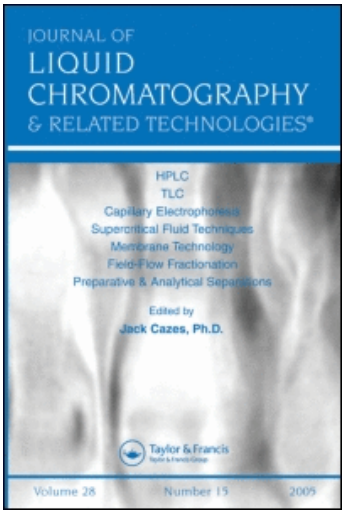

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EVALUATION OF MICRO-HPLC AND VARIOUS STATIONARY PHASES IN REVERSED-PHASE MODE FOR THE SEPARATION OF STYRENE OLIGOMERS

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ABSTRACT

The potential of the micro-HPLC technique and various reversed-phase packing materials for the separation of styrene oligomers is evaluated. The results indicate that longer carbon chains and/or copolymer materials with small-diameter particles are superior to other type packings for the separation of oligomers with methanol as mobile phase. Micro-HPLC promises the possibility of separating conformational isomers of styrene oligomers.

INTRODUCTION

Over the past few years, much effort has been directed toward increasing both selectivity and efficiency in liquid chromatography (LC). The introduction of various types of micro-HPLC columns (1-5) and smaller size packing materials represents a revolution in column technology (6-8).

In light of recent interest in micro-HPLC and small-dimension packing materials, it seems appropriate at this

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time to assess the utility of the new column technology for separation problems in polymer chemistry.

The purpose of this communication is to evaluate their ability for the separation of styrene oligomers, which is one of the typical chromatographic problems in polymer chemistry. The discussion, here, is restricted to an isocratic mode with methanol as mobile phase, using teflon micro columns.

EXPERIMENTAL

All measurements of micro-HPLC separation were made with the MF-2 microfeeder (Azuma Electric, Tokyo, Japan) to control the mobile phase flow. A Jasco (Tokyo, Japan) Uvidec-100 II ultraviolet spectrophotometer was used. Conventional HPLC measurements were made with a system consisting of a Jasco Trirotar III and Uvidec-100 III ultraviolet spectrophotometer.

The column packing materials evaluated here are listed in Table 1, in which carbon chain-length, particle size, column length and commercial name are shown for each. All of the micro columns used were constructed with teflon tubing, 0.5 mm inner diameter, packed with materials listed in Table 1 by a slurry technique. The conventional HPLC column was a 4.6 mm i.d. x 25 cm stainless steel tube packed with FineSIL C18 (Jasco, 10 μm).

The mobile phase was HPLC-grade methanol purchased from Kanto Chemicals (Tokyo, Japan). Flow rates were 8 μl/min for micro-HPLC and 0.5 ml/min for conventional HPLC, respectively.

Table 1

Packing Materials Used in This Work

Column No.	Carbon Chain Length	Particle Diameter	Column Length	Commercial Name
1	C 1	10 μm	162 mm	FineSIL C1
2	C 2	10	220	FineSIL C2
3	C 8	10	193	FineSIL C8
4	C 8	5	175	Develosil C8-5
5	C18	5	185	FineSIL C18-5
6	C18	10	211	FineSIL C18-10
7	C18	10	210	FineSIL C18 T*
8	C18	7	160	Chemcosorb ODS/H-7
9	C18	3	169	Develosil C18-3
10	C18	5	196	Develosil C18-5
11	C18	10	179	Develosil C18-10
12	C18	5	232	SC-01
13	copolymer, styrene-di-vinylbenzene	10	44	HP-01

* trimethylsililated after chemical bonding.

Test solute for column evaluation was styrene oligomers A-500 (purchased from Toyo Soda, Tokyo, Japan) which has an average molecular weight of 500 with a butyl side chain.

RESULTS AND DISCUSSION

The chromatograms obtained under identical chromatographic conditions, with micro-HPLC, are shown in Figures 1-A, 1-B and 1-C. The number of each chromatogram corresponds to that shown in Table 1. The chromatogram recorded with conventional HPLC is shown in Figure 2.

Effect of chain length: Obviously, materials bonded with shorter carbon chains will have smaller capacity factors

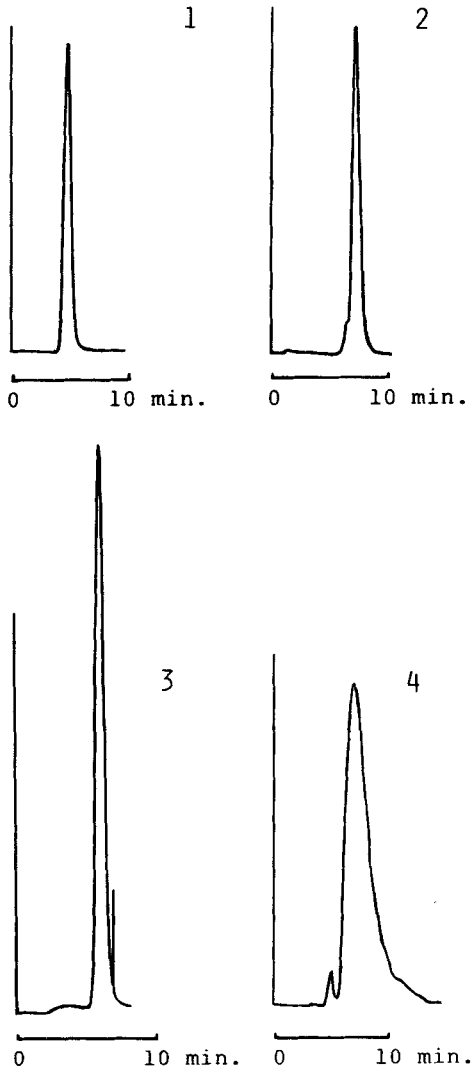

Figure 1 Separation of styrene oligomers with micro-HPLC
A: column No. 1-7 in Table 1.
B: column No. 8-11
C: column No. 12, 13
Chromatographic conditions:
Mobile phase; methanol 100 %
Flow rate; 8 µl/min
Sample injection; 0.3 µl
Column temperature; 25 °C
Detection; UV 207 nm
(n=2 means dimer).

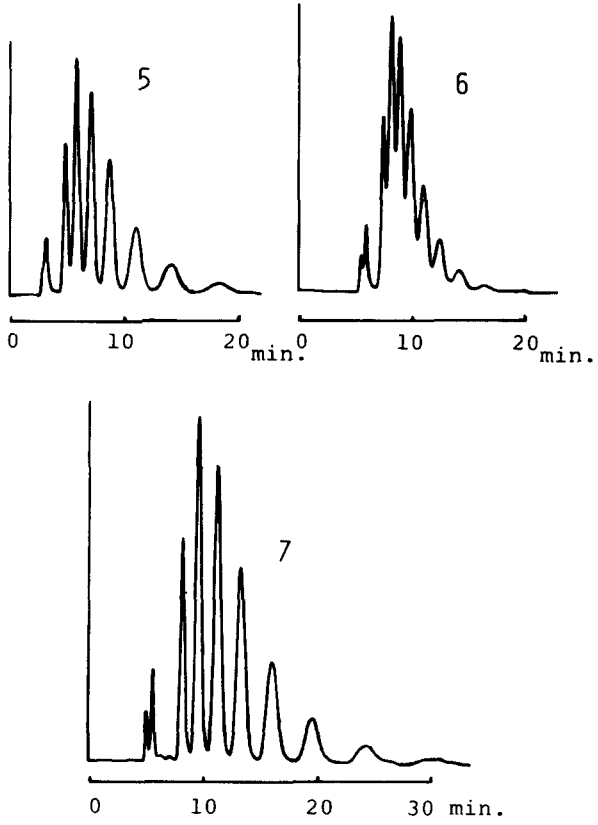

Figure 1 - continued

than those with longer carbon chains when used with the same mobile phase. However, in this instance, the retention times of oligomers with C2, C8 and C18 columns (No. 2, 3, 6 and 7 in Figure 1, all materials have the same particle diameter) are almost the same; this means that longer carbon-chain columns are more likely to resolve styrene oligomers. From the chromatograms shown in Figure 1, it is apparent that the separations with C1, C2 and C8 packings (group-1) are poor, whereas those with C18 and copolymer (group-2) are good.

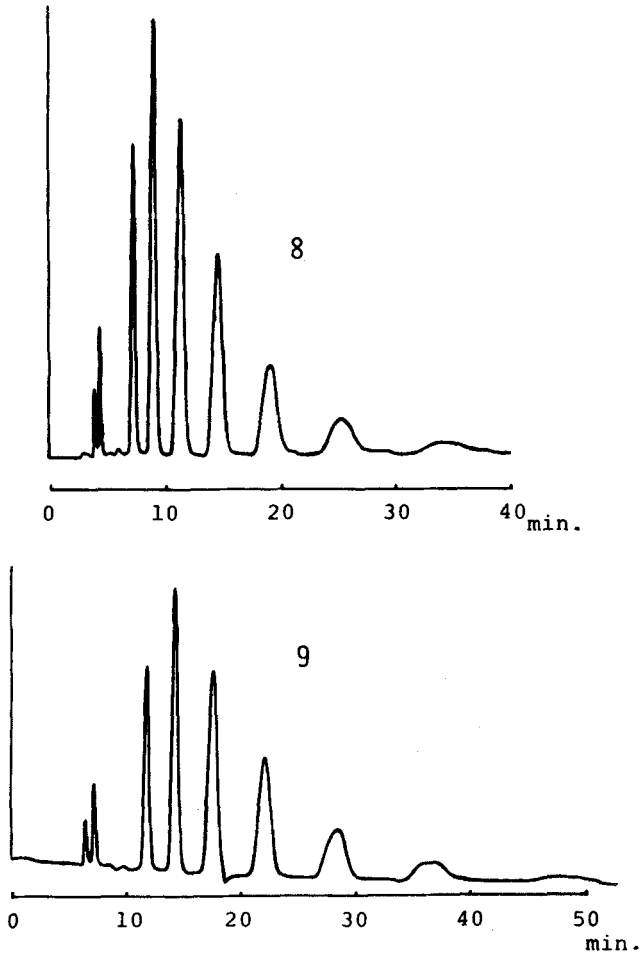

Figure 1 - continued

There have been a number of discussions concerning the retention mechanism in reversed-phase separation (9-24). Despite the popularity and wide applicability of reversed-phase separations, a complete description of the retention mechanism for bonded phases has not yet been formulated. However, it is well known that a major factor in determining

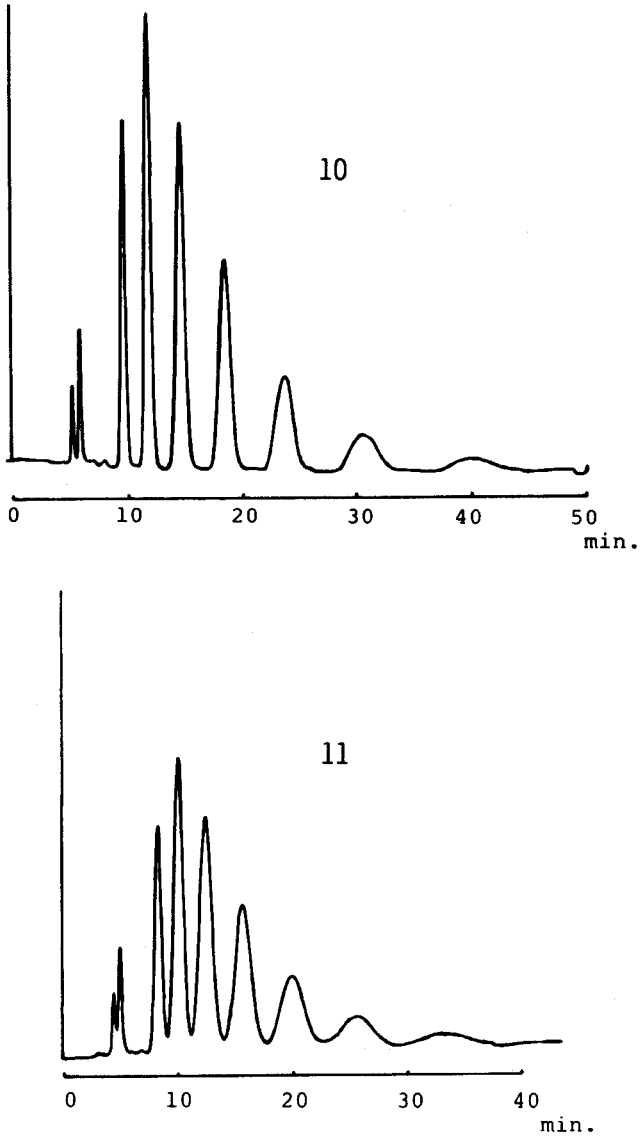

Figure 1 - continued

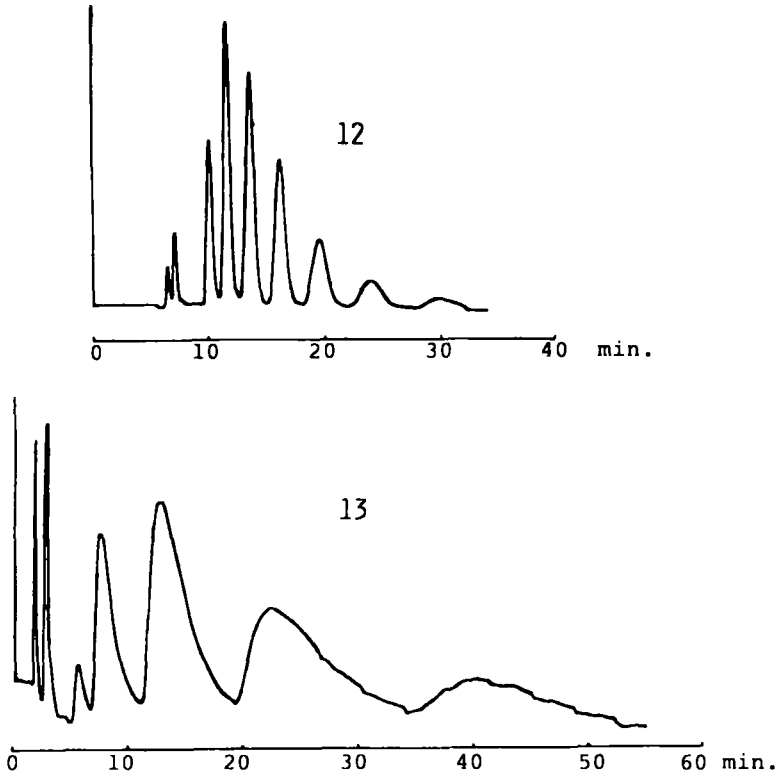

Figure 1 - continued

the selectivity of reversed-phase LC is the degree of aqueous character of the mobile phase; solute distribution has been modeled by invoking a solvophobic interaction (24-26).

In our previous paper (27), it was reported that the interactions between solute and stationary phases such as C2, C8 and C18 are similar to each other with mixtures of acetonitrile and water as mobile phases. However, it seems, in this instance, that some differences are present in retention mechanism between the stationary phases of group-1 and -2.

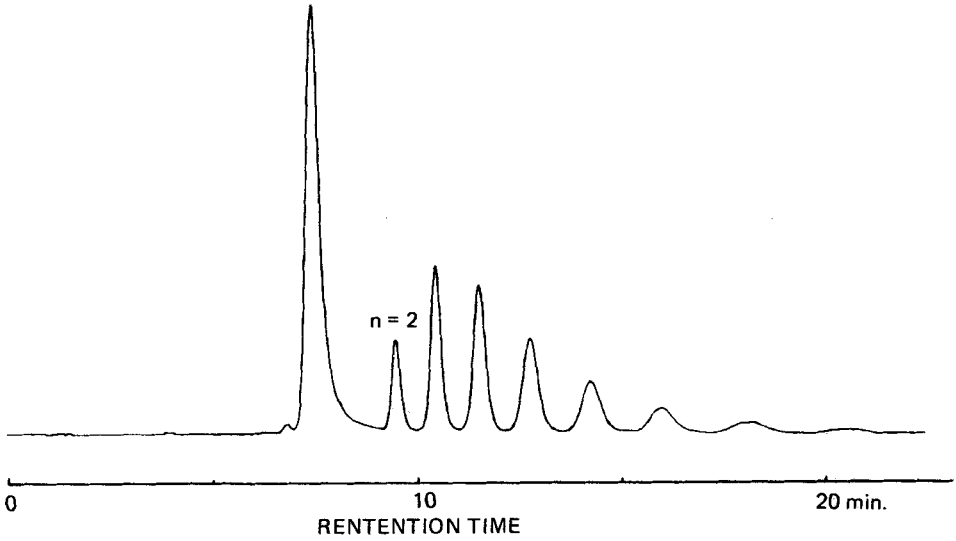

Figure 2 Separation of styrene oligomers with conventional HPLC
Chromatographic conditions:
Column; 4.6 mm i.d. x 25 cm, FineSIL C18
Mobile phase; methanol 100 %
Flow rate; 0.5 ml/min
Sample injection; 1 µl
Column temperature; 30 °C
Detection; UV 207 nm

Tanaka et.al. (28) have investigated the effect of the structure of the stationary phase on retention and selectivity in reversed-phase LC using chemically bonded stationary phases on silica gels. Their conclusions are as follows; in addition to the solvophobic interaction and the solvation of the solutes in the mobile phase, effects such as steric recognition and $\pi - \pi$ interaction between solute and the stationary phase were found to be important in determining retention in a reversed-phase system. Extended, longer carbon groups and large aromatic rings in the stationary phase contribute to the preferential retention of more planar solutes.

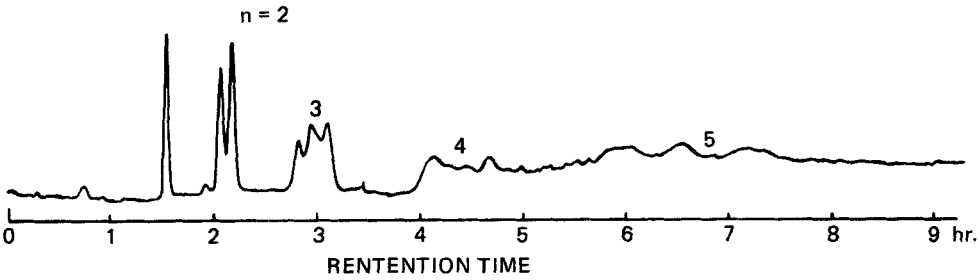

Figure 3 Separation of styrene oligomers with best optimized micro-HPLC
Chromatographic conditions:
Column; connected two columns of No. 8 and 10.
Mobile phase; acetonitrile 100 %
Flow rate; 2 ul/min
Sample injection; 0.1 µl
Column temperature; 25°C
Detection; UV 207 nm

The results we report exhibited a similar mechanism to that described above. The stationary phases with the longer carbon-chain (C18) and the aromatic rings (copolymer) can retain styrene oligomers more than those with shorter carbon chains. This means that there exists an effect of molecular shape and size to their retention.

The differences of separation ability between the stationary phases with the same carbon chain length might be caused from their other characteristics, e.g., internal porosity, specific surface area, treatments for chemical bonding, etc., which have not been determined for the materials investigated here.

Effect of particle size: The effect of particle size is seen in the results. Calculated k' values (capacity factor) for each oligomer are tabulated in Table 2 for Column No. 9, 10 and 11. The k' values are almost consistent each

Table 2

Logarithm of Capacity Factor (k') for Styrene Oligomers.

Column No.	Particle Diameter	log k' n=2	n=3	n=4	n=5	n=6
9	3 um	-0.198	-0.012	0.158	0.328	0.468
10	5	-0.215	-0.015	0.156	0.314	0.464
11	10	-0.194	-0.004	0.164	0.318	0.467

other for these columns. It is apparent that the decrease of particle diameter improves the resolution but does not change the retention. Smaller particles need more analysis time in some instances, although it is realized that the analysis time generally decreases in proportion to the square of particle diameter (29).

Performance of micro-HPLC: Micro-HPLC promises great improvements in selecting chromatographic conditions due to its advantageous features: smaller flow rates (in the order of microliters per minute), smaller required sample quantity (less than one microliter), and easier procedures for preparation of columns.

In order to evaluate the potential of micro-HPLC, a comparison of the chromatograms obtained with a conventional HPLC column and the micro-HPLC columns was examined.

It is clear, from No. 7 in Figure 1-A and Figure 2, that the resolution of the conventional column is not higher than those of the micro columns, and that there are no disadvantages in performance caused by column miniaturization.

It is concluded that micro-HPLC offers high potential for separations in polymer chemistry because of the above

features. Also, this technique drastically reduces system and running costs.

Figure 3 shows an optimized chromatogram for styrene oligomers by micro-HPLC in which conformational isomers of each oligomer can be resolved. Recent developments in micro-column technology in capillary LC (30-32) will bring higher resolution separations of isomers with shorter analysis times.

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