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RETENTION CHARACTERISTICS OF VARIOUS POLYMERS IN THERMAL FIELD-FLOW FRACTIONATION

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SUMMARY

The synthetic polymers, polystyrene, polyisoprene, polytetrahydrofuran, and polymethylmethacrylate, in the molecular-weight range from 7600 to 270,000, were successfully retained in a thermal field-flow fractionation (FFF) system. Two solvents, tetrahydrofuran and ethyl acetate, were employed. Retention and selectivity levels were found to be comparable between polystyrene and the other polymers.

The present results are the first to show decisively that thermal FFF is applicable to polymers other than polystyrene. Consequently, we consider the scope of thermal FFF in polymer analysis to be considerably enlarged by the present work.

INTRODUCTION

Field-flow fractionation (FFF) is an analytical separation method which has been proposed for the analysis and characterization of a wide range of polymeric and particulate systems¹⁻³. Our investigations have shown that FFF is applicable to a wide range of chemical structures and types, and we have demonstrated¹ applicability to species having effective molecular weights in the range from 10^3 to 10^{16} .

FFF is a chromatographic-like method in which solute retention is achieved by the application of a field or gradient across a narrow flow channel^{4,5}. Part of the versatility of FFF stems from the possibility of using different fields to retain particular chemical species. For example, an electrical field could clearly be used for the retention of any charged particles⁶. The separation of synthetic nonpolar polymers, on the other hand, cannot be achieved by electrical FFF, but several other subtechniques (each with a specific field) are capable of dealing with such polymers. Among these other subtechniques are thermal FFF⁷, sedimentation FFF⁸, and flow FFF⁹. The problems, prospects, and limits of the application of these various subtechniques to polymers have been outlined in some detail³.

The experimental realization of polymer fractionation by FFF has been limited largely to thermal FFF. Furthermore, most of the work has involved the

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application of thermal FFF to linear polystyrene polymers in ethylbenzene solvent, although a few other solvents have been briefly employed to demonstrate retention¹⁰. Although the results with polystyrene show excellent retention, resolution, range, and speed, this single polymer by itself does not justify a wide interest in polymer analysis by thermal FFF. Consequently, we have wanted for some time to examine the applicability of thermal FFF to other types of polymers. Our preliminary investigations of this matter have been hampered by limited solubility, high sample polydispersity, and detection problems³. Retention was indicated but not confirmed. Consequently, until this time there has been no proof of the retention and thus of the applicability of thermal FFF to polymers other than polystyrene.

In the present study, we have been able to employ improved polymer samples (decreased polydispersity) from various sources to demonstrate the clear retention of polyisoprene, polytetrahydrofuran, and polymethylmethacrylate in a thermal FFF system using tetrahydrofuran and in some cases ethyl acetate for a solvent. The molecular weight of the retained polymers ranged from 15,000 to 270,000. Polystyrene was retained in the same system for reference. The object of this paper is to report the results of this expansion in the scope of thermal FFF in polymer analysis.

THEORY

The theory of polymer retention in FFF has been adequately described and need not be repeated here^{1,5}. We will note only a few of the crucial equations and definitions needed to present and interpret our results. We will ignore the corrections that arise because of the change in viscosity and heat conductivity across the thickness of the channel^{10,11}. These corrections tend to be small in the case of small temperature increments like those used here (34°) and are not justified in the interpretation of the present data.

We note first of all that the theoretical parameter of greatest importance in FFF is the reduced thickness of the solute layer λ found compressed against the wall by the field

$$\lambda = D/Uw \quad (1)$$

where D is the diffusion coefficient for the polymer-solvent system, U is the mean velocity of the polymer molecules induced by the field, and w is the channel thickness (the distance between hot and cold walls). In the case of thermal FFF, this equation can be approximated by¹

$$\lambda = \frac{T_c}{\alpha \Delta T} \quad (2)$$

where ΔT is the difference between hot wall temperature T_H and cold wall temperature T_c , and α is the thermal diffusion factor—the underlying physicochemical parameter controlling retention and separation.

Parameter λ governs retention in FFF systems. The governing equation is

$$R = 6\lambda[\coth(1/2\lambda) - 2\lambda] \quad (3)$$

where R is the retention ratio, a quantity equal to the ratio of the elution volume (or time) of an unretained peak to the elution volume (or time) of the peak of interest. For small λ values, R approaches the limit $R = 6\lambda$.

The usefulness of a separation technique like thermal FFF or size exclusion chromatography in the characterization of polymers depends upon the ability of the technique to cleanly separate polymer molecules of a given molecular weight from those of a somewhat different molecular weight. The efficacy of this process is defined by the *selectivity*¹²

$$S = | d \ln V_r / d \ln M | = | d \ln t_r / d \ln M | \quad (4)$$

where V_r is the solute retention volume, t_r is the retention time, and M is the molecular weight of the solute. The value of S in size exclusion chromatography generally lies in the range 0.03–0.22 (ref. 12). The application of thermal FFF to linear polystyrenes yields a higher S with a maximum value in the range 0.5–0.6. This maximum value can be obtained from the equation¹²

$$S_{\max.} = | d \log \lambda / d \log M | \quad (5)$$

One object of this paper is to obtain some preliminary $S_{\max.}$ values for polymers other than polystyrene to see if selectivity (as well as retention) is of the same approximate magnitude as it is for polystyrene. To this end, eqn. 5 can be employed by obtaining experimental R values for polymers of several molecular weights and using eqn. 3 to obtain a corresponding value. The results will be shown in a later section.

EXPERIMENTAL

The "hairpin" thermal FFF column used for all measurements in this study has been described in detail in a previous paper¹³. The Mylar spacer determining the thickness (width) w of the channel was 0.127 mm thick. The temperature drop across the channel was kept at 34°, with the temperature of the cold wall maintained at 26°. These temperatures were chosen in order to keep the hot wall temperature below the boiling point of the solvents used at normal atmospheric pressure. This avoids the necessity of using more sophisticated experimental arrangements which involve working at elevated pressures and high hot wall temperatures¹⁴.

The solutions of polymer samples were injected by means of an 8-port injection valve (Carle Instruments, Fullerton, Calif., U.S.A.) with two loops of volumes 5 and 7 μ l. This injection system, normally used in liquid chromatography, is very convenient for our purposes. It provides a high reproducibility of injected volumes and it is also flexible for automation.

A differential refractometer R401 (Waters Assoc., Milford, Mass., U.S.A.) was used as a detector.

A constant flow-rate pump (Chromatronix CMP IV, Laboratory Data Control, Riviera Beach, Fla., U.S.A.) was used to deliver the solvents. The volumetric flow-rate was 3.36 ml/h in all cases, which corresponds to a mean linear velocity within the channel of $\langle v \rangle = 0.073$ cm/sec. Since the results of the previous study¹⁵ using the

same thermal FFF channel indicated relatively unimportant relaxation phenomena, we did not stop the flow for relaxation after the injection.

Two solvents were used in this investigation: reagent-grade tetrahydrofuran (THF) (Fisher Scientific, Fairlawn, N.J., U.S.A.), and reagent-grade ethyl acetate (EtAc) (Matheson, Norwood, Ohio, U.S.A.). The use of THF has the advantage of good solubility for many synthetic organophilic polymers. On the other hand EtAc has a slightly higher boiling point than THF, which allows one to increase the hot wall temperature for more efficient separation if necessary, especially for low-molecular-weight polymers. Another advantage of EtAc is its relatively high refractive index increment when used with most polymers¹⁶. EtAc, however, is not as universal a solvent for a variety of polymers as THF. In order to avoid any bubble formation due to dissolved gases in the solvents within the channel (which could complicate the flow pattern inside the channel and increase the noise of the detector), both solvents were kept in glass reservoirs heated to the hot wall temperature of the thermal FFF channel.

Various polymers were used in this work. All necessary parameters and designations are given in Table I. Concentrations of injected polymer solutions were in the range from 0.5 to 1.0% (w/v), with the lower limit applying to the high-molecular-weight samples. In this concentration range, no substantial distortions such as pronounced tailing or the occurrence of shoulders on the fractograms occurred.

The retention ratio R was calculated by comparing the polymer elution volume (or time) with the elution volume (or time) of unretained solute. The latter was a small amount of toluene added to the polymer solution for THF solvent, or THF added to the polymer solution for EtAc solvent.

TABLE I
DESCRIPTION OF POLYMER SAMPLES USED IN THIS STUDY

<i>Polymer</i>	<i>Supplier</i>	<i>Molecular weight</i>	<i>Polydispersity,</i> $\mu = \bar{M}_w/\bar{M}_n$
Polystyrene (PS)	Pressure Chemical Co., Pittsburgh, Pa., U.S.A.	200,000	<1.06
	Pressure Chemical Co.	110,000	<1.065
	Pressure Chemical Co.	37,000	<1.06
	Pressure Chemical Co.	20,400	<1.06
	Mann Research Labs., New York, N.Y., U.S.A.	51,000	Not given
Polyisoprene (PI)	Polymer Labs., Shawbury, Great Britain	210,000	<1.05
	Polymer Labs.	86,000	<1.05
	Polymer Labs.	54,000	<1.05
	Polymer Labs.	15,000	<1.05
Polytetrahydrofuran (PTHF)	Polymer Labs.	270,000	<1.20
	Polymer Labs.	7,600	<1.07
	Chrompack, Middelburg, The Netherlands	103,000	<1.10
	Chrompack	24,000	<1.09
Polymethyl- methacrylate (PMMA)	Chrompack	140,000	<1.1

RESULTS AND DISCUSSION

Fig. 1 shows typical elution diagrams obtained for several different polymers. In each case a sharp void (unretained) peak is shown alongside the polymer peak. Each of the polymer peaks is unmistakably retained with respect to the void peak, thus proving the existence of retention for these polymers in thermal FFF systems.

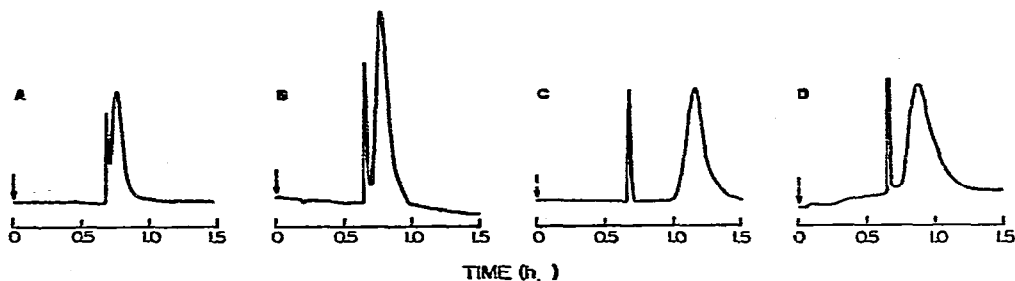


Fig. 1. Elution diagrams of various polymers in tetrahydrofuran. Injection points are indicated by arrows. (A) polytetrahydrofuran, mol.wt. 24,000; (B) polyisoprene, mol.wt. 54,000; (C) polystyrene, mol.wt. 110,000; (D) polymethylmethacrylate, mol.wt. 140,000.

In most cases, measurements were made with polymers of several different molecular weights in order to characterize general trends in retention and to prove the existence of selectivity (a capability to fractionate different molecular weights) as defined by eqn. 4. The results of the retention measurements are summarized in Table II and Figs. 2 and 3.

TABLE II

MEASURED VALUES OF RETENTION RATIO FOR VARIOUS POLYMERS OF DIFFERENT MOLECULAR WEIGHTS IN TETRAHYDROFURAN AND ETHYL ACETATE

The word "Retained" means that the polymer was not observed to elute even after a considerable time.

Polymer	Molecular weight	Retention ratio in tetrahydrofuran	Retention ratio in ethyl acetate
Polystyrene	20,400	0.872	0.861
	37,000	0.808	0.773
	51,000	0.775	0.761
	110,000	0.590	0.576
	200,000	0.483	0.500
Polyisoprene	15,000	0.933	Insoluble
	54,000	0.837	
	86,000	0.740	
	210,000	0.567	
Polytetrahydrofuran	7,600	1.000	1.000
	24,000	0.908	0.809
	103,000	0.720	0.591
	270,000	Retained	Retained
Polymethylmethacrylate	140,000	0.717	Insoluble

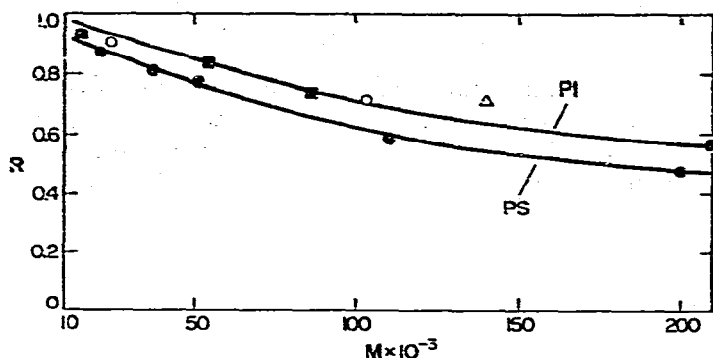


Fig. 2. Retention ratio, R , versus molecular weight, M , for various polymers in tetrahydrofuran. Temperature drop $T = 34^\circ$, $T_c = 26^\circ$. ●, PS; ■, PI; ○, PTHF; △, PMMA. The lines are drawn to represent the experimental points for PI (top) and PS (bottom).

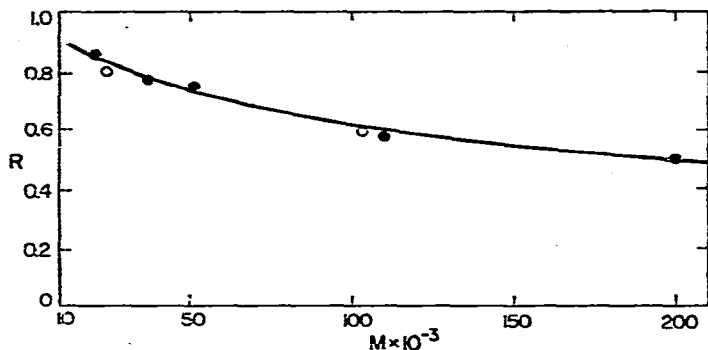


Fig. 3. Retention ratio, R , versus molecular weight, M , for polystyrene and polytetrahydrofuran in ethyl acetate. Conditions as in Fig. 2. ●, PS; ○, PTHF.

Fig. 2 demonstrates that all polymers are retained by thermal FFF using THF as solvent, but it shows that polystyrene has a small but distinct gain in retention (decrease in R) relative to the other three polymers. The advantage of polystyrene does not persist with EtAc solvent: Fig. 3 shows nearly identical retention levels for polystyrene and polytetrahydrofuran. The reasons for this inconsistency in solvent effect probably cannot be explained until there is a better fundamental understanding of the polymer-solvent interactions leading to thermal diffusion in the first place.

Figs. 2 and 3 show clearly that the R values vary with molecular weight, thus demonstrating the existence of a selectivity with respect to molecular weight. In order to ascertain the magnitude of selectivity, we use the experimental R values to obtain λ values via eqn. 3. We then plot $\log \lambda$ vs. $\log M$ as shown in Fig. 4. The absolute value of the slope of the line is equal to the maximum value of the selectivity as indicated by eqn. 5. These S_{\max} values are summarized in Table III. We see that the three selectivity values for non-polystyrene polymers lie in the range 0.43–0.50. Linear polystyrene results obtained in the same series of experiments (but not shown in Fig. 4) are also reported in Table III. We find $S_{\max} = 0.52$ in tetrahydrofuran and 0.46 in ethyl acetate. The polystyrene results are slightly lower than those suggested

by earlier work¹², perhaps due to the fact that the present experiments were all carried out under low retention conditions ($R > 0.48$). Most importantly, a comparison of the results for PS and the other two polymers (PI and PTHF) in Table III shows that all selectivities lie in the same general range.

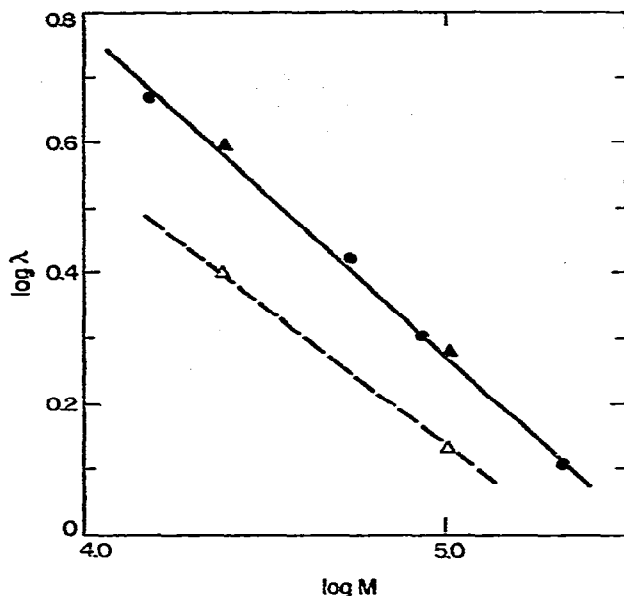


Fig. 4. Plot of $\log \lambda$ versus $\log M$ for various polymers in tetrahydrofuran and ethyl acetate. ●, PI in THF (linear regression analysis: —); ▲, PTHF in THF; △, PTHF in EtAc (---).

TABLE III

VALUES OF MAXIMUM SELECTIVITY, $S_{\max.}$, FOR VARIOUS POLYMERS AND SOLVENTS ACCORDING TO EQN. 5

Polymer	$S_{\max.}$ in THF	$S_{\max.}$ in EtAc
Polystyrene	0.52	0.46
Polyisoprene	0.50	—
Polytetrahydrofuran	0.50	0.43

In conclusion, the present experiments demonstrate rather conclusively that thermal FFF is applicable to polymers other than polystyrene, and that the relevant retention and selectivity parameters are comparable for all polymers tested. Thus polymer fractionation could be achieved, based on the present evidence, with approximately the same level of resolution and speed as we have demonstrated for polystyrene fractions. The experimental conditions, of course, would not mimic those used here: laboratory parameters would have to be adapted to suit the requirement of each polymer and experimenter, and might involve programming¹⁷, high temperature-high pressure controls¹⁴, ultrathin channels¹⁸, and other features we have employed in the past to amplify separation in thermal FFF.

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