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DETERMINATION OF POLYMER MOLECULAR
WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION
BY REVERSE PHASE THIN LAYER CHROMATOGRAPHY

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ABSTRACT

Reverse phase thin layer chromatography (RPTLC) and scanning densitometry was used to determine various molecular weight averages and the molecular weight distribution of broad molecular weight range samples of poly(styrene) and poly(methyl methacrylate). A basic program was developed which analyzes the analog signals from the scanner, calculates the desired parameters, prints the parameters, graphs the results and simultaneously displays the results on a CRT. The average molecular weight values obtained by this technique compare well to those obtained by other methods.

INTRODUCTION

The ability of RPTLC to efficiently fractionate a variety of synthetic polymers using a binary solvent mobile phase consisting of a thermodynamically "good" solvent and a thermodynamically "poor" solvent of the polymer was recently reported (1-3). The mechanism of fractionation was demonstrated to be a selective

precipitation of the polymer resulting from the continuous change in mobile phase composition during development (1,2,4). In RPTLC the depletion of the less polar "good" solvent can occur naturally via selective absorption (during development) by the nonpolar stationary phase.

In addition to its high resolving power, RPTLC has several other advantages over conventional normal phase TLC methods for the separation of polymers. It is applicable to a greater variety of polymers as well as to a greater molecular weight range (2,5). In this work the applicability of RPTLC for the analysis of polymer molecular weights and polydispersity is evaluated.

MATERIALS

Whatman KC18F reversed phase TLC plates (5 x 20 cm and 20 x 20 cm) were used in all fractionations. HPLC grade methanol, methylene chloride, tetrahydrofuran (from Waters Associate), ethylene glycol (from Sigma Co.) and resublimed iodine (from Fisher Scientific Co.) were used as received. The polymer standards, their manufacturers and the various average molecular weight values supplied by the manufacturer are listed in Table I.

METHODS

All polymer standards were dissolved in methylene chloride (5 mg/ml) and 2 μ l of the solution was deposited on the TLC plates via a Drummond 5 μ l micropipette. All TLC fractionations were done in an 11 3/4 in. long, 4 in. wide and 10 3/4 in. high Chroma-flex developing chamber. Both the narrow molecular weight range

TABLE I

Polymers Standards. The Average Molecular Weights are Certified by the Indicated Suppliers

Polymers	MW	Mw	Mn	Mw/Mn	Suppliers
Poly(styrene)	-	257800	-	2.1	NBS*
	-	37400	35800	1.04	NBS*
	900000	929000	850000	1.09	Poly Science
	233000	254000	217600	1.17	Poly Science
	100000	93050	926000	1.04	Poly Science
	100000	-	-	1.3	Poly Science
	3700000	-	-	1.2	Waters
	390000	-	-	1.04	Waters
	110000	-	-	1.1	Waters
	35000	-	-	1.04	Waters
17500	-	-	1.04	Waters	
Poly(methyl methacrylate)	-	81000	47000	1.7	Poly Science
	45000	-	-	1.09	Polymer Laboratories
	72000	-	-	1.08	Polymer Laboratories
	96000	-	-	1.10	Polymer Laboratories
	280000	-	-	1.15	Polymer Laboratories
	48000	-	-	1.16	Polymer Laboratories
	64000	-	-	1.16	Polymer Laboratories

* National Bureau of Standards

standards and the broad molecular weight range polymer (used as the unknown) were spotted on the same plate and the calibration curve was established using the elution data of the narrow molecular weight range standards. Typical calibration curves for poly(styrene) and poly(methyl methacrylate) are shown in Figure I.

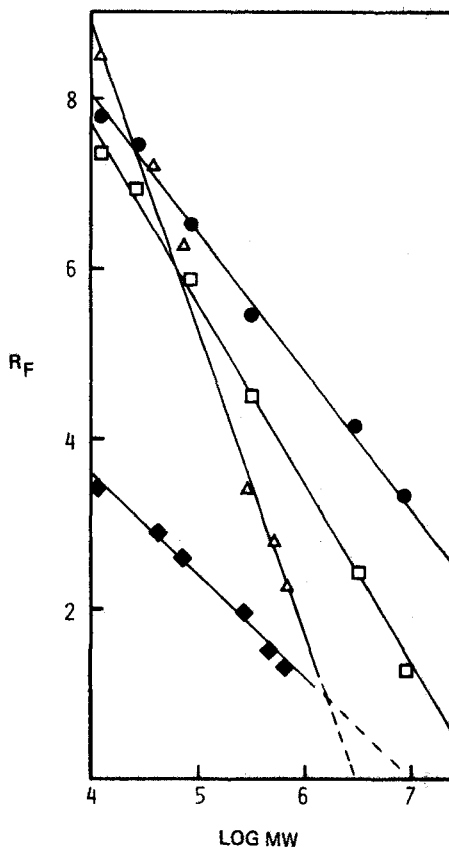


Figure 1. Typical TLC calibration curves for poly(styrene) developed with a 77.5:22.5 (v:v) MeCl₂:MeOH mobile phase (●) and with a 79:21 (v:v) MeCl₂:MeOH mobile phase (□). The poly(methyl methacrylate) calibration curves were obtained using a 76:24 (v:v) THF:ethylene glycol mobile phase (◆) and a 39:61 (v:v) MeCl₂:MeOH mobile phase (△).

It is apparent that for both polymer systems, there is a linear relationship between the R_f values (or elution distance) and the log of their molecular weight. Furthermore, this relationship holds for different mobile phase compositions and mobile phase systems. Consequently calibration can be done simply by linearly

correlating the molecular weight of the polymers to their elution values. Quantitative analysis of the polymer concentration along its elution path was performed via direct scanning densitometry using a Shimadzu model CS 910 dual wavelength TLC scanner. For polystyrene, maximum absorption occurs at wavelength of around 265 nm and almost no absorption occurs at 300 nm. Therefore, the sample wavelength was set at 265 nm and the reference wavelength was set at 300 nm. Detection was performed in the reflectance mode (Figure 3). Unusually high noise levels and baselines were observed (even under dual wavelength scan) when the KC 18 plates were scanned at 265 nm. This phenomenon is believed to be caused by the presence of the fluorescence indicator which has emission bands that extend into the UV. In the analysis of polydispersity of a polymer, this unusually high baseline is very deleterious since only the top portion of the peak (which protrudes above the base line) can be detected and the peak and hence the polydispersity of the polymer will appear to be artificially very narrow. Fortunately, the fluorescence indicator can be easily destroyed by spraying the plate with an 8% sulfuric acid/ethanol solution and heating the plate at 100°C for 10 minutes. Figure 2 shows that both the noise level and the baseline were considerably improved when the above treatment was performed on part of the plate. Consequently, the sensitivity of the detection is also enhanced with this treatment (Figure 3).

In order to visualize poly(methyl methacrylate), a 1% methanolic iodine solution was sprayed on the plate. After warming the plate at ~50°C for a few minutes and letting the yellow background

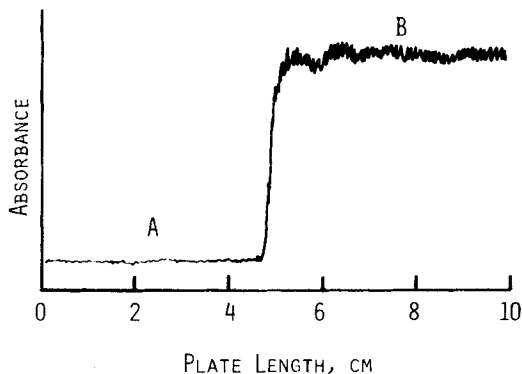


Figure 2: Scanning densitometric profile of a reversed phase TLC plate with fluorescent indicator. Part "A" of the plate was sprayed with $H_2SO_4/EtOH$ solution and Part "B" was untreated. Note that the baseline is lower and more stable when the fluorescent indicator has been inactivated. The magnitude of this effect is dependent on the scanning wavelength used.

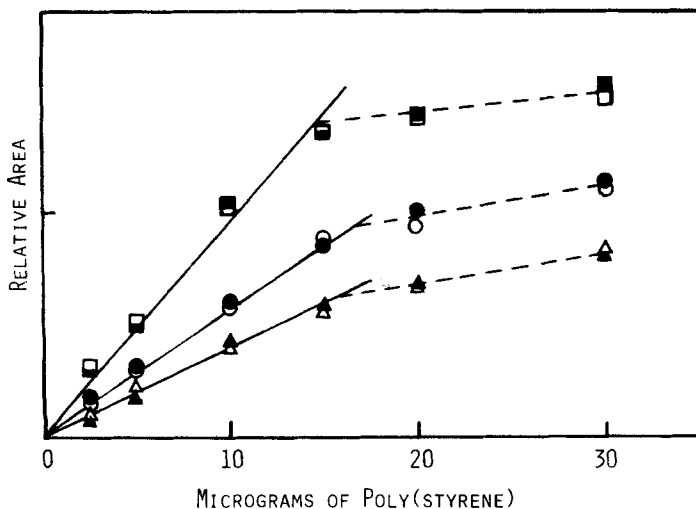


Figure 3: Plots of the weight of poly(styrene) spotted on a TLC plate versus densitometric peak area. The white symbols correspond to poly(styrene) of 35,000 Daltons and the dark symbols correspond to poly(styrene) of 10^6 Daltons. Three detection modes are shown:
 □, ■ = reflectance mode with H_2SO_4 treatment of plate
 ○, ● = reflectance mode without treatment of plate
 △, ▲ = transmission mode without treatment of plate

of the plate fade, poly(methyl methacrylates) appeared as yellow-brown spots. The maximum absorption of these spots occurred at 405 nm. Scanning densitometry of these spots, performed under single wavelength transmission mode provided the highest sensitivity (see Figure 4).

A Shimadzu Chromatopac model CR2A(X) data processor was used to analyze the analog data collected from the TLC scanner. The Chromatopac can function as a data processor as well as a per-

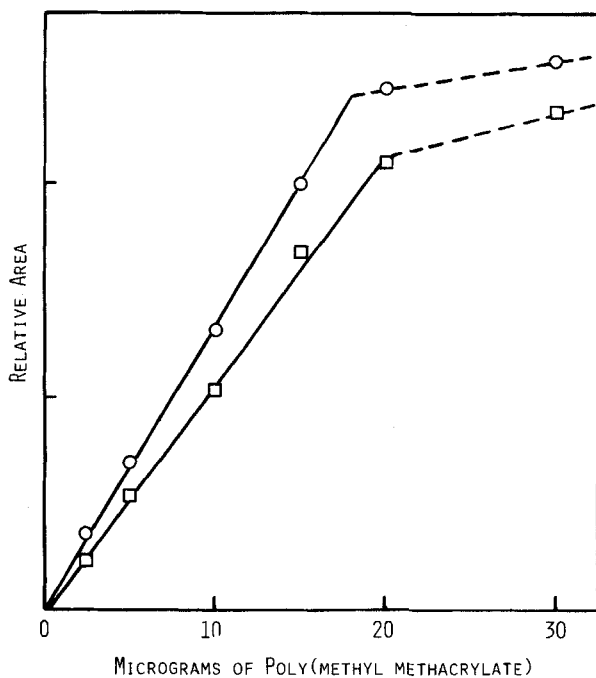


Figure 4: Plots of the weight of poly(methyl methacrylate) spotted on a TLC plate versus densitometric peak area. The circles (O) are for quantitation done in the transmission mode and the squares (□) are for quantitation of the same spots in the reflectance mode. The scanning wavelength was 405 nm (after spraying with iodine solution).

sonal computer. Data processed by the chromatopac such as peak retention time, peak area, area of a certain time band (slice area), retention time of the slice area, etc. can be manipulated freely as variables by a user defined Basic program. A Basic program was developed which permits calculations of the various average molecular weights and the polydispersity as well as the graphical display of the cumulative weight fraction molecular weight distribution and the weight fraction frequency distribution of the polymers. A listing of the program is provided in Appendix I.

RESULTS AND DISCUSSION

Figure 5 illustrates the scanning densitometric profile of a TLC chromatogram showing the fractionation of a mixture of 4 narrow disperse poly(styrene) standards and of a broad molecular weight range poly(styrene) standard (please note that these standards and standard mixtures were spotted on the same plate and developed under identical conditions). These scanning densitometric profiles are essentially a molecular weight size distribution of the polymer in weight concentration if and only if a detection method which is sensitive only to the weight concentration of the polymer and not the molecular weight of the polymer is used. Light absorption of polymers has been shown to be independent of the polymer molecular weight and to vary linearly with the concentration of the polymer in different solvent systems (when in sufficiently dilute solution) (6,7). Indeed Figure 3 shows that the UV absorption of poly(styrene) is independent of its molecular

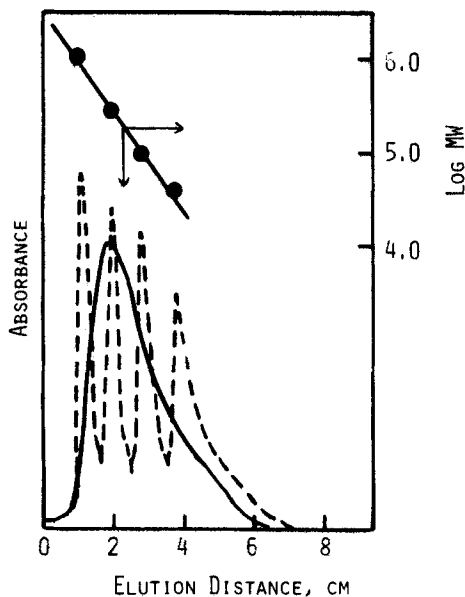


Figure 5: Two superimposed scanning densitometric profiles of a poly(styrene) unknown (i.e., the solid line, —) and poly(styrene) standards (i.e., the broken line, ---). Above the profiles is the calibration curve for the standards (i.e., log MW vs. elution distance).

weight and varies linearly with the concentration of the polymer (up to $\sim 15 \mu\text{g}$). Using the scanning densitometric profile of the mixture of narrow disperse standards, a calibration curve can be readily established. From this calibration curve, the scanning densitometric profile of the broad molecular weight range standard is converted into a molecular weight distribution curve and the respective molecular weight averages can be calculated (i.e., including number average, weight average and z-average molecular weights. See Appendix I).

The various molecular weight averages of broad distribution poly(styrene) and poly(methyl methacrylate) standards determined

TABLE II.

A Comparison of Polymer Molecular Weight Averages Obtained
by RPTLC and Other Traditional Methods

Polystyrene ⁽¹⁾ (NBS)	Average Mw by RPTLC	Standard Deviation	Average Mw given by Manufacturer
Mw	2.45×10^4	9000	2.58×10^4 (light scattering) 2.88×10^4 (sedimentation equilibrium)
Mn	1.20×10^4	9000	1.23 (fractionation)*
Mw/Mn	2.0	-	2.1

Polymethyl Methacrylate ⁽²⁾ (Poly Sciences)	Average Mw by RPTLC	Standard Deviation	Average Mw given by Manufacturer
Mw	8.0×10^4	3000	8.1×10^4 (light scattering)
Mn	5.4×10^4	3000	4.7×10^4 (osmometry)
Mw/Mn	1.5	-	1.7

* Based on fractionation value of Mw/Mn multiplied by Mn value for light scattering

- (1) Fractionated using 78:22 (v:v) MeCl₂/MeOH. Sample loading = 5 mg/ml. Analyzed in the reflectance mode at 265 nm after spraying with ethanolic sulfuric acid solution.
- (2) Fractionated using 30:70 (v:v) (MeCl₂/MeOH). Sample loading = 5 mg/ml. Analyzed in the transmission mode at 405 nm after spraying with methanolic iodine solution.

TABLE III.

Polymers Which Have Been Fractionated by RPTLC

Polymers	Solvent Pairs	Reference
Poly(styrene)	MeCl ₂ /MeOH	1
Poly(α -styrene)	MeCl ₂ /MeOH	2
Poly(methyl methacrylate)	MeCl ₂ /MeOH [*] ; THF:EG	2
Poly(ethylene glycol)	Dioxan/Ethylene glycol; MeOH/EG	2
Poly(ethylene oxide)	Dioxan/EG	2
Poly(vinyl chloride)	THF:EG	8
Poly(vinyl acetate)	THF:EG	8
Poly(isoprene)	MeCl ₂ /MeOH	2
Poly(butadiene)	MeCl ₂ /MeOH	2
Poly(tetrahydrofuran)	THF:EG	2

* This work

by this technique are compared to those given by the manufacturers in Table II. It is apparent that the average molecular weight values determined by this technique compare well to those given by the manufacturers in spite of the fact that no correction for band broadening due to processes other than the fractionation process was made (in TLC fractionation of polymer, band broadening can be caused not only by the polydispersity of the polymer but also by other processes such as eddy diffusion and mass transfer).

Table III lists all the polymers which have been fractionated by RPTLC and the solvent pairs used to fractionate them. It is

apparent that except for those polymers which exist in the crystalline state (where elevated temperature is needed to break up the crystalline bond forces before dissolution of these polymers can occur) this technique is readily applicable to the analysis of a variety of macromolecules.

ACKNOWLEDGEMENT

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APPENDIX I

LIST
BASIC PROGRAM

```

5 PRINT " *** MOLECULAR WEIGHT REPORT ***"
6 P.:P.
10 PRINT "CALIBRATION DATA"
20 PRINT "COEFFICIENT A":INPUT A

```

```

30     PRINT "COEFFICIENT B":INPUT B
40     PRINT "COEFFICIENT C":INPUT C
50     PRINT "COEFFICIENT D":INPUT D
60     P=MAXSL(1)
70     DIM AR(P),M(P),L(P),CU(P)
100    T=0:X=0:Y=0:ZA=0:ZB=0:ZC=0:AM=0
120    FOR J=1 TO P
130    T=T+SLAR(1,J)
140    NEXT J
145    PRINT
150    PRINT "Ret.      ":"Slice  ":"Mol.Wt  ":"Area ":"Cum"
155    PRINT "Time      ":" Area  ":" Slice  ":" %   ":"AR."
156    PRINT "-----"
157    PRINT
160    FOR I=1 TO P
170    M(I)=A+B*SLRT(1,I)+C*SLRT(1,I)^2+D*SLRT(1,I)^3
175    L(I)=10^M(I)
180    AR(I)=100*SLAR(1,I)/T
185    IF AM<AR(I) THEN AM=AR(I)
190    X=X+SLAR(1,I)
200    Y=Y+SLAR(1,I)/L(I)
210    ZA=ZA+SLAR(1,I)*L(I)
220    ZB=ZB+SLAR(1,I)*(L(I)^2)
230    ZC=ZC+SLAR(1,I)*L(I)^3
250    CU(I)=100*X/T
260    PRINT USING 261;SLRT(1,I),SLAR(1,I),L(I),AR(I),CU(I)
261    IMAGE;##.##  ####.## ***** ###.## ##.##
270    NEXT I
280    MW=ZA/X
290    MN=X/Y
300    MA=ZB/ZA
310    MB=ZC/ZB
315    MP=MW/MN
316    P.:P.:P.
317    PRINT "Distribution Averages:"
318    PRINT "Total Area =",T
320    PRINT "Mn =",MN
325    PRINT "Mw =",MW
330    PRINT "Mz =",MA
340    PRINT "MZ+1 =",MB
350    PRINT "MW/MN =",MP
355    P.:P.:P.
370    PRINT "Range of Log MW Plotted?"
380    PRINT "Minimum Log MW value":INPUT MI
390    PRINT "Maximum Log MW value":INPUT MX
392    P.:P.:P.
393    PRINT "4"
395    PRINT "                                AREA %"
396    PRINT
400    Q=MX-MI
410    PVL=0
420    MOVE PRINTER,0,0
440    MOVE CRT 400,10
445    MOVE PRINTER,900,0
446    PRINT USING 447;AM
447    IMAGE;##.##
448    MOVE CRT 70,20
449    DRAW CRT 450,20
450    MOVE PRINTER,120,100
455    DRAW PRINTER,920,100
456    FOR I=10 TO 0 STEP -1
457    MOVE PRINTER,80*I+120,100
458    DRAW PRINTER,80*I+120,140
459    MOVE CRT 38*I+70,24
460    DRAW CRT 38*I+70,20
461    NEXT I

```

```

462 DRAW CRT 70,180
463 DRAW CRT 450,180
469 DRAW PRINTER 120,2300
470 DRAW PRINTER,920,2300
472 FOR I=10 TO 0 STEP -2
474 MOVE CRT 38*I+70,180
475 DRAW CRT 38*I+70,176
476 MOVE PRINTER,80*I+120,2300
477 DRAW PRINTER,80*I+120,2260
478 NEXT I
480 MOVE PRINTER,920,2300
481 DRAW PRINTER,920,100
482 MOVE CRT 450,180
483 DRAW CRT 450,20
500 FOR I=0 TO Q
510 MOVE PRINTER,50,(2200*I/Q)+100
512 MOVE CRT 30,(160*I/Q)+20
520 PRINT USING 530;MX-I
530 IMAGE;#
540 MOVE PRINTER,120,(2200*I/Q)+100
550 DRAW PRINTER,130,(2200*I/Q)+100
551 MOVE CRT 70,(160*I/Q)+20
552 DRAW CRT 75,(160*I/Q)+20
554 MOVE PRINTER,910,(2200*I/Q)+100
555 DRAW PRINTER,920,(2200*I/Q)+100
556 MOVE CRT 445,(160*I/Q)+20
557 DRAW CRT 450,(160*I/Q)+20
560 NEXT I
650 MOVE PRINTER,120,(2200*(MX-M(1))/Q)+100
651 MOVE CRT 70,160*(MX-M(1))/Q+20
660 FOR I=1 TO P
670 DRAW PRINTER,8*CU(I)+120,2200*(MX-M(I))/Q+100
671 DRAW CRT 3.8*CU(I)+70,160*(MX-M(I))/Q+20
690 NEXT I
695 MOVE PRINTER,120,2200*(MX-M(1))/Q+100
696 MOVE CRT 70,160*(MX-M(1))/Q+20
700 FOR I=1 TO P
710 DRAW PRINTER,800*AR(I)/AM+120,2200*(MX-M(I))/Q+100
711 DRAW CRT 380*AR(I)/AM+70,160*(MX-M(I))/Q+20
720 NEXT I
730 MOVE PRINTER,0,2400
731 MOVE CRT 0,190
740 P. USING 750;"LOG MU","0","20","40","60"
750 IMAGE;##### * ** ** **
760 MOVE PRINTER,720,2400
765 MOVE CRT 350,190
770 PRINT " 80 100"
775 PRINT
780 PRINT " CUM. AREA %"
900 END

```