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## SOLVENT SELECTIVITY STUDIES USING ISOMERS OF POLYSTYRENE

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### SUMMARY

The order of elution of isomeric trimers of polystyrene has been found to be independent of the dominant solvent-solute interaction as indicated by the location of the solvent in a Snyder triangle. The pure solvents were nitromethane, propylene carbonate, N-methylformamide, acetonitrile, the mixtures were trifluoroethanol with chloroform, methylene chloride and trichlorotrifluoroethane and also one of 2-methoxyethanol with water. Likewise, mixtures of acetonitrile with solvents near each of the corners of that triangle (chloroform, methylene chloride, and trifluoroethanol did not change the order of isomer elution). Substitution of trifluoroethanol for ethanol in mixtures with chloroform, methylene chloride, or trichlorotrifluoroethane led to improved isomer fractionations.

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### INTRODUCTION

The Snyder triangle<sup>1</sup> is a classification scheme for solvents used in reversed-phase liquid chromatography that classifies them according to three dominant interactions: polarity, hydrogen donating ability, and hydrogen accepting ability. It has been used very successfully by many investigators in liquid chromatography. When Lewis *et al.*<sup>2</sup> examined the separations of isomers of small polystyrene *n*-mers, solvents in different regions of the triangle were observed to lead to fractionation. Hence, there was the possibility that the order of elution of isomers was different, depending upon the dominant type of interaction with the solvent. The present study has examined that question. There was the possibility of identifying the order of elution of isomers in different solvents using NMR spectroscopy of isolated fractions. However, the decision was made to base the identification upon retention times of known isomers when compared to those peaks found in a sample of MW 800 polystyrene that contained a mixture of oligomers. The identifications could be done either in separate runs or by the addition of one isomer to a regular polystyrene sample and noting which peak was affected. Chromatographic method of identification had the advantage that it did not require as high a purity of individual isomers as the NMR approach and, therefore, permitted badly overlapped peaks to be readily identified.

An additional goal of the present study was to examine the solvents strengths of two fluorinated species, trifluoroethanol and trichlorotrifluoroethane. In the first

case, trifluoroethanol was compared with ethanol while in the second case the halogenated ethane was compared with chloroform and with methylene chloride.

## EXPERIMENTAL

### *Chemicals*

All solvents were used as received unless otherwise noted. Acetonitrile, chloroform, methanol, methylene chloride, nitromethane, and toluene were either "pho-trex" or reagent grade (J. T. Baker, Phillipsburg, PA, U.S.A.). Propylene carbonate, N-methylformamide, and 2-methoxyethanol were purchased from Aldrich (Milwaukee, WI, U.S.A.). 2,2,2-Trifluoroethanol was obtained from PCR (Gainesville, FL, U.S.A.). Absolute ethanol was purchased from U.S. Industrial Chemicals (New York, NY, U.S.A.). 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon) was purchased from DuPont (Wilmington, DE, U.S.A.). House distilled water was passed through a deionizing system and a Corning Mega-Pure 1-1 still (Corning Glass Works, Corning, NY, U.S.A.) before collection in glass bottles. All solvents were degassed with helium before use.

Monodisperse MW 800 polystyrene was purchased from Pressure Chemical (Pittsburgh, PA, U.S.A.). A C<sub>18</sub> column (IBM Instruments, Yalesville, CT, U.S.A.) (25 cm × 4.6 mm I.D.) packed with spherical, 5- $\mu$ m particles having an average pore size of 100 Å, was used as received.

### *Apparatus*

The chromatographic system consisted of two Varian Model 8500 pumps (Palo Alto, CA, U.S.A.), a Model ACV-6UHPa injection valve (Valco Instruments, Houston, TX, U.S.A.), a Beckman Model 155 variable-wavelength detector (Fullerton, CA, U.S.A.) and a Linear Model 585 (Reno, NV, U.S.A.) chart recorder.

An RI detector from LDC, Model 1107 (Riviera Beach, FL, U.S.A.), together with an Altex Model 110A solvent metering pump (Berkeley, CA, U.S.A.) and an air-actuated six-port valve, Model ACV-6UHPa (Valco Instruments, Houston, CA, U.S.A.) having a 10- $\mu$ l loop, was used to perform the separations in which the mobile phases absorbed strongly at 254 nm.

### *Procedure*

An amount of 2 g of monodisperse MW 800 polystyrene standard sample (Pressure Chemical, Pittsburgh, PA, U.S.A.) were dissolved in a minimum amount of *n*-hexane. This solution was then applied to a low pressure column containing approximately 200 ml of silica gel (J. T. Baker, Phillipsburg, NJ, U.S.A.). The silica column was eluted successively with 10% toluene in hexane (which contained impurities plus the monomer), 20% (*n*-mers 2 through 5), 40% (*n*-mers 5 through 8) and 60% (to clean the column). The toluene-hexane (20:80) fraction contained oligomers up to the pentamer. The solvent was removed by fractional distillation, and the polystyrene was redissolved in pure acetonitrile. This sample was then used for all of the following experiments without further modification.

Trimer fractionation was performed by injecting the above sample into a Vydac semi-prep C<sub>18</sub> column (25 cm × 10 mm I.D., 10  $\mu$ m particle size), (Separations Group, Hesperia, CA, U.S.A.) using pure acetonitrile as eluent. The collected frac-

tions were analyzed by  $^{13}\text{C}$  NMR for stereoisomer identification. Those fractions were later reinjected into different mobile phases to confirm the elution order. Sample injections of 10  $\mu\text{l}$  were made when the baseline stabilized. The mobile phase flow-rate was held at 0.8 ml/min for all separations. The capacity factor,  $k'$ , was calculated by the following equation:

$$k' = \frac{t_{\text{R}} - t_0}{t_0}$$

where  $t_{\text{R}}$  is the retention time of interested component and  $t_0$  is the value for an unretained peak. The value of  $t_0$  was obtained from the solvent peak as done in the previous paper<sup>2</sup>.

## RESULTS AND DISCUSSION

### *Solvent studies*

Chloroform, water and trifluoroethanol are classified in the same group (Group VIII) in the Snyder triangle diagram<sup>3</sup>, but they give quite different results in separations of polystyrene. Chloroform acted like a strong solvent and eluted all of the isomers together, without separation. In contrast, no peak was eluted in 20 min when water or trifluoroethanol was used as the mobile phase. Both acted as weak solvents. These and other results are reported in Table I. Clearly, the location of a solvent in the Snyder triangle diagram does not have a simple relation to its ability for isomer separation.

Methylene chloride (Group V) and 1,1,2-trichloro-1,2,2-trifluoroethane, like chloroform, did not produce isomer separation of polystyrene on the  $\text{C}_{18}$  column, as a result of being strong solvents for the polystyrene. However, when a small percentage of one of these solvents was mixed with trifluoroethanol, isomer fractionation as well as oligomer separation was observed (Table I, Fig. 1).

Note that only oligomer separation was observed when the mobile phase was pure ethanol. The presence of 5% chloroform only slightly shortened the retention times of the oligomers whereas 20% chloroform eluted all of the polystyrene oligomers together in a yet shorter time. These data indicated that chloroform was a stronger solvent than ethanol. However, ethanol was stronger than 2,2,2-trifluoroethanol, because when using the trifluoroethanol, no peak eluted in 20 min after polystyrene had been injected into the column.

### *Elution order of trimers*

In the polystyrene study of Lewis *et al.*<sup>2</sup>, the dominant solvent interaction in the fractionations of the isomers appeared to be different with the result that the elution order might also differ with the solvent. Hence, the order of elution of isomers was determined by reinjecting separately the two isolated fractions of the isomers of the trimer and comparing their retention times with those for peaks in a mixture. The data in Table II clearly show that the elution order was not affected by these different mobile phases.

Another set of experiments was based upon acetonitrile which has been found to be a good mobile phase for separations of polystyrene isomers on a  $\text{C}_{18}$  column.

TABLE I  
 FRACTIONATIONS OF OLIGOMERS AND ISOMERS USING ELUENTS CONTAINING 2,2,2-TRIFLUOROETHANOL OR ETHANOL

Solvent composition	Retention time (min)			Comments
	n = 2	n = 3	n = 4	
Ethanol (100%)	4.4	4.6	4.7	Oligomer separation; some isomer separation
Ethanol-acetonitrile (95:5)	4.3	4.5	4.6	Poor oligomer separation*
Ethanol-acetonitrile (80:20)		(4.1)**		No separation
Ethanol-methylene chloride (95:5)	4.3	4.4	4.6	Poor oligomer separation**
Ethanol-methylene chloride (80:20)		(4.1)**		No separation
2,2,2-Trifluoroethanol-acetonitrile (80:20)	7.5	10.1, 10.4	13.7	Isomer separation
2,2,2-Trifluoroethanol-methylene chloride (80:20)	6.8	8.8, 9.2	11.4	Isomer separation
2,2,2-Trifluoroethanol-Freon (80:20)	7.6	9.7, 10.2	-***	Isomer separation

\* Not baseline separation of oligomers.

\*\* All polystyrene oligomers came out together.

\*\*\* Flushed out without being measured.

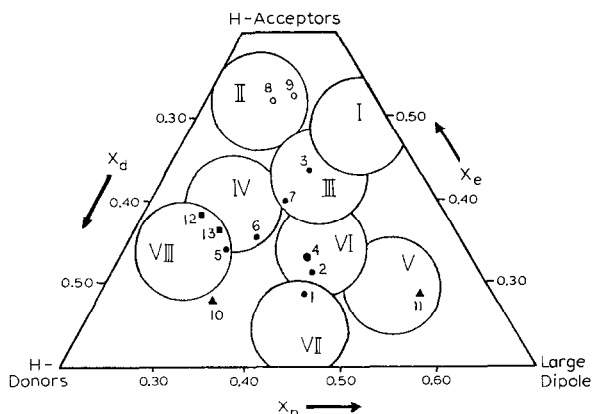


Fig. 1. Snyder selectivity triangle for the solvents studied. The numbers correspond to: 1, nitromethane; 2, propylene carbonate; 3, N-methylformamide; 4, acetonitrile; 5, 2,2,2-trifluoroethanol-chloroform (80:20); 6, 2,2,2-trifluoroethanol-methylene chloride (80:20); 7, 2-methoxyethanol-water (90:10); 8, ethanol; 9, methanol; 10, chloroform; 11, methylene chloride; 12, water; 13, 2,2,2-trifluoroethanol. The symbols correspond to different degrees of polystyrene separation: (●), isomer separation; (○), oligomer separation (partial isomer separation); (▲), no fractionation of oligomers; (■), solutes retained more than 20 min.

It is classified as Group VI, in the central part of Snyder selectivity triangle diagram. Hence, acetonitrile was mixed with a solvent located near each corner of the Snyder selectivity triangle diagram. Methanol, water and methylene chloride were chosen as H-acceptor, H-donor and large dipole solvents respectively.

When acetonitrile was mixed with water, isomer separation of polystyrene was obtained. The retention time of each isomer was longer than that in pure acetonitrile. As the concentration of water went up to 20% (v/v), the resolution became worse than in pure acetonitrile. It seems that water acted only as a weak solvent, but did not contribute to the selectivity. This confirms the report of Lewis *et al.*<sup>2</sup>

When methylene chloride was added at 3, 5 and 10% (v/v) in acetonitrile, the retention times of the first trimer isomer were 6.8, 6.5 and 5.6 min, respectively. As the retention time became shorter, the resolution became worse as can be seen in Fig. 3.

Methanol was chosen as the H-acceptor phase mixed with acetonitrile. Methanol alone gave only a partial separation of isomers that could best be detected in the large oligomers. Fig. 4 shows that as the concentration of acetonitrile increased, the isomer separation improved. Acetonitrile itself gave much better resolution of the isomers.

2,2,2-Trifluoroethanol, like water, is classified in Group VIII of the Snyder selectivity triangle<sup>3</sup>. As the concentration of trifluoroethanol increased from 0% (v/v) to 40% (v/v) in acetonitrile, the retention time was increased. However, the resolution got noticeably worse at the 5% level and then remained about the same up to 40% (Fig. 5).

Finally, it was interesting to find that 15% (v/v) trichlorotrifluoroethane in acetonitrile also gave shorter retention times and only partial isomer separations.

TABLE II  
ELUTION ORDER OF TRIMERS\*

Solvents	Group	Capacity factors of trimers**		Capacity factors of trimers***		Detector type
		$k'(I)$	$k'(II)$	$k'(I)$	$k'(II)$	
Propylene carbonate	VI	2.99	3.33	2.96	3.33	RI
Nitromethane	VII	3.80	4.11	3.80	4.11	RI
2,2,2-Trifluoroethanol-acetonitrile (80:20)	VIII/VIII	3.39	2.62	3.39	2.62	UV
2,2,2-Trifluoroethanol-methylene chloride (80:20)	VIII/V	1.30	1.39	1.30	1.37	UV
2,2,2-Trifluoroethanol-Freon (80:20)	-§	1.53	1.66	1.53	1.66	UV
2-Methoxyethanol-water (90:10)	III/VIII	4.35	4.56	4.35	4.56	RI
N-Methylformamide	III	2.29	2.39	2.29	2.37	RI

\* The capacity factors were averaged values of three injections.

\*\* Polystyrene MW 800 sample.

\*\*\* Samples of the individual isomers.

§ Not defined.

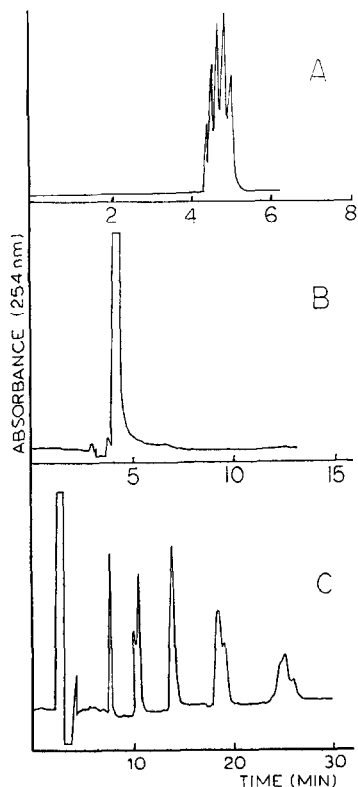


Fig. 2. Chromatograms of MW 800 polystyrene (up to end-mer 6) separation on (A) 100% ethanol, (B) ethanol-chloroform (80:20), (C) 2,2,2-trifluoroethanol-chloroform (80:20).

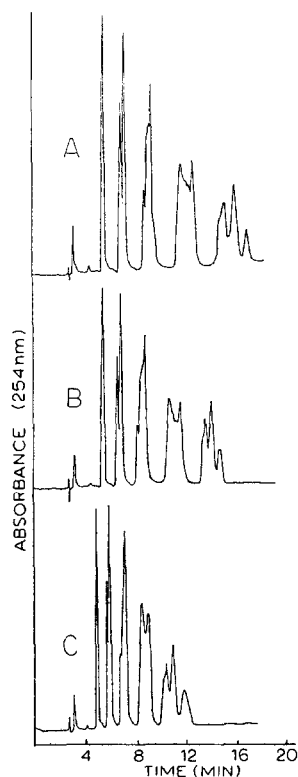


Fig. 3. The effect of methylene chloride concentration in polystyrene separation. The mobile phase compositions are: (A) methylene chloride-acetonitrile (3:97), (B) 5:95, (C) 10:90.

However, as shown in Table I, a mixed solvent of these two fluorinated mobile phase, trifluoroethanol-Freon (80:20), gave very good isomer fractionations even though, when alone with acetonitrile, each degraded the fractionation.

## CONCLUSIONS

All of the pure solvents examined in this study produced the same order of isomers of *n*-mer 3. Similarly, mixing acetonitrile with solvents that exhibited different types of primary interactions with the solutes failed to change the elution order of the trimers. This suggested that a change in the type of dominant interaction, as indicated by the position of each solvent in the Snyder diagram, was not the controlling factor or that the interaction with acetonitrile was much stronger than the others.

Weaker solvents, when added to acetonitrile, which itself gave good isomer resolution, only lengthened the retention times; the resolutions were not improved. Mixing a weaker solvent, trifluoroethanol, or a stronger solvent, methylene chloride,

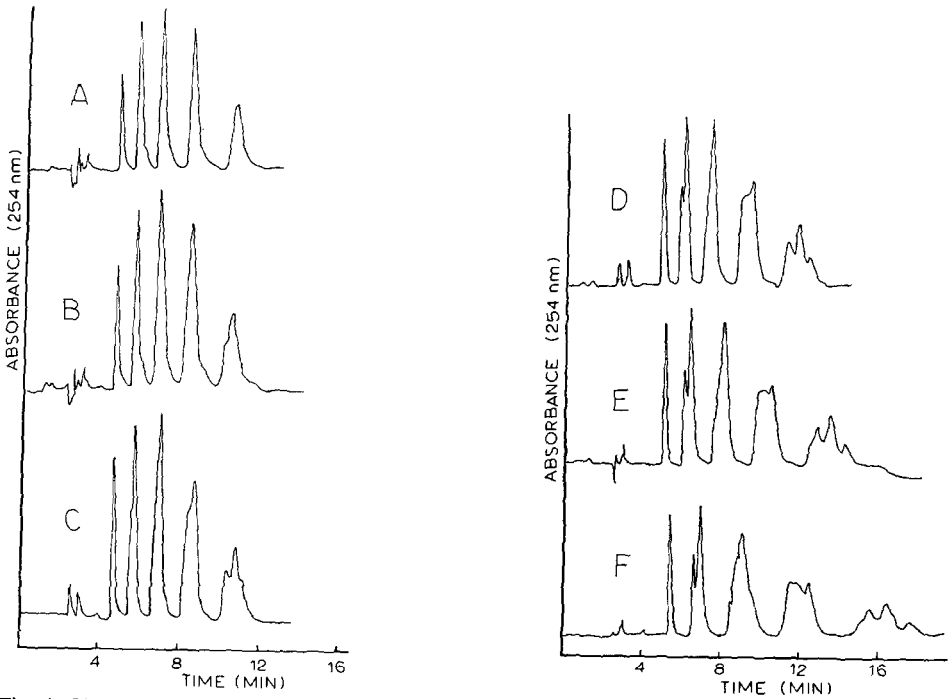


Fig. 4. Chromatograms of polystyrene fractionation for different composition ratios of methanol and acetonitrile. (A) 100% methanol, (B) methanol-acetonitrile (80:20), (C) 60:40, (D) 40:60, (E) 20:80, (F) 100% acetonitrile.

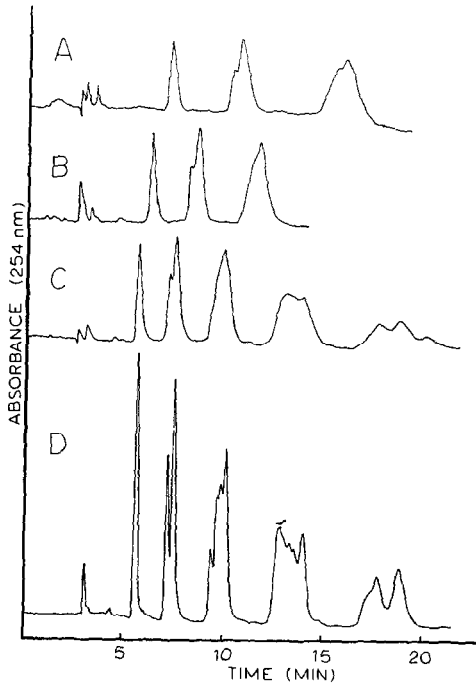


Fig. 5. The effect of 2,2,2-trifluoroethanol on separations of polystyrene isomers using mixtures of acetonitrile and 2,2,2-trifluoroethanol. The composition ratios of acetonitrile and 2,2,2-trifluoroethanol are: (A) 60:40, (B) 80:20, (C) 95:5 and (D) 100% acetonitrile.



with acetonitrile did not improve the resolution over that obtained using pure acetonitrile. However, in mixtures of ethanol with chloroform or methylene chloride substitution of a weaker solvent, trifluoroethanol, improved resolution. Hence, the question of the dominant interaction is complex.

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