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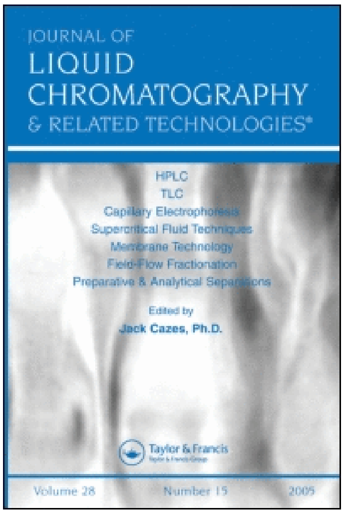

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Selectivity and the Separation of Isomers of Low Molecular Weight Polystyrenes

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ABSTRACT

The separation of diastereoisomers of polystyrene has been investigated on carbon-clad zirconia (CCZ), C_{18}, and diamond C18 stationary phases using eluents of widely different properties. Eluents were chosen according to their selectivity, solvent polarity index, and polymer solubility constants. Acetonitrile mobile phases in combination with CCZ produced the best diastereoisomer separations, however, when methanol was employed as the mobile phase, the separation profiles were very similar, except that retention was greatly increased. Retention and isomer separation decreased when isopropanol was employed. Surprisingly, some diastereoisomer separation was still apparent using the CCZ column and a 99% hexane/1% isopropanol mobile phase,

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although none was observed for the same solvent mixture on a C_{18} column. Indeed, significant diastereoisomer separation was only obtained on the C_{18} column-using acetonitrile as the mobile phase, but the resolution was far inferior to that observed on the CCZ column. The diamond C18 surface, which is a hybrid of C_{18} and CCZ, gave separations that were intermediate between those of the parent surfaces, with enhanced molecular weight selectivity in comparison with CCZ, but slightly less discrimination on the basis of stereochemistry. Polystyrenes eluted unretained if either dichloromethane or tetrahydrofuran were used as the mobile phases on all stationary phases.

Key Words: Diastereoisomers; Carbon-clad zirconia; Reversed phase LC; Polystyrene.

INTRODUCTION

The separation of oligomers of low molecular weight polymers, such as polystyrene, has been studied for several decades (see Refs.[1–12] and references cited there in). The retention of these oligomers in different chromatographic systems may be explained using thermodynamic arguments, where enthalpic interactions dominate in thermodynamically poor solvents and the oligostyrenes undergo retention on the chromatographic surface. In thermodynamically strong solvents, entropic exclusion dominates and the oligostyrenes elute according to the principles of size exclusion chromatography. Separations in which the enthalpic interactions dominate over the entropic exclusion have been reported in reversed phase[1–9] and normal phase[6,10–12] liquid chromatography, as well as supercritical-fluid chromatography.[13,14]

Subtle changes in molecular interactions may be controlled by judiciously varying the stationary and mobile phases. These changes in chromatographic selectivity may allow isomeric components to be separated on the basis of their different stereochemistries. For example, although a C_{18} column with a methanol mobile phase can give good separation for low molecular weight oligostyrenes, the different stereoisomers (isotactic, syndiotactic, and atactic forms) are poorly separated, if at all.[5] However, by changing from methanol to acetonitrile as a mobile phase, isomeric components are clearly apparent, although not fully separated.[5] Similar effects are observed in various normal phase systems employing silica columns.[10] Nevertheless, in all such cases the separation of isomers for the oligomeric fractions is dominated by the molecular weight of the oligomeric fractions,[1–12] and the isomers elute within confined regions depending upon their molecular weight.

Retention of low molecular weight polystyrenes in reversed phase chromatography is governed by the relative solvent strength with respect to the chromatographic stationary phase surface, or from a thermodynamic point of view the relative contribution of enthalpic interactions to entropic factors. Solvent strength may be gauged according to the solvent polarity index and the Hildebrand solubility constant, which takes into account the endoergic process of forming cavities in the solvent that are large enough to accommodate the solute. Selectivity in a separation is not entirely independent of the solvent strength, but is a term used to define individual solvent characteristics that relate to aspects of the solute, rather than the solvent averaged group effects. For example, the solvent selectivity triangle (SST) and the solvochromic modified version of the SST, which takes into account more precisely defined contributions from hydrogen bonding, acidity, basicity, and dipole/polarisability, are useful for estimating changes in selectivity.[15] In this triangle, solvents with similar attributes are grouped together, making it possible for the analyst to anticipate changes in selectivity. For example, solvents may have vastly different polarities (and/or polymer solubility constants), yet be contained in the same region of the SST. The alcohols, methanol, ethanol, and isopropanol decrease in polarity as the alkyl chain length increases, and offer similar selectivity; consequently, they are grouped together in the selectivity triangle. The increase in solvent polarity from isopropanol to methanol should give an increase in retention in a reversed phase separation, but with little change in selectivity. In contrast, methanol and acetonitrile, which have similar polarities, belong to different groups in the selectivity triangle and, consequently, different selectivities, and this is observed for the separation of oligostyrenes.[15]

Prior investigations on the separation of oligostyrenes found that C_{18} gave the best separations for reversed phase systems, but native silica also yielded excellent normal phase separations.[10,11] In all cases, the stereoisomer resolution is secondary to the molecular weight separation, and isomers are resolved within the distinct regions specific to that particular molecular weight. More recently, the separation of stereoisomers of low molecular weight polystyrenes on carbon-clad zirconia (CCZ) has been studied, which has demonstrated a high degree of selectivity towards diastereoisomers. Using this surface, Sweeney and coworkers[16–18] were able to provide high-resolution diastereoisomer separations of low molecular weight polystyrenes. In these separations retention was dominated by the stereochemistry of the polymer, so more than just the molecular weight. In fact, the molecular weight separations of oligostyrenes resulted in chaotic band displacement, with retention being more dependent on the isomeric form than on the molecular weight. Although the C_{18} and CCZ columns both behave as reversed phase surfaces, their surface chemistries are vastly different, which changes the selectivity of these two surfaces. The current study focuses on changes in selectivity on both CCZ and C_{18} stationary phases, and incorporates the retention behaviour of oligostyrenes on a third column referred to as the diamond C18 column, which is essentially a hybrid column containing an underlying carbon clad surface and an outer C_{18} moiety.

EXPERIMENTAL

Chemicals

HPLC grade dichloromethane, methanol, isopropanol, tetrahydrofuran, acetonitrile, and HPLC/GC grade hexanes were obtained from Mallinckrodt Australia. All hexane mobile phases were 50% saturated with water prior to use (Millipore Ultra Pure Water obtained in-house and filtered through a 0.22 μm filter). All mobile phases were sparged continuously with helium. A narrow molecular weight distribution polystyrene standard ($M_n/M_w = 1.13$) with an average molecular weight of 580 Da and *n*-butyl end group was obtained from Polymer Laboratories Inc. CCZ stationary phase (3 μm particle size) was purchased from ZirChrom Separations, Inc., Anoka, MN.

Instrumentation

All chromatographic experiments were performed on a Shimadzu liquid chromatograph (Shimadzu Scientific Instruments, Rydalmere, NSW Australia) incorporating a LC-10ATvp pumping system, SIL-10ADvp auto injector, SPD-10Avp UV detector set at 262 nm, SCL-10Avp system controller, and Shimadzu Class-VP version 5.03 software on a Pentium II 266 PC. Because of incompatibility between pump seals and dichloromethane, the dichloromethane mobile phases were delivered using a Hewlett Packard Series 1050 LC pump. Data acquisition was achieved using a Lawson Labs model 203 serially interfaced 20-bit data acquisition system with a custom ± 1 V gain range operated at 10 Hz (Lawson Labs Inc., Malvern, PA). All chromatographic separations were carried out in a thermostated water jacket at 20.0 ± 0.2°C using a LKB Bromma 2219 Multitemp II thermostatic circulator.

Chromatographic Columns

CCZ columns (50 × 4.6 mm) were prepared in-house using a downward slurry packing technique in which 6 g of stationary phase was slurried in 35 mL of a 90% hexane and 10% isopropanol solvent mixture.[16] The slurry was stirred for 30 min followed by 20 min of ultrasonication and a further 10 min of stirring. A dichloromethane displacement solvent was employed in the column tubing and the column was packed at 7000 psi using an isopropanol packing solvent. Packing continued until 100 mL of isopropanol passed through the bed.

A Valupak C18 column (250 × 4.6 mm, 5 μm P_d) (Activon, Australia—no longer in operation) was used for conventional reversed phase separations. The diamond C18 column (100 × 4.6 mm, 3 μm P_d) was a gift from ZirChrom Separations, Inc.

Sample Pretreatment

Narrow molecular weight polystyrene standards contain a distribution of oligomers. The focus of this study was the behaviour of stereoisomers of these oligomers on three different stationary phase surfaces. Individual oligomer fractions with numbers of configurational repeating units (n) ranging from $n = 2$ to $n = 5$, were collected and purified using a semi-preparative (250 × 10 mm) C_{18} column and a methanol mobile phase.[16–18] All oligomer fractions were contained in methanol, except for the separations carried out in the hexane mobile phase, in which case the oligomer fractions were blown dry and the polystyrene was redissolved in an appropriate volume of n-hexane.

Separations

Sample injection volumes were either 20 or 10 μL. Flow rates were 1 mL/min for all mobile phases, except for those containing high concentrations of isopropanol, in which case the flow rate was 0.5 mL/min.

RESULTS AND DISCUSSION

In this study, three types of stationary phase surfaces were employed. The first surface was a conventional C_{18} reversed phase, the second was reversed phase CCZ, and the third surface was essentially a hybrid of the first two: a CCZ column with an overlay of C_{18} bonded ligands (diamond C18 column). The solvents employed in this study were chosen according to the factors described in the introduction—solvent polarity index, Hildebrand polymer solubility constant (δ), and selectivity, according to the modified Snyder selectivity triangle.[15] The solvents are listed in Table 1, with the relevant solvent descriptors. They are arranged in order according to their Hildebrand polymer solubility constant. The solubility constants show that

Table 1. Hildebrand polymer solubility constant and polarity index for each of the solvents employed in this study.

Chemical name	Hildebrand polymer solubility constant (δ) (MPa)$^{1/2}$	Polarity index
Hexane	14.9	—
Tetrahydrofuran	18.6	4.0
Dichloromethane	19.8	3.1
Isopropanol	23.5	3.9
Acetonitrile	24.3	5.8
Methanol	29.7	5.1
Polystyrene	17.4–19.8	—

the two most thermodynamically favourable solvents for polystyrene are tetrahydrofuran and dichloromethane. When these solvents were employed no oligomer retention was observed on any of the three columns. The next most thermodynamically favourable solvent is hexane followed by isopropanol, acetonitrile, and lastly, methanol. For the two strongest solvents, dichloromethane and tetrahydrofuran, elution of the polystyrene oligomers should be dominated by entropic exclusion, regardless of the stationary phase surface. However, the remaining four solvents are less thermodynamically favourable for polystyrene, and hence some degree of retention in a reversed phase system was expected, depending upon the surface of the stationary phase.

The Hildebrand polymer solubility constants in Table 1 indicate that hexane should be a mediocre solvent for polystyrene, so retention should be greater than THF. However, the retention behaviour of low molecular weight polystyrenes, which were to some extent expected to behave as relatively large organic molecules, their retention behaviour may be determined by the polarities of both the mobile and the stationary phases. Hexane, as a non-polar solvent in combination with a non-polar stationary phase, might elute the oligostyrenes from the stationary phase with little or no retention. Consequently, hexane was expected to be an interesting solvent for making comparisons between these different types of reversed phase surfaces.

Almost all solvents in this study came from different regions of the selectivity triangle, the exception being methanol and isopropanol. Within this selectivity grouping, these two solvents represent changes in both solvent polarity and Hildebrand polymer solubility constant. Thus, isopropanol should be a more thermodynamically favourable solvent than methanol and hence retention should decrease when isopropanol is employed as the mobile phase. Methanol and acetonitrile have similar polarities and hence similar solvent strengths, but they differ in both their Hildebrand polymer solubility constants and their selectivity grouping. Acetonitrile and tetrahydrofuran belong to similar regions of the SST, but tetrahydrofuran is a more thermodynamically strong solvent with a lower polarity. Tetrahydrofuran and isopropanol have similar polarities but are from different regions of the SST and they also have very different polymer solubility constants.

The chromatogram illustrated in Fig. 1(a) is typical of a reversed phase oligomeric separation that results when a C_{18} column and a methanol mobile phase are employed for the analysis of low molecular weight polystyrenes. In this figure, we see a systematic increase in retention with an increase in molecular weight. The appearance of some isomeric resolution is apparent for the higher oligomers ($n > 5$). By changing the solvent to acetonitrile (which is a more polar but a more thermodynamically favourable solvent than methanol), greater resolution of the isomeric components within the oligomer fractions is apparent [see Fig. 1(b)]. This is consistent with results obtained by Men et al.[5] The resolution of these isomers is largely due to the change in selectivity. Improved isomer resolution would not be expected if the mobile phase were changed from methanol to isopropanol, as both solvents belong to the same group in the selectivity triangle. Such a change would simply represent an increase in solvent strength, with a corresponding reduction in retention. The isomer separation shown in Fig. 1(b) could be further improved by optimisation of the elution conditions using gradient chromatography,[17] but at the expense of increasing the analysis time. In any case, the separation remains dominated by the molecular weight component of the sample.

In comparison, when a CCZ column was employed, the separation of the oligostyrenes was chaotic.[17] No information regarding the molecular weight distribution was immediately apparent. For example, the separation in Fig. 1(c) illustrates the complex separation on a CCZ column employing an acetonitrile mobile phase. These types of separations have been previously described.[16–18] The diamond C18 column gave substantially greater resolution of components using acetonitrile than on the C_{18} column, as shown by the chromatograms in Fig. 1(d). If the mobile phase is changed to methanol, the corresponding oligostyrenes separate into more defined groups of diastereoisomers of the same molecular weight [Fig. 1(e)]. Within each of these diastereoisomers resolution was also substantially greater than that observed on the C_{18} column, particularly when methanol was the mobile phase. In contrast, the stereoisomer resolution on the C_{18} column was very poor and only observed for $n > 5$ when the mobile phase was changed from acetonitrile to methanol. The pyrolised carbon layer on the surface of the diamond C18 column had a significant effect on the retention process.

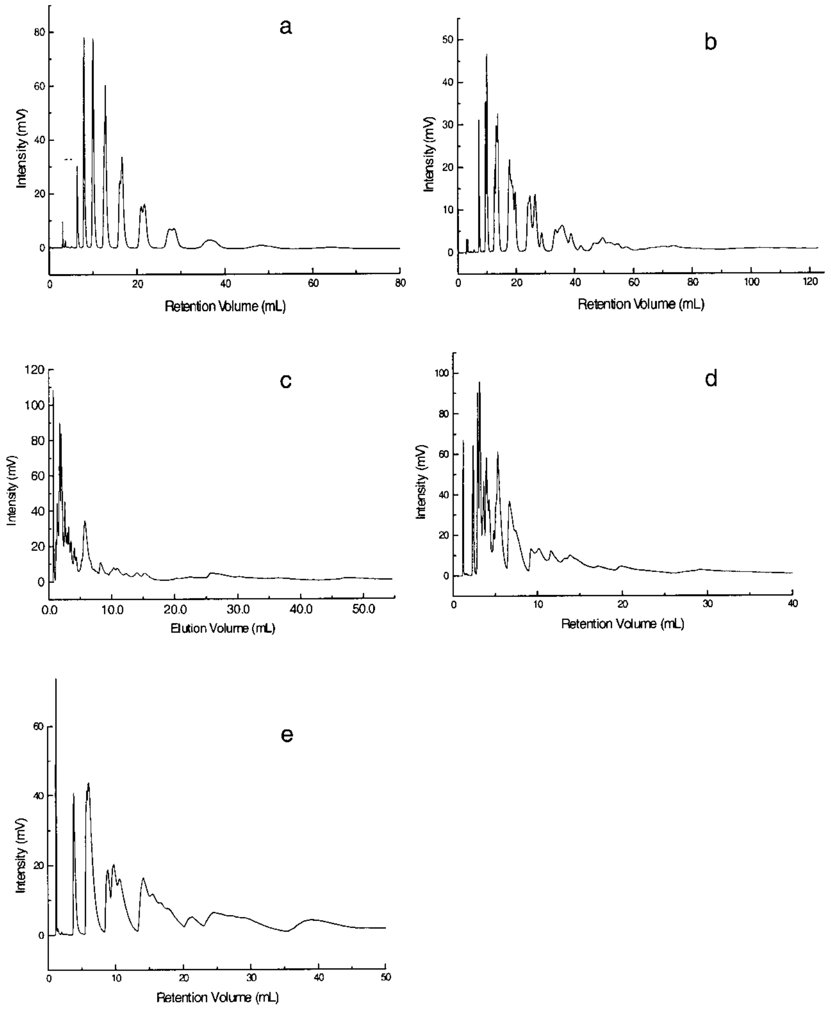

Figure 1. Oligomeric separations of polystyrene ($M_w = 580$ Da) on: (a) a Valupak C18 column (250 × 4.6 mm) with a 100% methanol mobile phase. (b) A Valupak C18 column (250 × 4.6 mm) with a 100% acetonitrile mobile phase. (c) A CCZ column (50 × 4.6 mm) with a 100% acetonitrile mobile phase. (d) A diamond C18 column (100 × 4.6 mm) with a 100% acetonitrile mobile phase. (e) A diamond C18 column (100 × 4.6 mm) with a 100% methanol mobile phase. All flow rates were 1.0 mL/min. Column temperature 20°C. Injection volumes 10 μL.

The chaotic chromatographic elution profile observed on the CCZ column was further evaluated by individually injecting each of the oligomeric components, following fractionation on a C_{18} column with a methanol mobile phase. The chromatogram shown in Fig. 2(a) illustrates a high-resolution separation of the diastereoisomers for an $n = 5$ oligostyrene that was obtained when acetonitrile was employed as the mobile phase. Eight diastereoisomers are visible, which is the expected number of isomers for an oligostyrene of this molecular formula. In comparison, the number of isomers, which had previously been resolved on a C_{18} column did not exceed 4 or 5.[17] When the CCZ mobile phase was changed to methanol, the isomeric separation is shown in Fig. 2(b), which was in complete contrast to the separation on the C_{18} column, where this component eluted as a single peak. Note that for both mobile phases the separations on the CCZ column are strikingly similar, except that the retention in the methanol system is greatly increased. Once again, this is in complete contrast to the behaviour observed for the C_{18} column, where retention decreased (rather than increased) when methanol was employed as the mobile phase and the stereoisomer selectivity also greatly decreased.

When individual oligomeric fractions were injected into the diamond C18 column, the separation and retention was better than found for the C_{18}, but worse than the results for the CCZ column. Using acetonitrile on the CCZ column, the four diastereoisomers for an $n = 4$ oligomer were baseline resolved [Fig. 3(a)], but on the diamond C18 column only two of the diastereoisomers were resolved (at 1/3 peak height criteria) [Fig. 3(b)]. For the $n = 5$ oligomer, only six of the eight diastereoisomers were observed on the diamond C18 column [Fig. 3(c)]. Retention was also reduced on the diamond C18 column, for example, the diastereoisomers of the $n = 5$ oligomer eluted within 18 mL from the diamond C18 column whereas around 80 mL was required for the CCZ column. Changing the mobile phase of the diamond C18 column to methanol resulted in a reduction in the diastereoisomer resolution. The reduction in resolution as the solvent was changed from acetonitrile to methanol was in keeping with the trend observed on the C_{18} stationary phase, however, retention on the diamond C18 column increased when methanol was employed as the mobile phase. The last of the four diastereoisomers eluted with a peak maximum corresponding to 22 mL of methanol. In comparison, elution of the last diastereoisomer from the diamond C18 column with an acetonitrile mobile phase occurred after passage of only 6.5 mL. This trend was in keeping with the behaviour observed on the CCZ column.

No retention of the oligostyrenes was observed on the C_{18} column if a 99% hexane/1% isopropanol mobile phase was employed. This was surprising because hexane is a "poor solvent" for polystyrene. We concluded that in the presence of a C_{18} surface, hexane acts as a good solvent for the low

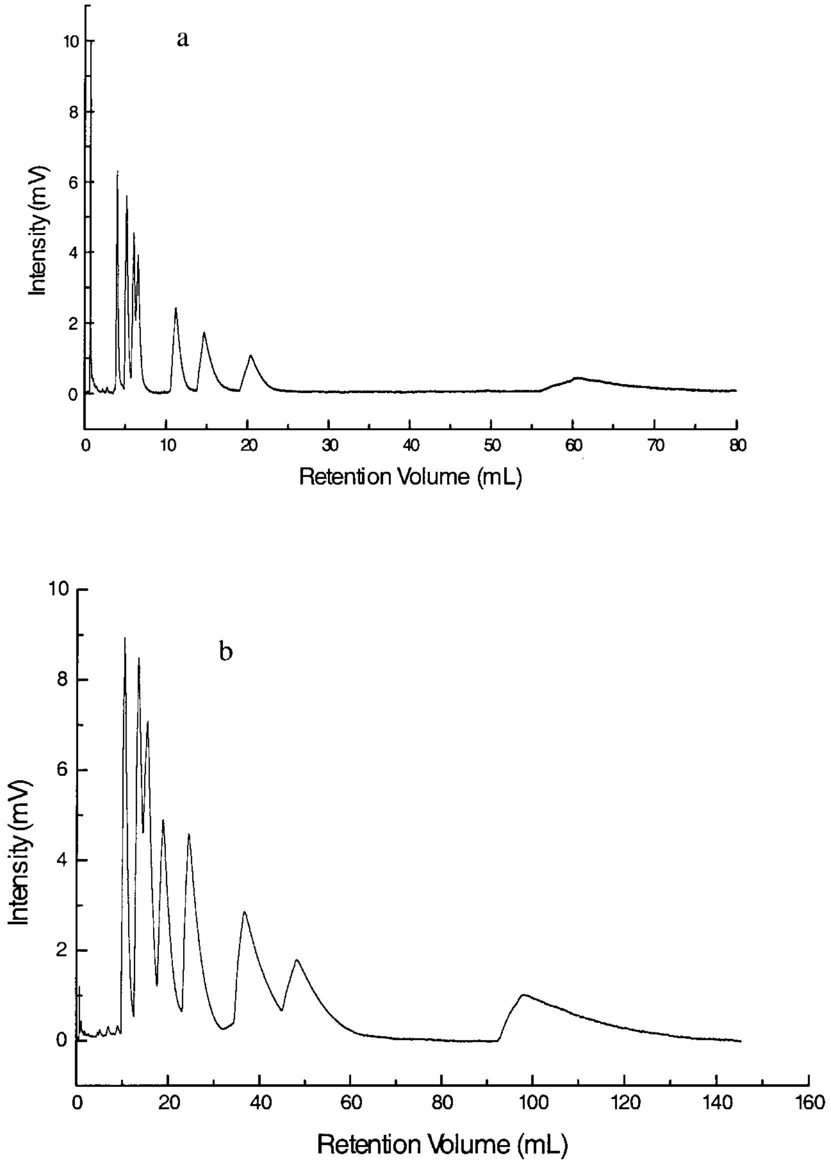

Figure 2. Chromatograms of a $n = 5$ oligostyrene on a CCZ column (50 × 4.6 mm). Flow rate = 1.0 mL/min, column temperature 20°C. Injection volume 20 μL. Mobile phase 100% acetonitrile. Mobile phase 100% methanol.

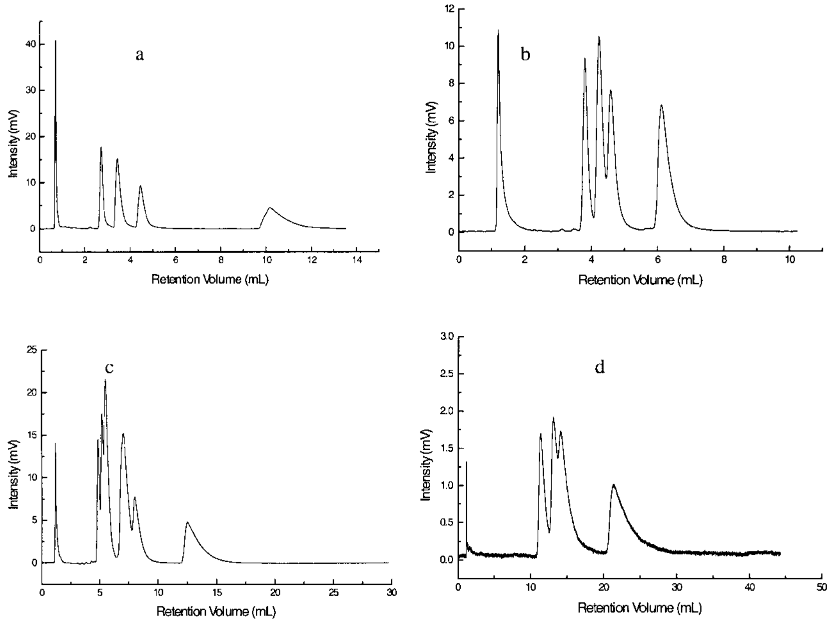

Figure 3. Comparison in the diastereoisomer separations between the CCZ column and the diamond C18 column. (a) Diastereoisomer separation of the $n = 4$ oligostyrene on the CCZ column with a 100% acetonitrile mobile phase. (b) Diastereoisomer separation of the $n = 4$ oligostyrene on the diamond C18 column with a 100% acetonitrile mobile phase. (c) Diastereoisomer separation of the $n = 5$ oligostyrene on the diamond C18 column with a 100% acetonitrile mobile phase. (d) Diastereoisomer separation of the $n = 4$ oligostyrene on the diamond C18 column with a 100% methanol mobile phase. All flow rates were 1.0 mL/min. Column temperatures 20°C. Injection volumes 20 μL.

molecular weight polystyrene oligomers and elution occurs according to the processes of conventional reversed phase systems. In contrast, when the CCZ column was used with the 99% hexane/1% isopropanol mobile phase, stereoisomer selectivity was apparent (see Fig. 4). While the resolution of the stereoisomers was not substantial, and there was virtually no discrimination between isomers of different molecular weights, these separations do illustrate the vast difference in separation behaviour afforded by the CCZ and C_{18} columns. This contrast between the two columns is even more apparent when the stereoisomer separation of the $n = 5$ oligostyrene is observed in a predominantly hexane mobile phase, as shown in Fig. 5. No retention was observed on the C_{18} column, while retention and stereoisomer selectivity was evident on the CCZ column. The diamond C18 column

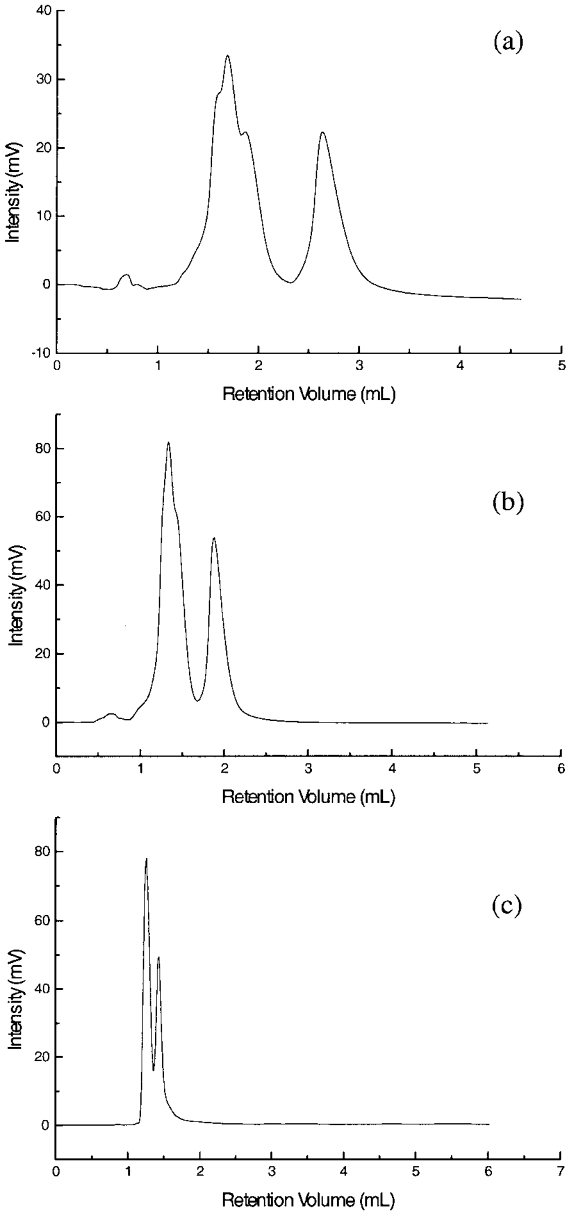

Figure 4. Diastereoisomer separations of oligostyrene $n = 4$ on a CCZ column in an isopropanol/hexane mobile phase. (a) 10% Hexane/90% isopropanol, (b) 20% hexane/80% isopropanol, and (c) 99% hexane/1% isopropanol.

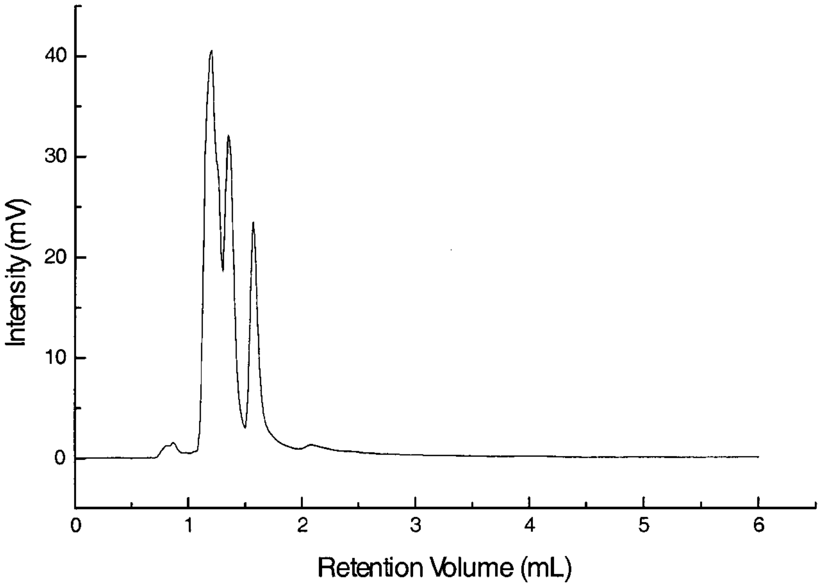

Figure 5. Diastereoisomer separation of oligostyrene $n = 5$ on a CCZ column using 99% hexane/1% isopropanol mobile phase.

yielded retention behaviour that was essentially the same as on the C_{18} column. That is, the oligomers eluted unretained with no stereoisomer resolution.

We have shown in the previous papers, that CCZ is an exceptionally good stationary phase for separation of the stereoisomers of polystyrene oligomers.[16–18] It is sensitive to quite subtle differences in molecular stereochemistry and, thus, has potential for separating other mixtures of isomers, either on its own or as a component of a multidimensional chromatographic system.

This ability of CCZ to separate polystyrene oligomers largely on the basis of their stereochemistry can be contrasted with the more commonly used C_{18} surface, which separates the oligostyrenes principally on the basis of molecular weight. To improve our understanding of the CCZ and to optimise its use in practice, we have carried out a systematic qualitative study of its chromatographic selectivity for different mobile phases, with C_{18} as a comparison. The selectivity of C_{18} for polystyrene oligomers can be reasonably well understood in terms of simple thermodynamic theory and solvent properties, although the results for hexane confirm that for some solvents the balance between the properties of the stationary and mobile phases is important.

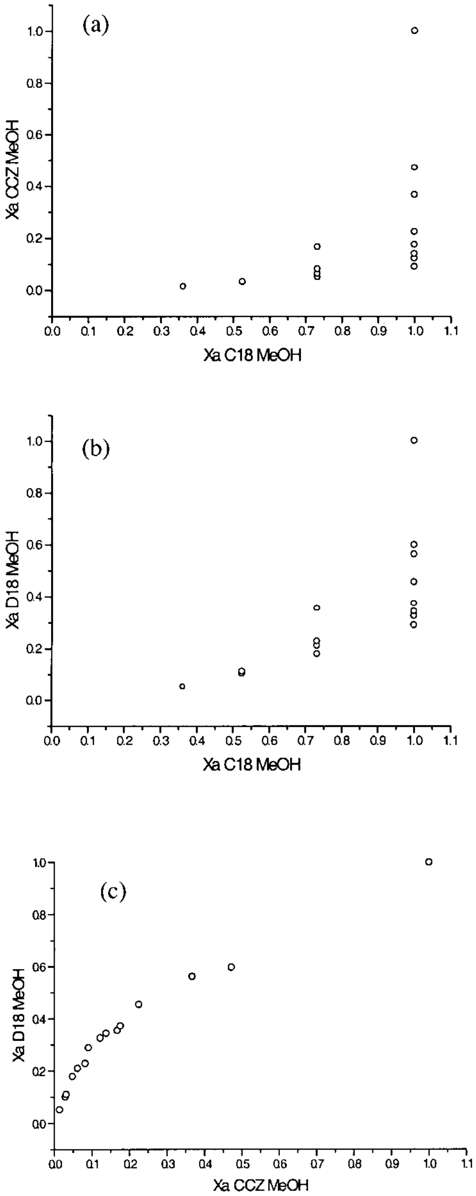

Figure 6. Normalised retention plots illustrating the retention correlation between each of the three different chromatographic columns using methanol as a mobile phase in each column: (a) C_{18} and CCZ columns; (b) C_{18} and diamond C_{18} columns; (c) CCZ and diamond C_{18} columns.

The behaviour of the CCZ surface is also reasonably consistent with these basic principles, except in the case of very good solvents, where the selectivity appears to be dominated by the sensitivity of the surface–solute interactions to the molecular shape of the polystyrene oligomers.

The diamond C18 column, which is a hybrid design of the C_{18} and CCZ columns, yielded retention behaviour that was intermediate between the C_{18} and CCZ surfaces. Reasonably good isomer selectivity was apparent and the separation of these isomers occurred in a more ordered elution process than that observed on the CCZ column—atleast with respect to molecular weight discrimination. The normalised retention plots shown in Fig. 6 offer a means of comparing the relative retention behaviour of each of these three surfaces. The *Xa* factor relates to the scaled or normalised retention data according to the method discussed by Steuer et al.[20] Alignment of the polystyrene retention along a diagonal is an indication that the retention process on each column is highly correlated. When methanol was employed as the mobile phase no isomer resolution was found using the C_{18} column, and there was obviously very little correlation in the retention behaviour between the C_{18} column and the CCZ column [Fig. 6(a)]. Slightly more correlation was apparent between the diamond C18 column and the conventional C_{18} column [Fig. 6(b)]. There was, however, a high degree of correlation in the retention behaviour of the polystyrenes betweenz the CCZ and the diamond C18 columns [Fig. 6(c)]. Even when the mobile phase was changed to acetonitrile on all three columns and some diastereoisomer separation was apparent on the C_{18} column, there was high correlation between the diamond C18 and the CCZ columns, but the retention behaviour between the diamond C18 and CCZ columns were divergent from the retention behaviour observed on the conventional C_{18} column.

One important factor may make the use of the diamond C18 column more attractive for the separation of diastereoisomers than the CCZ column. That is, the elution order on the diamond C18 column was less chaotic than on the CCZ column, multidimensional separations may be feasible in which the component displacement between the dimensions may be more easily defined. It is noteworthy that acetonitrile gave the best isomeric separations on all three columns. Furthermore, the increase in the bandwidth for separations in methanol, [see, for example, Fig. 3(b) and 3(d)] illustrated the importance of solvent optimisation strategies prior to employing these carbon based surfaces.

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