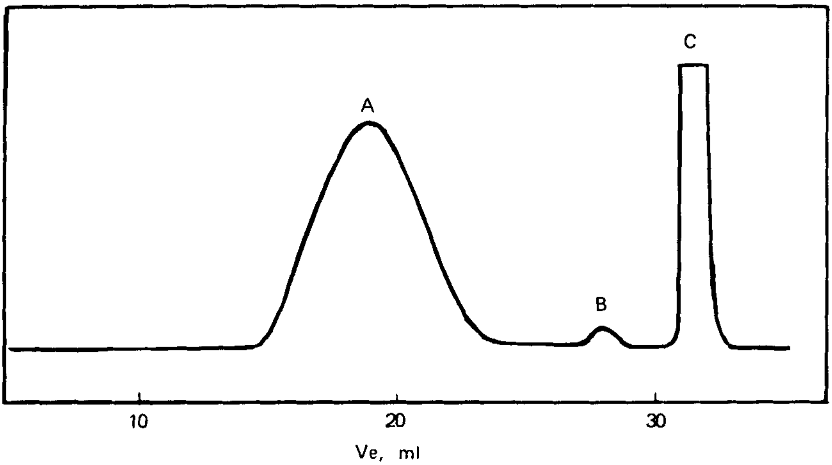

Figure 1. A typical chromatogram of PET in mixed solvent. (A - PET Polymer: B - PET oligomer; C - o-Chlorophenol).

the peak for o-chlorophenol is far behind that of the PET sample. A typical chromatogram is shown in Figure 1.

GPC Calibration Curves

The elution volumes of two sets of PET standards and PS standards, measured in two GPC systems, under conditions described above, are listed in Table 3 and Table 4.

The corresponding calibration curves for the two column systems are illustrated in Figure 2 and Figure 3.

TABLE 3

Data for Calibration Curve of Spheron Column

Standard Sample of PS	$\overline{M}_w$	V_e,ml	Standard Sample of PET	$\overline{M}_\eta$	V_e,ml
1	2.0×10^6	16.0	1	3.43×10^4	26.0
2	4.98×10^5	16.0	2	2.78×10^4	28.0
3	1.10×10^5	23.0	3	2.46×10^4	29.0
4	5.0×10^4	28.0	4	2.14×10^4	30.0
5	3.7×10^4	30.0	5	1.61×10^4	32.5
6	1.75×10^4	34.5	6	1.13×10^4	35.0
7	4.0×10^3	44.0	7	8.85×10^3	37.0
8	2.2×10^3	45.0	8	6.70×10^3	38.5
			9	5.93×10^3	40.5

Universal Calibration

Standard samples of PET are not available commercially. The preparation of PET standard samples by fractionation is troublesome and time-consuming. If the universal calibration proposed by Benoit is applicable in this new solvent system, we can then use PS samples, which are commercially available, to calibrate our column. In the universal calibration treatment, Mark-Houwink equations for both polymers in the same

TABLE 4

Data for Calibration Curve of Styragel Column

Standard Sample of PS	$\bar{M}_n$*	V_e,ml	Standard Sample of PET	$\bar{M}_\eta$	V_e,ml
1	1.50×10^6	13.3	1	2.99×10^4	18.2
2	3.50×10^5	15.2	2	2.11×10^4	19.6
3	2.18×10^5	16.0	3	1.75×10^4	20.0
4	1.11×10^5	17.7	4	7.67×10^3	21.5
5	3.60×10^4	19.8	5	4.57×10^3	23.6
6	9.05×10^3	23.8	6	4.22×10^3	23.8
7	3.57×10^3	25.1			
8	1.79×10^3	25.9			
9	8.11×10^2	27.6			
10	6.00×10^2	28.1			

* Peak Molecular Weight by GPC.

solvent are required. Therefore, intrinsic viscosities of some standard samples of PET and of PS were measured in the mixed solvent, o-chlorophenol - chloroform (1:9) at 25 deg. C. The log$[\eta]$ vs log M plots are shown in Figure 4. The corresponding Mark-Houwink equations were calculated by a least square method:

$$[\eta]_{PET} = 5.84 \times 10^{-5} M_{PET}^{0.91}$$

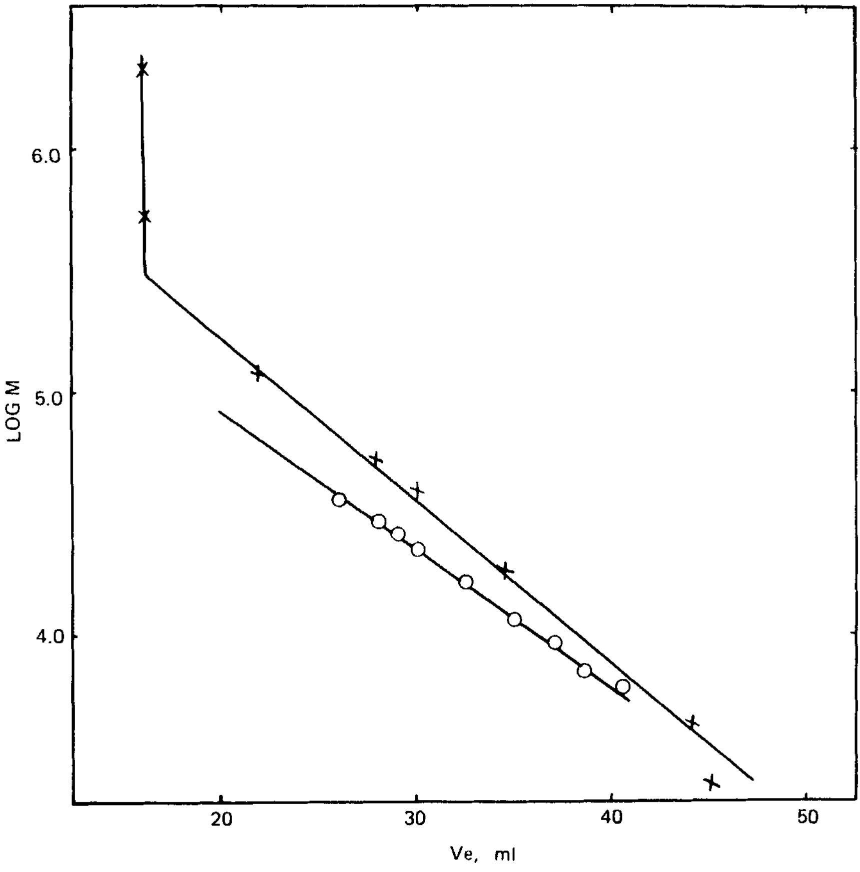

Figure 2. GPC calibration curves for Spheron column.
(o PET x PS)

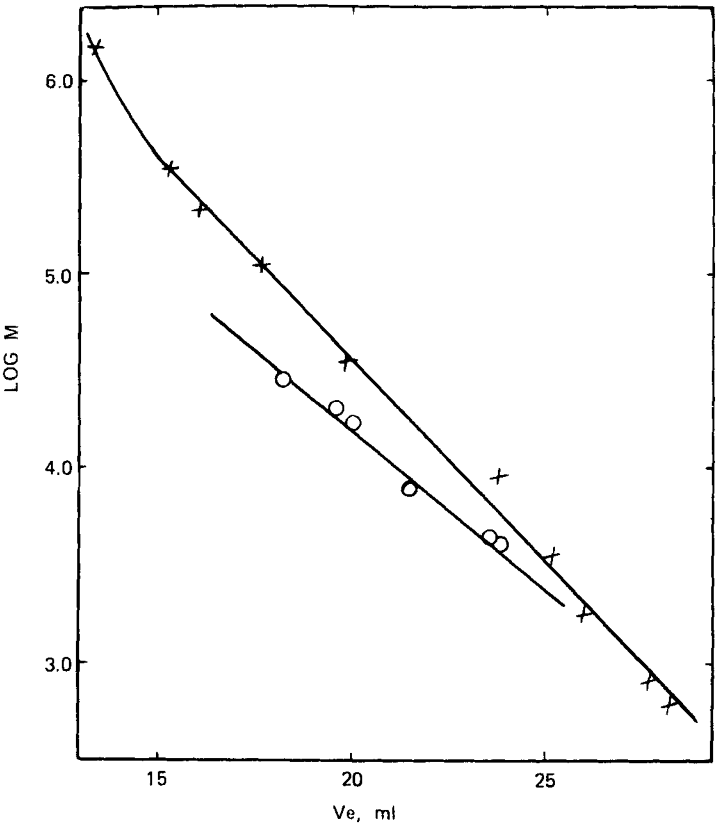

Figure 3. GPC curves for Styragel column.
(o PET x PS)

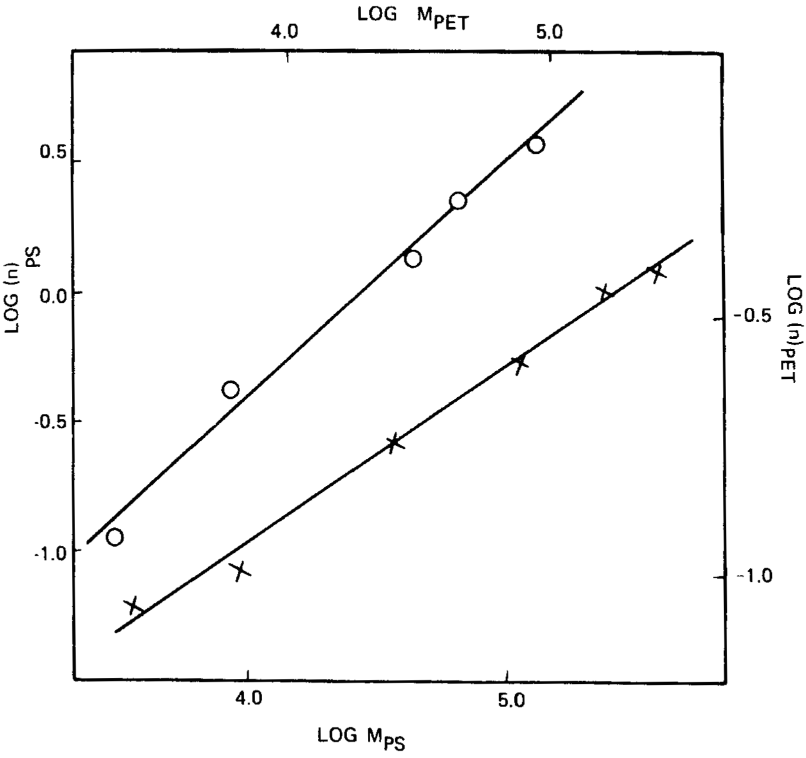

Figure 4. The log $[\eta]$ vs log M plots for PET and PS in a mixed solvent of o-chlorophenol and chloroform (1:9).
(o PET x PS)

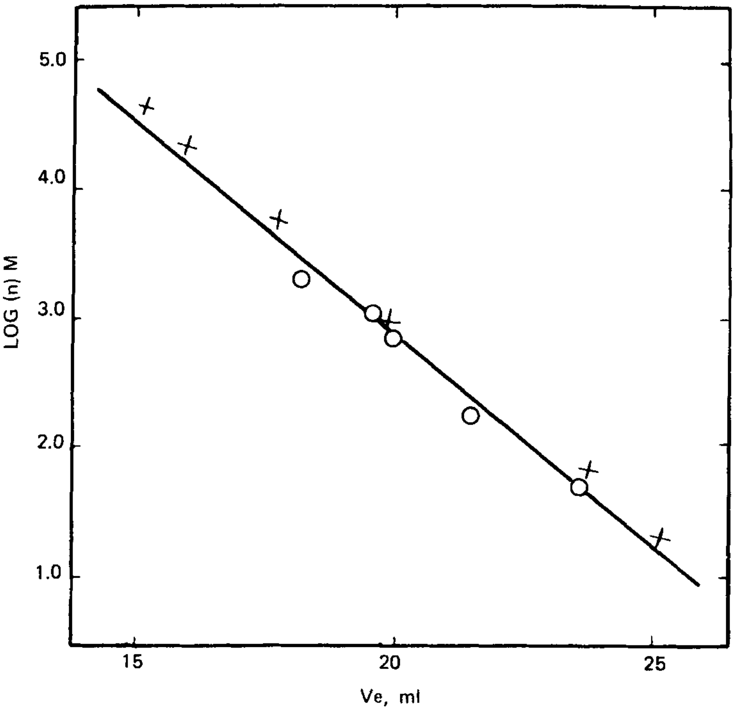

Figure 5. Log [η] vs Ve plot for PET and PS in a mixed solvent of o-chlorophenol and chloroform (1:9).
(o PET x PS).

$$[\eta]_{PS} = 2.0 \times 10^{-4} M_{PS}^{0.68}$$

The log [η] vs Ve plots of PET and PS were obtained from the data given above. All the points fall on the same straight line as shown in Figure 5. This shows that universal calibration is applicable in this system.

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