Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Liquid Chromatographic Fractionations of Mixtures of Polystyrene Oligomers

Michael A. Curtis[a]; James W. Webb[ab]; Doris C. Warren[ac]; Vernon O. Brandt[ad]; Francis G. Gerberich[ae]; K. B. Raut[af]; L. B. Rogers[a]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA ATHENS, GEORGIA [b] Department of Chemistry, Illinois State University, Normal, Illinois [c] Department of Chemistry, Houston Baptist University, Houston, Texas [d] Ethyl Corporation, Baton Rouge, Louisiana [e] Monsanto Company, Missouri [f] Department of Chemistry, Savannah State College, Savannah, Georgia

To cite this Article Curtis, Michael A. , Webb, James W. , Warren, Doris C. , Brandt, Vernon O. , Gerberich, Francis G. , Raut, K. B. and Rogers, L. B.(1980) 'Liquid Chromatographic Fractionations of Mixtures of Polystyrene Oligomers', Separation Science and Technology, 15: 7, 1413 — 1428

To link to this Article: DOI: 10.1080/01496398008056094

URL: http://dx.doi.org/10.1080/01496398008056094

SEPARATION SCIENCE AND TECHNOLOGY, 15(7), pp. 1413–1428, 1980

Liquid Chromatographic Fractionations of Mixtures of Polystyrene Oligomers

---

MICHAEL A. CURTIS, JAMES W. WEBB,*
DORIS C. WARREN,† VERNON O. BRANDT,‡
FRANCIS G. GERBERICH,§ K. B. RAUT,¶ and L. B. ROGERS

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF GEORGIA
ATHENS, GEORGIA 30602

Abstract

Oligomer mixtures of 800, 2200, and 4000 molecular weight polystyrene have been fractionated using silica and bonded phase columns under similar conditions of solvent gradient and flow rate. Using a hexane tetrahydrofuran gradient, the silica and nitro phases were best in that they separated 41 and 43 oligomers, respectively. At the other extreme, a phenyl bonded phase column gave virtually no resolution using a water/THF gradient, and a cyano bonded phase column, using the earlier hexane/tetrahydrofuran system, resolved only 10 oligomers. Amino and octadecyl bonded phase columns gave results intermediate between these two extremes. The strength of the solvent used to dissolve the sample was found to be of critical importance. Use of too good a sample solvent seriously degraded the attainable resolution. When number-average and weight-average molecular weights for an 800 molecular weight polystyrene sample were calculated from the oligomer distribution, the silica column gave values which were most consistent with those reported from other methods.

*Present address: Department of Chemistry, Illinois State University, Normal, Illinois 61761.

†Present address: Department of Chemistry, Houston Baptist University, 7502 Fondren Road, Houston, Texas 77074.

‡Present address: Ethyl Corporation, Box 341, Baton Rouge, Louisiana 70821.

§Present address: Monsanto Company, St. Louis, Missouri 63166.

¶Present address: Department of Chemistry, Savannah State College, Savannah, Georgia 31404.

INTRODUCTION

There is considerable interest in separating oligomers of polymeric systems. Much of the recent work has been concerned with polystyrene due to its sensitivity to ultraviolet detection and to the availability of well-characterized samples. Thus polystyrene can serve as a model for future work on the fractionation of oligomers of other polymers.

The most extensive work on the separations of oligomers of polystyrene has been with supercritical fluid chromatography (SFC) (*1–8*). In a recent report (*1*) 49 oligomers in a 2200 molecular weight (MW) sample were separated by SFC; however, separation times were long (17 hr) and required special instrumentation. Separations of 18 oligomers by gel permeation have also been reported within 12 hr (*9–11*) using 2-m long columns.

There has been relatively little work utilizing high performance liquid chromatography (HPLC) to separate polystyrene oligomers. Kirkland (*12*) reported the separation of about 12 oligomers on octadecyl columns using acetonitrile at 50°C. However, since he used isocratic conditions, the first peaks to elute were poorly resolved and the last peaks to elute were broad. Advertising literature has indicated that either a silica columns used with a hexane/tetrahydrofuran (THF) gradient (*13*) or a reverse phase (Zorbax ODS) column used with a methanol/THF gradient (*14*) was a good system for separating polystyrene oligomers.

One objective of this investigation was to compare different column packings and solvent combinations for the eventual optimization of the resolution of polystyrene oligomers. A second objective was to compare them with the results from SFC techniques and to provide a basis for separations of other polymers. Finally, the number-average molecular weight ($\overline{M}_N$) of a polystyrene standard having a nominal $\overline{M}_N$ of 800 was calculated from the oligomer distribution using methods previously reported (*4*, *15*).

EXPERIMENTAL

Apparatus

Two Varian Model 8500 pumps, one equipped with a solvent programmer (Varian Instrument Division, Palo Alto, California), were used to generate mobile phase gradients. Samples were introduced into the columns by means of an air-actuated six-port Valco valve, Model AC V-6UHPA (Valco Instrument Co., Houston, Texas), having a 12.5 μL sample loop. The detector was a Perkin-Elmer LC-55 variable wavelength detector (Perkin-Elmer Corp., Norwalk, Connecticut) set at 265 nm. Chromatograms were recorded using a Sargent Model SR recorder (Sargent Welch Scientific Co., Skokie, Illinois).

Chemicals

Hexanes (a mixture of hexane isomers) and methyl alcohol, both J. T. Baker reagent grade, were used as mobile phases as received. Isopropanol, chloroform (both J. T. Baker reagent grade), and tetrahydrofuran (Fisher, histological grade) were used as packing solvents as received. Tetrahydrofuran (THF) that was used as a mobile phase or to dissolve the samples was distilled over 5:1 potassium-sodium alloy to remove water and butylated hydroxytoluene. The latter had been added to the THF as a stabilizer. Water, used both as a mobile phase and a packing solvent, was deionized, then doubly distilled. It was degassed by heating under a water-aspirator vacuum immediately prior to use.

Monodisperse polystyrene samples (800, 2200, and 4000 MW) were obtained from the Pressure Chemical Company (Pittsburgh, Pennsylvania). Sample mixtures were prepared using the two Varian 8500 pumps and solvent programmer. Samples of the 800 MW polystyrene that were used on the amino, cyano, nitro, and silica columns were usually dissolved in a hexanes/THF mixture. The 800 MW polymer was dissoved in 1: 99 THF/hexanes at a concentration of 25 mg/mL. However, all samples used with the octadecyl and phenyl columns were dissolved in pure THF at a concentration of 100 mg/mL. In all cases, new samples were prepared every 2 weeks.

Column packings were obtained from E. Merck Laboratories (octadecyl, amino), Waters Associates (phenyl), Whatman (silica, cyano), and Rainin Instrument Co. (nitro). Physical data for the columns are given in Table 1.

TABLE 1

Physical Data for Chromatographic Columns

Packing	Source	Particle size (μ)	Packing solvent
Octadecyl	E. Merck	10	1:1 *i*-PrOH:MeOH
Amino	E. Merck	10	3:1 $CHCl_3$:THF
Silica	Whatman	10	H_2O
Nitro	Machery-Nagel	10	*i*-PrOH
Cyano	Whatman	10	1:4 MeOH:$CHCl_3$
Phenyl	Waters	37–75	Dry-packed

PROCEDURES

Column Preparation

All columns were constructed from 316 stainless steel tubing (25 cm × 4.1 mm i.d., Alltech Associates, Arlington Heights, Illinois) that had been washed with 6 *M* nitric acid, followed by distilled water, methanol, and finally THF. Dry nitrogen was then blown through the tubing.

All columns, except the phenyl bonded phase, were packed at 4500 psi using a Micromeritics Model 705-P slurry packer (Micromeritics, Norcross, Georgia) and one of the Varian pumps. After the packing pressure had been reached, slurry was passed into the column until it was full. The column of phenyl bonded phase was dry packed using the conventional tap-and-fill method.

The packed columns were prepared for sample injection by passing 20–30 column volumes of distilled THF through at a rate of 1 mL/min and then ramping down the solvent composition at a rate of 5%/min until the mobile phase composition corresponded to that used for injection on that particular column.

Sample injection was done in the following manner. After the baseline had stabilized, the sample loop was filled. The air-actuated valve was then switched to the "sample" position and, at the same time, the solvent gradient was initiated. After 2.5 min the valve was switched back to the "load" position.

For the silica column, the initial mobile phase composition was 3:97 THF/hexanes. After sample injection the solvent gradient was increased at 0.2% THF/min until elution of the separated oligomers had occurred and the signal had returned to the baseline. For the amino, cyano, and nitro columns, the initial percentages of THF in the hexane/THF mobile phase were 1, 3, and 5%, respectively. Elution was performed by increasing the concentration of THF at 0.2%/min until all of the sample had eluted.

For the octadecyl and phenyl columns, the initial solvent composition was 60:40 THF/water, and the percentage of THF was increased at 0.2%/min.

At the end of each run the following reconditioning procedure was performed prior to the next injection. After the signal had returned to the baseline, the percentage of THF in the eluent was increased to 100% at 10%/min. Pure THF was then passed through the column for 10 min to insure complete elution of sample components. Then the solvent gradient was decreased at 5%/min to the initial solvent composition where the baseline was allowed to stabilize before the next injection. For the octadecyl and phenyl columns, a faster downramp (10%/min) was used.

During the entire injection, elution, and regeneration sequence, the flow rate of the mobile phase was held at 1.0 mL/min for all columns.

Calculations

Peak retention volumes were calculated by mutliplying the distance measured from the injection point to the peak by the flow rate and dividing by the chart speed. Reproducibility of retention volumes in triplicate chromatograms were generally within a range of −2.5% or ±2 min, whichever was smaller.

Chromatographic peak areas were measured using a Keuffel and Esser Model 62000 compensating polar planimeter. The total peak areas from each chromatogram were summed, and each peak area was reported as its percentage of the total area.

Since the chromatograms used for molecular weight determinations did not exhibit baseline resolution of all oligomers, two methods of determining peak area were used. In Method *A*, a line drawn between the lowest point of the valley on each side of the peak served as the baseline. In Method *B*, a vertical line was extended from the lowest point of the valley on each side of the peak through the envelope to the baseline of zero signal so as to include that portion of the envelope in the area for that peak.

Each polystyrene oligomer had a butyl end group resulting from the polymerization process in which butyllithium was added as an initiator (*3–5*, *15*, *16*). Consequently, the molecular weight of an oligomer was determined by

$$M_x = 104n + 58 \tag{1}$$

where n was the degree of oligomerization and M_x was the molecular weight of the oligomer.

The weight-average ($\overline{M}_W$) and number-average ($\overline{M}_N$) molecular weights for 800 molecular weight polystyrene were calculated from the oligomer distribution in a manner similar to that used by Klesper and Hartmann (*4*) and Altares (*15*). The relative area of each peak was divided by n, the degree of oligomerization; the resulting value was proportional to N_x, the number of molecules of that degree of oligomerization. Thus

$$\overline{M}_W = \frac{\Sigma N_x M_x^2}{\Sigma N_x M_x} \tag{2}$$

and

$$\overline{M}_N = \frac{\Sigma N_x M_x}{\Sigma N_x} \tag{3}$$

RESULTS

Preliminary Studies

It was found that the sample solvent composition was critically important to the success of the separation. Use of too strong a sample solvent tended to elute the sample rapidly without allowing it sufficient interaction with the stationary phase. The "wash off" effect was characterized by a sharply rising front followed by poorly resolved peaks. No such effect was observed on the octadecyl or phenyl columns.

The effect of sample solvent can be seen in Fig. 1 where samples of 800 MW polystyrene in pure THF, 1:1, 1:3, and 1:9 THF/hexanes

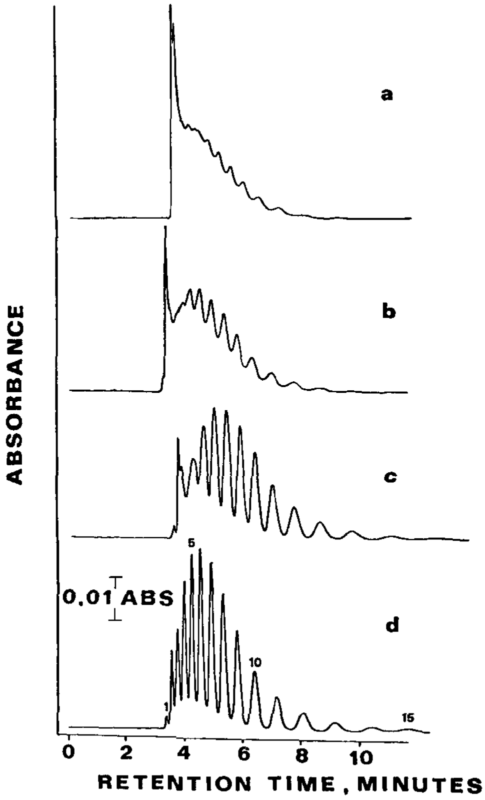

FIG. 1. Separations of 800 MW polystyrene on a nitro-bonded phase column using different sample solvents. (a) 100% THF, (b) 1:1 THF/hexanes, (c) 1:3 THF/hexanes, (d) 1:9 THF/hexanes. Gradient: 5% THF in hexanes to 8% THF at 0.2%/min.

(1a through 1d, respectively) were injected on the nitro column. Plainly, a trend toward improved resolution occurred as the sample solvent strength was decreased. An effect of sample solvent on the resolution of mixtures of simple compounds has been noted previously (*17*). Since the 800 MW sample was soluble in 1:99 THF/hexanes, this solvent was used for further work on the amino, cyano, nitro, and silica columns.

The 2200 and 4000 MW polystyrenes were not soluble in 1% or even 5% THF. Although they could be dissolved with some difficulty in 1:9 THF/hexanes by warming and shaking for several minutes, a solvent mixture of 1:3 THF/hexanes was used because it dissolved the molecular weight polystyrenes more easily and, in addition, the resulting separations appeared to be identical to those obtained using the 1:9 composition. Hence the 1:3 solvent mixture was used for all further work with the 2200 and 4000 MW polystyrenes on the amino, nitro, and silica columns.

Another exploratory experiment tested the feasibility of substituting cyclohexane for the mixture of hexanes in the mobile phase. Using 800 MW polystyrene and the nitro column under otherwise identical conditions, the time required to elute all of the oligomers in the sample (approximately 12 min) was not changed but the resolutions of the peaks were seriously degraded. Seven broad peaks eluted over a large envelope instead of 15 peaks.

QUALITATIVE RESULTS

Nitro and Silica Columns

These columns gave excellent separations, resolving 15 and 14 oligomers, respectively, for the 800 MW polystyrene (see Figs. 2a and b and Table 2), and 43 and 41 oligomers, respectively, for the 2200 MW (see Figs. 4a and b and Table 2). Approximately 40 oligomers were discernible with the 4000 MW polymer on these columns (see Figs. 5a and b).

The peaks corresponding to higher molecular weight species in the 2200 and 4000 MW polystyrenes appeared on a "hump" or envelope that has been observed in other separations of polystyrenes involving supercritical fluid chromatography (*1–3*, *7*). The hump is probably due to unresolved oligomers since the fractional change in molecular weight due to the addition of a monomer unit becomes progressively less.

There was also a marked difference in appearance between the separations of 2200 and 4000 MW polystyrenes. In the latter, the envelope constituted most of the area reflecting the fact that there were larger relative concentrations of the higher molecular weight oligomers present.

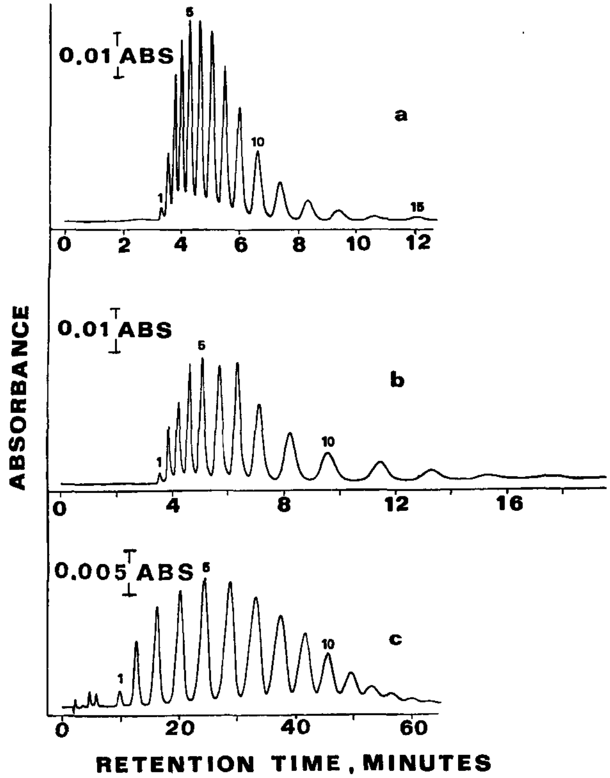

FIG. 2. Separations of 800 MW polystyrene. (a) Nitro-bonded phase, sample solvent: 1:99 THF/hexanes, gradient: 5% THF in hexanes to 8% THF at 0.2%/min; (b) silica column, sample solvent: 1:99 THF/hexanes, gradient: 3% THF in hexanes to 7% THF at 0.2% min; (c) octadecyl-bonded phase, sample solvent: THF, gradient: 60% THF in water to 75% THF at 0.2%/min.

Amino Column

Separation of the 800 and 2200 MW polystyrenes resulted in 13 and 25 oligomers, respectively (Figs. 3a and 4c). Peak symmetry tended to be poor with the amino column such that even the peaks for the 800 MW sample showed pronounced tailing. The poor peak symmetry was especially noticeable for the 2200 MW sample.

Octadecyl Column

Hexane could not be used as a mobile phase because the 800, 2200, and 4000 MW polystyrenes each eluted as one peak with the solvent

TABLE 2

Retention Volumes of Species in Polystyrene Samples of Molecular Weights 800 and 2200 on Silica, Nitro Bonded Phase, and C-18 Bonded Phase Columns

	Retention volumes (mL)					
	Silica		Nitro		Octadecyl	
Peak no.	800 MW	2200 MW	800 MW	2200 MW	800 MW	2200 MW
1	3.48	3.5	3.34	3.3	9.8	10.0
2	3.81	3.6	3.54	3.5	12.7	12.0
3	4.15	4.0	3.75	3.7	16.1	15.8
4	4.54	4.5	4.00	3.9	20.0	19.5
5	4.99	4.9	4.28	4.3	24.3	23.2
6	5.57	5.5	4.62	4.7	28.6	27.1
7	6.10	6.1	5.02	5.1	32.7	31.3
8	6.76	6.8	5.47	5.6	37.1	35.5
9	7.79	7.7	5.95	6.3	41.2	39.7
10	9.30	9.0	6.55	7.0	45.2	43.5
11	11.08	10.5	7.27	7.8	49.1	46.9
12	12.95	12.0	8.15	8.9	52.5	51.1
13	14.98	13.9	9.21	10.2	55.9	54.9
14	17.53[a]	15.9	10.42	11.7	59.4[a]	57.8
15		18.0	11.67[a]	13.0		61.1
16		20.3		14.8		64.4
17		22.7		16.7		66.9
18		25.2		18.7		69.9
19		27.7		20.9		72.1
20		30.8		23.2		
21		33.0		25.7		
22		35.8		28.0		
23		38.3		30.5		
24		41.0		33.2		
25		43.6		35.8		
26		46.2		38.2		
27		48.7		40.6		
28		51.2		43.2		
29		53.8		45.8		
30		56.1		48.2		
31		58.4		50.6		
32		60.7		52.9		
33		62.9		55.3		
34		65.0		57.4		
35		67.2		59.6		
36		69.3		61.8		
37		71.3		63.9		
38		73.4		65.9		
39		75.3		67.9		
40		77.3		70.0		
41		79.9[a]		71.9		
42				73.7		
43				75.8[a]		

[a] No higher oligomers resolved.

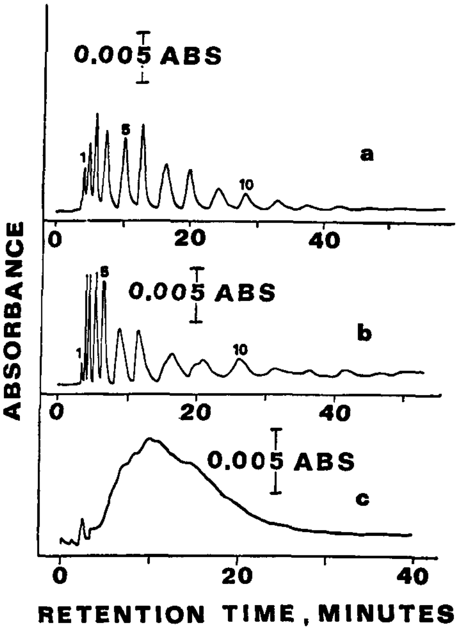

FIG. 3. Separations of 800 MW polystyrene. (a) Amino-bonded phase, sample solvent: 1:99 THF/hexanes, gradient: 1% THF in hexanes to 13% THF at 0.2%/min; (b) cyano-bonded phase, sample solvent: 1:99 THF/hexanes, gradient: 3% THF in hexanes to 13% THF at 0.2%/min; (3) phenyl-bonded phase, sample solvent: THF, gradient: 60% THF in water to 68% THF at 0.2%/min.

front. However, using a water/THF gradient, the 800 MW sample produced 16 peaks of which only the first three were baseline resolved (Fig. 2c and Table 2). The remaining 13 peaks eluted on an envelope. The 2200 MW polystyrene gave 19 oligomers, the rest of the sample having eluted as a broad, unresolved band (Fig. 4d and Table 2).

Substituting methanol for water in the eluent decreased the resolution of the 800 MW sample. Under the same gradient conditions as above, i.e., starting at 60: 40 THF/methanol and increasing the THF at 0.2%/min, the sample eluted as one peak. Even when the gradient was initiated with 100% methanol and run isocratically for 10 min, the oligomers eluted rapidly and produced 8 poorly resolved peaks.

Cyano and Phenyl Columns

These columns were not investigated throughly since the initial results

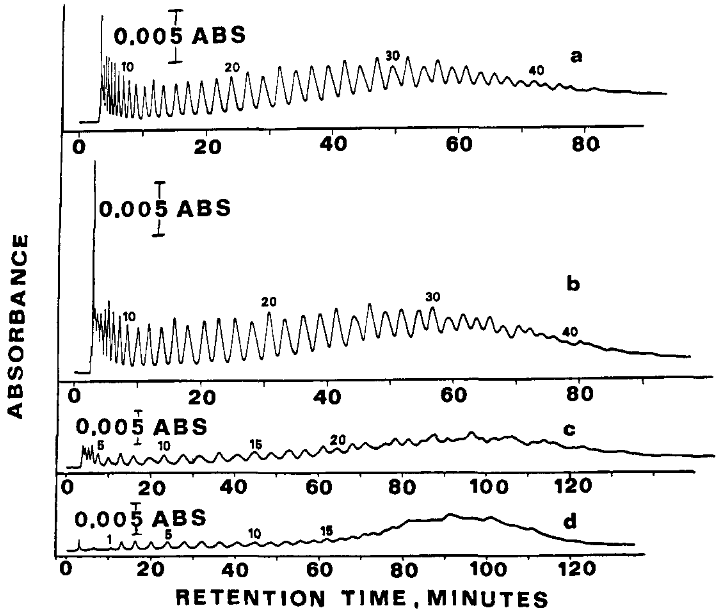

FIG. 4. Separations of 2200 MW polystyrene. (a) Nitro-bonded phase, sample solvent: 1:3 THF/hexanes, gradient: 5% THF in hexanes to 23% THF at 0.2%/min; (b) silica, sample solvent: 1:3 THF/hexanes, gradient: 3% THF in hexanes to 23% THF at 0.2%/min; (c) amino-bonded phase, sample solvent: 1:3 THF/hexanes, gradient: 1% THF in hexanes to 31% THF at 0.2%/min; (d) octadecyl-bonded phase, sample solvent: THF, gradient: 60% THF in water to 85% THF at 0.2%/min.

were not promising. For the cyano phase, the same solvents and gradient were used as with the silica column. The 800 MW sample showed about 10 oligomers (see Fig. 3b). The first few peaks were sharp but resolution and peak symmetry degraded rapidly for the larger oligomers. There was an irregular envelope with no clear resolution of any oligomers of the 2200 MW sample. The phenyl column showed an unresolved hump for the 800 MW sample using the same solvents and gradient as used with the octadecyl column (see Fig. 3c).

Quantitative Aspects

The 800 MW polystyrene was used to check molecular weight determinations since virtually all of the sample components were well resolved on more than one column. In order to extract quantitative information from the chromatograms, the following assumptions were made, based

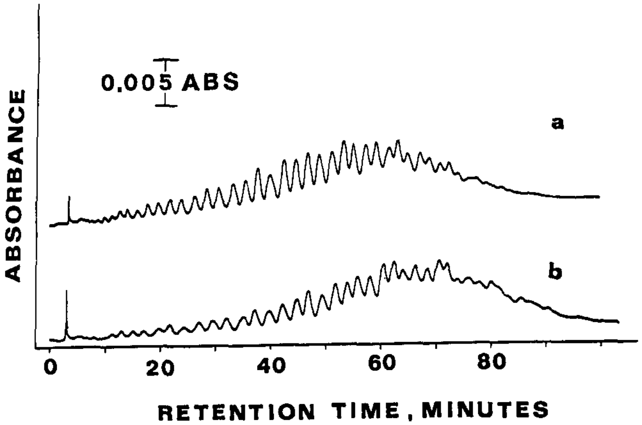

FIG. 5. Separations of 4000 MW polystyrene. (a) Nitro-bonded phase, sample solvent: 1:3 THF/hexanes, gradient: 5% THF in hexanes to 23% THF at 0.2%/min; (b) silica, sample solvent: 1:3 THF/hexanes, gradient: 3% THF in hexanes to 23% THF at 0.2%/min.

on earlier SFC work. First, the first two peaks to elute after the solvent peak from the 800 MW sample on the octadecyl column were not considered to be part of the oligomeric series of polystyrene since they were not consistent with the pattern of increasing area for the next four peaks in the polystyrene homologous series. Thus the first peak so identified as an oligomer is numbered 1 in Fig. 2(c) and Table 2.

Second, the first oligomer to elute was the dimer, based upon the work of Jentoft and Gouw (*5*) and Altares (*15*) who collected early fractions of a 600 MW polystyrene and found no monomer present. Each subsequent peak was assumed to be the next highest member of the oligomeric series.

Finally, there was assumed to be a direct proportionality between the absorbance at 265 nm and the concentration of each oligomer (*15*).

Relative peak areas of 800 MW polystyrene for the silica, nitro, and octadecyl columns are given in Tables 3A, 3B, and 3C, respectively. Relative areas calculated using Method *B* were more consistent among the three columns. Furthermore, when the envelope areas were included, oligomers 6 and 7 gave peaks with the largest relative areas on all three columns.

Table 4 gives calculated values for $\overline{M}_W$ and $\overline{M}_N$. Although the results show that $\overline{M}_W/\overline{M}_N$ ratios from all three columns were similar and below the maximum of 1.3 given by Pressure Chemical Co., the individual $\overline{M}_W$ and $\overline{M}_N$ values for the octadecyl column were lower than those for the nitro and silica columns. Again, the $\overline{M}_W$ and $\overline{M}_N$ values for the three columns showed better agreement using Method *B*.

TABLE 3A

Relative Peak Areas of 800 Molecular Weight Polystyrene on the Silica Column

		Method *A*		Method *B*	
Peak no.	n	Area %	N_x[a]	Area %	N_x
1	2	0.5	0.25	0.6	0.3
2	3	3.1	1.0	3.1	1.0
3	4	5.5	1.4	6.0	1.5
4	5	8.3	1.65	8.9	1.8
5	6	11.2	1.87	11.5	1.92
6	7	12.9	1.85	13.5	1.93
7	8	13.1	1.63	13.7	1.72
8	9	11.9	1.33	12.9	1.43
9	10	10.1	1.01	9.6	0.96
10	11	7.7	0.70	7.0	0.64
11	12	6.0	0.50	5.1	0.43
12	13	4.4	0.34	3.7	0.31
13	14	2.9	0.21	2.4	0.17
14	15	2.3	0.15	1.9	0.13
15	16	[b]		[b]	

[a] N_x = % area/n.

[b] Not found on this column.

TABLE 3B

Relative Peak Areas of 800 Molecular Weight Polystyrene on the Nitro Column

		Method *A*		Method *B*	
Peak no.	n	Area %	N_x	Area %	N_x
1	2	0.4	0.2	0.5	0.2
2	3	2.9	1.0	3.2	1.1
3	4	4.7	1.2	6.1	1.5
4	5	7.7	1.5	9.1	1.8
5	6	10.4	1.73	11.6	1.93
6	7	13.1	1.87	13.5	1.93
7	8	13.8	1.72	13.8	1.73
8	9	12.9	1.44	12.7	1.41
9	10	10.7	1.07	10.2	1.02
10	11	8.0	0.73	7.5	0.68
11	12	5.4	0.45	4.3	0.36
12	13	3.9	0.30	2.9	0.23
13	14	2.6	0.19	2.0	0.14
14	15	2.0	0.13	1.5	0.10
15	16	1.3	0.08	0.9	0.06

TABLE 3C

Relative Peak Areas of 800 Molecular Weight Polystyrene on the Octadecyl Column

		Method *A*		Method *B*	
Peak no.	*n*	Area %	N_x[a]	Area %	N_x
1	2	0.9	0.4	0.7	0.3
2	3	4.2	1.4	3.3	1.1
3	4	8.0	2.0	6.6	1.7
4	5	11.2	2.24	9.2	1.8
5	6	13.8	2.29	12.1	2.01
6	7	15.3	2.18	13.8	1.97
7	8	14.6	1.83	13.9	1.74
8	9	14.5	1.61	13.3	1.36
9	10	9.0	0.90	9.9	0.99
10	11	5.6	0.51	7.2	0.65
11	12	2.9	0.24	4.8	0.40
12	13	1.4	0.10	3.0	0.23
13	14	0.7	0.05	1.8	0.13
14	15	0.3	0.02	1.1	0.07
15	16	[b]		[b]	

[a] N_x = % area/*n*.

[b] Not found on this column.

TABLE 4

Molecular Weights Calculated for 800 Molecular Weight Polystyrene from Separations Obtained on Silica, Nitro, and Octadecyl Columns Using Two Different Baselines for Calculating Areas

	Silica		Nitro		Octadecyl	
	A	*B*	*A*	*B*	*A*	*B*
$\bar{M}_W$	917	897	930	893	818	876
$\bar{M}_N$	806	795	821	786	727	770
$\bar{M}_W/\bar{M}_N$	1.14	1.13	1.13	1.14	1.12	1.14

Pressure Chemical Co. reported a number-average molecular weight for the 800 MW polystyrene of 811 ± 5% that was calculated by vapor phase osmometry. Note that both the nitro and silica columns gave molecular weights that were highly consistent with that previous datum.

DISCUSSION

The separations of 2200 and 4000 MW polystyrenes on the nitro and silica columns demonstrate the potential of liquid chromatography for resolving oligomeric mixtures. The chromatograms show resolution approaching that attainable with state-of-the-art supercritical fluid chromatography but using commercially available equipment and involving much shorter separation times (80 min versus 17 hr).

In order to obtain reproducible results with the amino, cyano, nitro, and silica columns, a small concentration of THF in the mobile phase was necessary to overcome the "displacement effect" (*18–20*) that occurs upon introduction of a polar solvent (THF) into a nonpolar mobile phase (hexanes). Otherwise, polar solvent adsorbs on the stationary phase initially, resulting in little change in polarity of the mobile phase to which the remainder of the column is exposed. However, once the entire packing has been saturated, there is a sudden change in polarity of the mobile phase; any solutes eluted at that time are usually unresolved.

In some of our chromatograms this phenomenon took the form of elution of the first few oligomers followed by a sharply rising front plus two or three fused peaks. The displacement effect was overcome by using the minimum concentration of THF in the initial mobile phase that would eliminate the problem. For each column with which the hexanes/THF eluent was used, the minimum concentration of THF was found by trial and error.

In addition to eliminating the displacement effect, THF in the mobile phase also served to moderate the activity of the silica column (*21*). Saunders (*22*) has shown that mixed solvents, consisting of nonpolar solvents, such as *n*-alkanes, and small percentages of a moderately polar solvent, such as THF or acetonitrile, are superior to water-moderated solvents for controlling the activity of the stationary phase. This is due both to the difficulty of preparing and storing nonpolar solvents having a constant water content (*21*) and to the long reequilibration times required of such solvents (*23*).

For analysis of the 800 MW polystyrene, the octadecyl column gave results complementary to those obtained with the nitro and silica columns; i.e., the low molecular weight oligomers were better resolved by the former column while the higher molecular weight oligomers showed baseline resolution with the latter columns. This trend was also evident with the 2200 MW polystyrene in that the first few oligomers were baseline resolved with the octadecyl column whereas they were not as well resolved on the nitro and silica columns. However, the latter two gave a much larger number of peaks since the higher molecular weight oligomers in the hump were at least partly resolved. A mixture of the two phases (or two columns in series) is not a practical alternative because of the different eluting conditions used for each column.

One difference between the separations of the 800 and 2200 MW can be seen in the retention data in Table 2. While the retention volumes for the first few oligomers in both the 800 and 2200 MW samples showed agreement on a given column, those of the higher molecular weight oligomers in the 800 MW sample did not agree with the retention volumes of the same species in the 2200 MW sample. This may reflect an effect of the high molecular weight oligomers on the retentions of the low molecular weight oligomers.

Finally, it should be noted that while the nitro and silica columns showed superior performance under the conditions used, a change in operating conditions (e.g., use of a nonlinear gradient) might have improved the performances of the other stationary phases.

Acknowledgments

We wish to thank Bruce Semonian for carrying out some of the preliminary experiments. We are indebted to the Division of Basic Energy Sciences, Department of Energy, for partial support of this study through Contract No. EY–76–S–09–854 and to the University of Georgia Graduate School for a Graduate Assistantship (to M.A.C.).

REFERENCES

1. E. Klesper and W. Hartmann, *Eur. Polym. J.*, *14*, 77 (1978).
2. E. Klesper and W. Hartmann, *J. Polym. Sci., Polym. Lett. Ed.*, *15*, 9 (1977).
3. E. Klesper and W. Hartmann, *Ibid.*, *15*, 707 (1977).
4. E. Klesper and W. Hartmann, *Ibid.*, *15*, 713 (1977).
5. R. E. Jentoft and T. H. Gouw, *Ibid.*, *7*, 811 (1969).
6. R. E. Jentoft and T. H. Gouw, *J. Chromatogr. Sci.*, *8*, 138 (1970).
7. J. E. Conaway, J. A. Graham, and L. B. Rogers, *Ibid.*, *16*, 102 (1978).
8. T. H. Gouw and R. E. Jentoft, *J. Chromatogr.*, *68*, 303 (1972).
9. D. J. Harmon, in *Gel Permeation Chromatography* (K. H. Altgelt and L. Segal, eds.), Dekker, New York, 1971, p. 13.
10. W. Heitz and H. Ullner, *Makromol. Chem.*, *120*, 58 (1968).
11. W. Heitz, B. Bomer, and H. Ullner, *Ibid.*, *121*, 102 (1969).
12. J. J. Kirkland, *Chromatographia*, *8*, 661 (1975).
13. Perkin-Elmer Advertising Brochure, 1976.
14. DuPont Instruments Advertisement, *Anal. Chem.*, *50*, 331A (1978).
15. T. Altares, *J. Polym. Sci., Part B*, *8*, 761 (1970).
16. T. Altares, D. P. Wyman, and V. R. Allen, *J. Polym. Sci., Part A*, *2*, 4533 (1964).
17. P. K. Tseng and L. B. Rogers, *J. Chromatogr. Sci.*, *16*, 436 (1978).
18. R. E. Majors, *Anal. Chem.*, *45*, 755 (1973).
19. R. P. W. Scott and P. Kucera, *Ibid.*, *45*, 749 (1973).
20. H. Engelhardt and H. Eglass, *J. Chromatogr.*, *112*, 415 (1975).
21. H. Engelhardt, *J. Chromatogr. Sci.*, *15*, 380 (1977).
22. D. L. Saunders, *J. Chromatogr.*, *125*, 163 (1976).
23. J. J. Kirkland, *Ibid.*, *109*, 297 (1975).

Received by editor December 14, 1979