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Retention characteristics of high-molecular-weight compounds in capillary supercritical fluid chromatography

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ABSTRACT

The separation of oligomers of two different polymers using capillary supercritical fluid chromatography was studied. Pressure programming was used to achieve optimum separation of the oligomers. From a comparison of the separation of these oligomers with different length columns it was demonstrated that oligomer solubility was primarily controlling the separation. Accordingly, changing the stationary phase, shortening the column or not even using a stationary phase had minimal effect on the separation of the oligomers.

INTRODUCTION

Supercritical fluid chromatography (SFC) provides a powerful technique for the separation of oligomers in polymer samples. A wide variety of natural and synthetic polymers have been separated. Many combinations of mobile phase, stationary phase, and operating conditions are available for use. Such diversity may make it possible to separate polymers that are presently problematic when using other techniques.

Interactions between the mobile phase and the oligomers are of primary importance to polymer separations in SFC. While the stationary phase affects retention, the mechanism by which it contributes is unclear [1]. For packed SFC columns the postulated separation process involves continuous reprecipitation and redissolution of the oligomers as they move down the column [2]. As a result of the pressure drop across the column and the existence of threshold pressures or threshold densities for each oligomer [3], the higher-molecular-weight oligomers follow the smaller ones down the column. The validity of this retention mechanism has been substantiated by experimental results showing that the nature of the stationary phase has little impact on the selectivity of the oligomer separation [4]. Due to the nature of the retention mechanism in packed-column SFC of oligomers, gradient programming is required to achieve optimum separation of the oligomers [5]. Pressure programming and the resultant density programming were the first gradient methods used to separate polymers [3] and remains the most common gradient methods used for oligomer separations.

Capillary columns of the dimensions used in this study have negligible pressure drop across the column. The retention mechanism based on precipitation–redissolution as a function of pressure drop is therefore not applicable to capillary columns. This paper illustrates the relative importance of oligomer solubility and oligomer–stationary phase interac-

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tions for two very different polymer systems: a polydisulfide and a methylmethacrylate(MMA)–*n*-butylacrylate (BA) copolymer.

EXPERIMENTAL

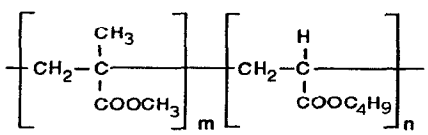
Polymers and samples

Thiokol LP-3 is a polydisulfide elastomer that is produced by Morton Thiokol. It is used as a sealant and as an additive for high molecular weight polymer synthesis. The polydisulfides are good sealants because they exhibit high resistance to organic solvent, *i.e.* the solubility of these elastomers in organic solvents is minimal. However, we have recently demonstrated that the LP-3 polymer is soluble in supercritical CO_2 [6]. The approximate molecular structure of the polydisulfide repeating unit is as follows (this structure does not include any subunits due to cross-linking reactions):

$$HS\text{–}(C_2H_4O\text{–}CH_2O\text{–}C_2H_4\text{–}SS)_n\text{–}C_2H_4O\text{–}CH_2O\text{–}C_2H_4\text{–}SH$$

Thiokol LP-3 was obtained from Polysciences (Warrington, PA, USA) and was used without further purification.

The repeating unit of the MMA–BA copolymer has the following molecular structure:



where m usually ranges from 10 to 18 and n values vary between 0 and 7, with $n = 2$ being the most common [7]. Oligomers ranging in molecular weight from 600 to 3500 have been identified using mass spectroscopy [7]. There are at least 72 oligomers theoretically possible in the molecular weight range from 1000 to 2700. These copolymers are used for the manufacture of many types of plastics. The specific MMA–BA copolymer studied was made by combining 80% (w/w) MMA and 20% (w/w) BA of the monomers. The polymer was obtained from the Marshall Laboratories of E.I. du Pont de Nemours & Co.

Table I shows other properties of the two oligomer systems used in this study. The analyzed samples were made by diluting bulk polymer to 10% (w/w) with reagent-grade carbon disulfide (J. T. Baker). This concentration, although high, was necessary because many of the oligomers in the samples were not detectable at lower bulk sample concentrations.

Instrumentation: MMA–BA studies

The chromatograph in the MMA–BA studies consisted of a Varian 3700 gas chromatographic oven and a Varian flame ionization detector. A 20 m × 100 μm I.D. DB-17 (polyphenylmethylsiloxane) open tubular column with a film thickness of 0.2 μm was used as purchased (J&W Scientific). A 20 m × 100 μm I.D. DB-225 (polycyanopropylphenylmethylsiloxane) open tubular column with a film thickness of 0.1 μm was also used as purchased (J&W Scientific). The mobile phase consisted of SFC-grade carbon dioxide (Matheson) modified with 0.5–1.3% (v/v) of 95–97% formic acid (Aldrich). An ISCO 260D syringe pump was used to deliver the mobile phase. Sample introduction was accomplished with a Valco CI4W injector with a 60-nl sample loop. Upon injection the sample loop was left in line with the column for the duration of the run. This is to prevent discrimination against high-molecular-weight analytes. Cycling of the valve introduces a pressure drop in the injection loop, and the concomitant density reduction may render the mobile phase solvent strength inadequate for solvation of heavier components in a sample.

Instrumentation: polydisulfide studies

The chromatographic system and operating conditions used have been described in detail elsewhere [6]. A Hewlett-Packard 5890A gas chromatograph and a Hewlett-Packard Model 19256A flame pho-

TABLE I

PHYSICAL PROPERTIES OF POLYMERS STUDIED

M_n = Number-average molecular weight; M_w = weight-average molecular weight; D (polydispersity) = M_w/M_n.

	M_n	M_w	D
Thiokol LP-3	540	1500	2.8
MMA–BA	750	1300	1.70

tometric detector served as the system oven and detector. A 12.2 m × 220 μm I.D. BP-10 (polyphenylmethylsiloxane) open tubular column with a film thickness of 0.25 μm was used (Scientific Glass Engineering, Austin, TX, USA). The stationary phase was cross-linked with azo-*tert.*-butane before exposure to a supercritical fluid mobile phase. A 12.2 m × 250 μm I.D. fused-silica capillary (Polymicro Technologies, Phoenix, AZ, USA) was also employed as a column. The fused-silica tubing was rinsed with methylene chloride and then flushed with dry nitrogen before use. The mobile phase used in the polydisulfide studies consisted of supercritical-grade carbon dioxide (Scott Specialty Gases). An ISCO μLC500 syringe pump delivered the mobile phase. Sample introduction was accomplished with a Valco CI4W injector with a 200-nl sample loop. As in the MMA–BA studies, upon injection the sample loop was left in line with the column for the duration of the analysis.

In all studies, integral restrictors constructed from 50 μm I.D. fused-silica tubing (Polymicro Technologies) were used to regulate pressure and to control flow. The orifice diameter of the restricting capillary was approximately 5 μm.

RESULTS AND DISCUSSION

Polydisulfide studies

The chromatographic separation of Thiokol LP-3 on the BP-10 column is shown in Fig. 1. Fig. 2 shows separation of the Thiokol LP-3 when the column is replaced with a fused-silica open tube with the same internal diameter and length as the column. Identical chromatographic conditions were used in the separation of LP-3 with the column and the fused-silica tube. These conditions included using carbon dioxide as the mobile phase, an oven temperature of 100°C, and an initial pressure of 102 atm for 15 min, followed by a pressure ramp of 3.4 atm/min to a final pressure of 306 atm. The polydisulfide was crudely separated in the fused-silica open tube, without the benefit of interaction with a stationary phase. The resulting chromatogram mimicked the results obtained when the BP-10 column was used under the same experimental conditions. The BP-10 column separation produced three sets of peaks, each peak being composed of one or more oligomers. The fused-silica tube separation lacked the resolution of the column chromatogram, but reproduced the three principle peak clusters.

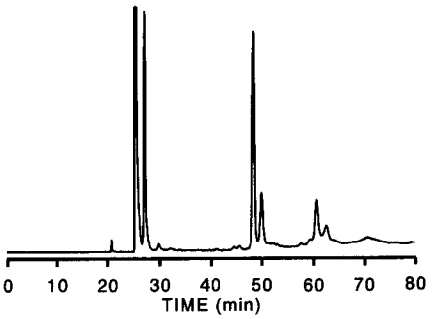


Fig. 1. Separation of Thiokol LP-3 on the 12.2-m BP-10 column. Oven temperature: 100°C. Mobile phase: carbon dioxide. Initial pressure: 102 atm for 15 min. Pressure ramp: 3.4 atm/min. Final pressure: 306 atm. Detector gas flows: 240 ml/min hydrogen, 45 ml/min oxygen. From ref. 7.

These results give insight into the retention mechanism of polymers in capillary SFC. The separations observed in the fused-silica tube can be attributed to the selective solvation of oligomers as the mobile phase density was ramped. Isobaric conditions did not permit a satisfactory separation to occur. If the initial pressure was too low, there was no sample elution. If the initial pressure was too high, the oligomers coeluted. With isobaric runs at an intermediate pressure, fewer peaks were observed. We attribute the separation achieved without stationary phase in the fused-silica tube to the selective solvation of the oligomers by the supercritical fluid. The polydisulfide must initially precipitate out onto the

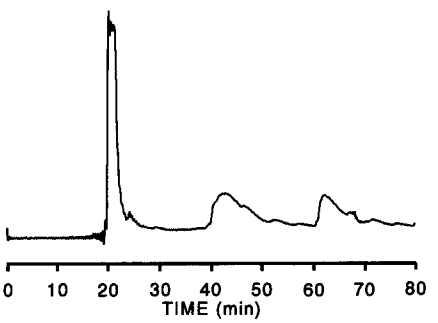


Fig. 2. Separation of Thiokol LP-3 on the 12.2-m fused-silica tube. Oven temperature: 100°C. Mobile phase: carbon dioxide. Initial pressure: 102 atm for 15 min. Pressure ramp: 3.4 atm/min. Final pressure: 306 atm. Detector gas flows: 240 ml/min hydrogen, 45 ml/min oxygen.

head of the column, due to the low solubility of the oligomer in supercritical carbon dioxide under the initial low-pressure conditions. By scanning through the threshold densities of the oligomers with a pressure or density program, selective solvation occurs. There are active sites found on fused-silica surfaces which can interact with and slow the migration of oligomers, but the number of sites is too small to be wholly responsible for the observed separations.

MMA–BA studies: DB-17 column

Fig. 3 shows the chromatogram resulting from the separation of the MMA–BA (80:20, w/w) copolymer on the 20-m DB-17 column. After completing initial studies on this 20-m column, the first meter was detached and used in further experiments. This was done to see if the efficiency and the resolution of the separations changed when a shorter column with a lesser amount of active stationary phase surface was used. Fig. 4 shows the separation of the MMA–BA copolymer on the 1-m column. When using either of the DB-17 columns a typical chromatogram contained from 30 to 40 peaks. The fifteen most prominent peaks on the chromatograms of both the 20-m and the 1-m columns were selected, and the chromatographic selectivities relative to one another were calculated to ensure that the same peaks were being compared between chromatograms.

The height equivalent to a theoretical plate (HETP) was calculated for each of the peaks using triangulation and is shown in Table II. In general,

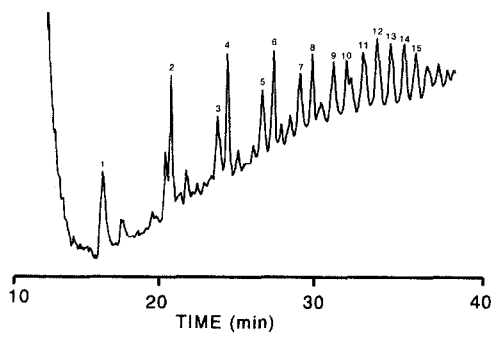


Fig. 3. Separation of MMA–BA on the 20-m DB-17 column. Oven temperature: 140°C. Mobile phase: carbon dioxide with 0.8% (v/v) formic acid. Initial pressure: 88 atm. Pressure ramp: 6.8 atm/min. Final pressure: 374 atm. Detector gas flows: 455 ml/min air, 45 ml/min hydrogen.

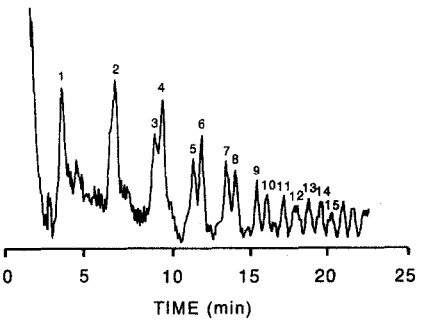


Fig. 4. Separation of MMA–BA on the 1-m DB-17 column. Oven temperature: 140°C. Mobile phase: carbon dioxide with 0.8% (v/v) formic acid. Initial pressure: 88 atm. Pressure ramp: 6.8 atm/min. Final pressure: 374 atm. Detector gas flows: 455 ml/min air, 45 ml/min hydrogen.

the 1-m column was as efficient or more efficient than the 20-m column. The same restrictor was used for the 1-m column and the 20-m column. Therefore since all other chromatographic conditions remained the same for the two separations, the linear velocity at a given pressure was also the same in each column. Minimal variation in plate height would therefore be expected with change in column length. The difference in measured plate heights for the two columns was also greatest for the compounds that

TABLE II

HETP (μm) PER PEAK

Peak No.	HETP	
	20-m column	1-m column
1	2000	1400
2	550	920
3	420	680
4	100	250
5	530	180
6	320	110
7	290	130
8	70	120
9	250	60
10	530	70
11	500	60
12	210	80
13	200	70
14	190	50
15	180	40

TABLE III

CAPACITY FACTORS (k') AND SELECTIVITIES (α) FOR 20-m DB-17, 20-m DB-225 AND 1-m DB-17 COLUMNS

Peak	k'			α		
	DB-17 (20 m)	DB-225 (20 m)	DB-17 (1 m)	DB-17 (20 m)	DB-225 (20 m)	DB-17 (1 m)
1	0.50	3.30	6.00	–	–	–
2	0.80	8.90	11.10	1.6	2.7	1.9
3	1.10	13.00	15.80	1.4	1.5	1.3
4	1.20	13.70	15.50	1.1	1.1	1.1
5	1.40	16.70	18.40	1.2	1.2	1.2
6	1.45	17.70	19.30	1.0	1.1	1.0
7	1.50	19.90	21.50	1.0	1.1	1.1
8	1.60	20.90	22.30	1.1	1.1	1.0
9	1.80	22.60	24.50	1.1	1.1	1.1
10	1.85	23.90	25.40	1.0	1.1	1.0
11	1.95	25.10	27.10	1.1	1.1	1.1
12	2.00	26.30	28.30	1.0	1.1	1.1
13	2.10	27.40	29.60	1.1	1.0	1.1
14	2.15	28.60	30.70	1.0	1.0	1.0
15	2.20	29.40	31.90	1.0	1.0	1.0

eluted latest. For these oligomers the plate height was significantly lower on the 1-m column than on the 20-m column.

Table III shows the capacity factors and selectivities for the 15 most prominent peaks in the chromatogram for both the 20- and 1-m columns. Since the two columns were identical in every way except in length, the capacity factor for a given oligomer should not change between the two columns. However, the measured capacity factor of a given oligomer was much larger for the longer column. This is a logical result if selective solvation significantly controls the separation of the oligomers. The dead time, t_0, of the 1-m column is 1/20 that of the longer column, while the dissolution time of an oligomer at a given pressure should be the same in each column.

The resolution for the two columns was also determined. Fig. 5 shows a comparison of these values. The long column, the less efficient of the two columns, provided superior resolution for oligomers 1–9. In typical chromatographic separations resolution is related to the square root of the total number of plates generated by a column. Although it was less efficient, the longer column still generated a far greater total number of theoretical plates. In Table IV the efficiency and the resolution of the two columns are compared. If the experimental efficiency of each chromatographic peak on the 20-m column is divided by 20 and substituted into the resolution equation below

$$R_s = \left(\frac{\sqrt{N}}{4}\right)\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k'}{k' - 1}\right)$$

along with the experimental selectivity and capacity factor value for the 1-m column, then the expected resolution on the 1-m column can be calculated. This is shown in Table IV. These data show that the experimental resolution obtained on the 1-m column is always higher than that expected for the larger oligomers found for peak 8 and later. We believe the major cause of this enhanced resolution to be that the separation of the higher molecular weight oligomers is predominately determined by their selective solvation in the supercritical fluid at well defined densities; this is the same mechanism as was described for the polydisulfide polymer. Interactions between the lower-molecular-weight oligomers and the stationary phase had a greater impact on their resolution. This further illustrates the relationship between the stationary phase and differential solvation in polymer separations. As seen in

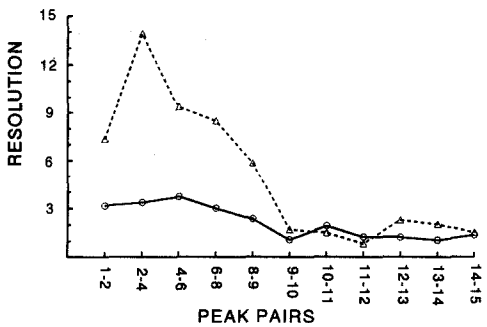


Fig. 5. Chromatographic resolution of the (○) 1-m DB-17 column and on the (△) 20-m DB-17 column.

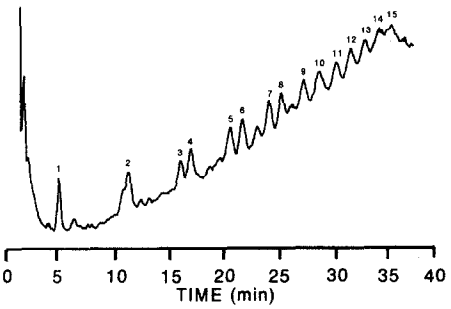


Fig. 6. Separation of MMA–BA on the 20-m DB-225 column. Oven temperature: 130°C. Mobile phase: carbon dioxide with 0.9% (v/v) formic acid. Initial pressure: 88 atm. Pressure ramp: 10.2 atm/min. Final pressure: 272 atm. Detector gas flows: 455 ml/min air, 45 ml/min hydrogen.

the polydisulfide studies, stationary phase must be present to achieve anything better than a crude separation of oligomers. The interactions between the stationary phase and oligomers serve to enhance the separation that is initiated by their differential solvation in the mobile phase. At the same time, a column that is needlessly long may increase the measured plate height of the separation (as shown in Table II) because selective solvation of the oligomers is controlling the separation, especially for the higher molecular weight compounds.

MMA–BA studies: DB-225 column

MMA–BA separations were obtained on a DB-225 column. Fig. 6 shows a chromatogram resulting from the separation. It resembles those obtained on the 20-m DB-17 column. The fifteen most prominent peaks on the DB-225 chromatogram were measured and found to have the same relative selectivity, α, as the fifteen most prominent peaks observed on the 20-m DB-17 column. In Table III a comparison of the capacity factors (k') and the selectivities (α) for the 20-m DB-225 and the 20-m

TABLE IV

A COMPARISON OF THE NUMBER OF THEORETICAL PLATES (N) AND RESOLUTION (R_s) OBSERVED FOR THE 20-m DB-17 AND 1-m DB-17 COLUMNS

Peak pair	N		R_s		
	DB-17 (20 m)	DB-17 (1 m)	DB-17 (20 m)	DB-17 (1 m)	DB-17[a] (20 m)
1–2	36 000	1 100	9.2	3.2	4.5
2–4	199 000	4 000	18.0	3.4	6.6
4–6	62 000	8 800	6.4	3.7	2.6
7–8	296 000	8 100	10.9	3.0	4.0
8–9	81 000	17 100	3.9	2.4	1.3
9–10	38 000	14 800	1.4	1.1	0.4
10–11	40 000	16 900	1.5	1.9	0.7
11–12	95 000	12 700	1.0	1.3	0.7
12–13	101 000	13 900	2.3	1.2	0.8
13–14	106 000	21 400	2.	1.1	0.6
14–15	109 000	23 100	1.5	1.4	0.7

[a] Calculated values.

DB-17 columns is shown. The elution order of the oligomers was the same regardless of the stationary phase used. These results corroborate the premise that the selectivity is controlled by selective solvation of the oligomers. Oligomer–stationary phase interactions are of lesser importance in determining retention order.

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