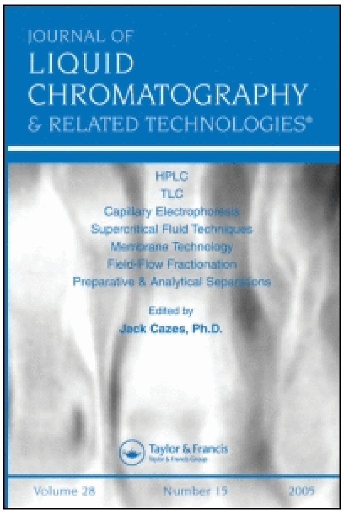

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RETENTION BEHAVIOR OF COPOLYMERS IN THERMAL FIELD-FLOW FRACTIONATION AND GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

Retention behavior of polystyrene copolymers having different structures and compositions was investigated for measuring thermal diffusion coefficient (D_T) using thermal field-flow fractionation (ThFFF). Samples were random poly(styrene-co-methylmethacrylate)s, poly(styrene-co-isoprene) block copolymers having molecular weights ranging from 10^4 to 10^5. It was found that the ThFFF retention of copolymers is related to the composition as well as the molecular size of copolymers. For random copolymers, D_T was a linear function of the monomer composition, and it was possible to determine the molecular weight of polymers by use of calibration curve of log(wt % $M[\eta]$) versus $\log(D/D_T)$. For block copolymers, D_T values of diblock copolymers were greater than those of triblock. It was found that the thermal diffusion varies with the copolymer structure as well as the composition.

INTRODUCTION

Various methods, including reversed phase chromatography (RPC), affinity chromatography, gel permeation chromatography (GPC), electrophoresis, and field-flow fractionation (FFF)[1] have been used to separate and characterize macromolecules.

Among those, FFF is a relatively new method. FFF is an elution method suited for high resolution separation of macromolecules[2,3] and various colloidal particles.[4,5] In FFF, differential retention (thus separation) is obtained by applying a perpendicular field across a thin ribbon-shaped flow channel within which the separation takes place.[6] The external field forces different components into the different stream laminae of the near parabolic flow, causes differential migration, which is followed by elution of the separated components into a detector.

As one of subtechniques of FFF, thermal field flow fractionation (ThFFF) is useful for analysis of various synthetic polymers.[7-9] ThFFF uses a temperature gradient established in a channel confined between two parallel plates, hot wall and cold wall, held at different temperatures. Under the temperature gradient, solute molecules are driven toward the channel wall by thermal diffusion process. Accumulation of solute is counteracted by ordinary diffusion of molecules and a steady-state layer is eventually established near the channel wall.

The distribution of molecules in the steady-state layer is of an exponential form. The layer thickness is expressed in a dimensionless form, $\lambda = \ell / w$, where ℓ is the effective thickness of the layer and w is the channel thickness. In FFF, retention ratio, R is defined as the channel void volume (V_0) divided by the observed retention volume (V_r) and is generally given by

$$R = \frac{V_0}{V_r} = 6\lambda\left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda\right] \qquad (1)$$

In ThFFF, eqn. (1) needs to be modified to account for the asymmetry of the channel flow caused by the temperature gradient and attendant viscosity change across the channel, which results in

$$R = \frac{1}{\sum_{i=1}^{5} \frac{h_i}{(i+1)}}\left\{\frac{1}{(1 - e^{1/\lambda})}\left[\sum_{i=1}^{5} h_i \sum_{j=0}^{i-1} \frac{i!}{(i-j)!}\lambda^j\right] + \sum_{i=1}^{5} i!\, h_i \lambda^i\right\} \qquad (2)$$

Table 1

Characteristics of Polymers Used in This Study

Polymer		**M_w**	**μ[a]**	**Weight %**	**Arrangement**	**Supplier**
PS	1	28,600[b]	1.03	100	Linear	Shodex
	2	66,400[b]	1.03	100	"	
	3	156,000[b]	1.03	100	"	
	4	455,600[b]	1.04	100	"	
PI	1	252,000[b]	1.05	---	"	Polyscience, Inc.
	2	500,000[b]	1.10	---	"	
PMMA	1	27,000	≤ 1.10	---	"	Polymer Labs, Ltd.
	2	60,000	≤ 1.10	---	"	
	3	107,000	≤ 1.10	---	"	
	4	185,000	≤ 1.10	---	"	
	5	330,000	≤ 1.10	---	"	
	6	590,000	≤ 1.10	---	"	
	7	845,000	≤ 1.10	---	"	
p(SI)	1	123,000[c]	1.04	26(35)	Linear, Diblock	Pohang Univ. of Sci. & Tech.
	2	140,000[c]	1.07	49(60)	"	
	3	228,000[c]	1.08	66(75)	"	
p(SIS)	1	79,000	1.03	31(41)	Linear, Triblock	Pohang Univ. of Sci. & Tech.
	2	39,000[c]	1.03	50(60)	"	
	3	78,000[c]	1.04	59(69)	"	
	4	52,000[c]	1.03	72(80)	"	
p(SM)	1	369,000[d]	1.9	29(30)[e]	Linear, Random	Pohang Univ. of
	2	116,000[d]	2.2	48(49)[e]	"	
	3	188,000[d]	3.0	49(50)[e]	"	
	4	108,000[d]	1.7	66(67)[e]	"	

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[a] Polydispersity, $\mu = M_w/M_n$; [b] GPC results in THF; [c] Light scattering results; [d] GPC results in $CHCl_3$; [e] Measured by NMR.

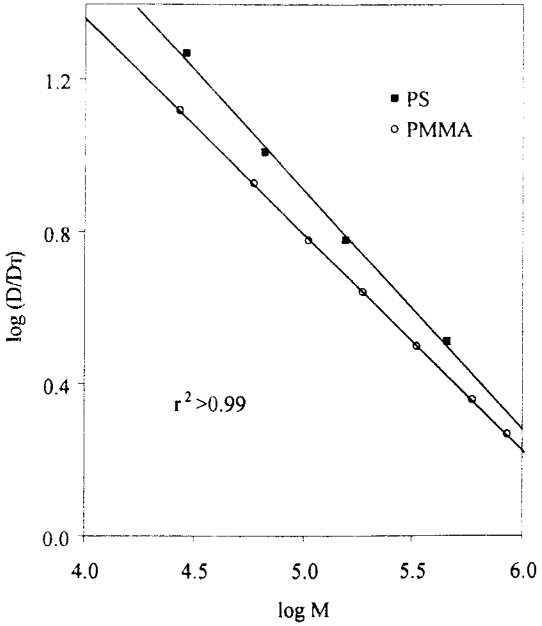

Figure 1. Plot of log (D/D$_T$) vs. log M for homopolymers.

where the hi's are composite constants(dependent on a_0-a_3, k, and dk/dT) reflecting the positional dependence of the viscosity and temperature gradient.[10] As those constants are different for different solvents, they must be obtained for the solvent used in the ThFFF experiment.

It is one of merits of FFF that retention is directly related to physicochemical parameters of solutes. In ThFFF, λ is given by

$$\lambda = \frac{D}{wD_T(dT/dx)} \cong \frac{D}{D_T \cdot \Delta T} \tag{3}$$

where dT/dx is the temperature gradient across the channel, and D the diffusion coefficient and D_T the thermal diffusion coefficient for the given polymer-carrier combination. Thus the solute retention parameter λ depends on both D and D_T , and the ratio of the two coefficients is the determining factor for the solute retention. At infinite dilution, the diffusion coefficient D is related to the intrinsic viscosity,[η] by[11]

Table 2

Molecular Weights and Intrinsic Viscosities of Copolymers

Polymer		**M_w** **Reported**[a]	 **PS Std. Cal.**[b]	**Intrinsic Viscosity**[c] **(dL/g)**
p(SI)	1	123,000	44,000	0.07
	2	140,000	96,000	0.16
	3	228,000	226,000	0.82
p(SIS)	1	79,000	54,500	0.47
	2	39,000	22,900	0.38
	3	78,000	78,800	0.33
	4	52,000	56,300	0.24
p(SM)	1	369,000	113,000	0.79
	2	116,000	198,000	0.39
	3	188,000	176,000	0.53
	4	108,000	111,000	0.40

---

[a] Same as Table 1; [b] Molecular Weight of copolymers measured by PS standard calibration; [c] Measured at 30°C.

$$D = \frac{RT}{6\pi\eta N}\left(\frac{10\pi N}{3M[\eta]}\right)^{1/3} \tag{4}$$

where R is the gas constant, T temperature, η the carrier viscosity, M polymer molecular weight, and N Avogadro's number, and $[\eta]$ intrinsic viscosity. Eqn. (4) shows that D is a function of the product $M[\eta]$ which is a measure of the hydrodynamic volume of polymer. Once λ and D are determined, D_T can be obtained using eqn. (3). Unlike in ThFFF, separation in GPC is obtained based on the hydrodynamic volume (or D) alone.

As seen in eqns. (1) and (3), thermal diffusion coefficient D_T is an important parameter for the understanding of solute retention in ThFFF. Only a limited number of studies have been reported on the thermal diffusion phenomenon in ThFFF.[12-14]

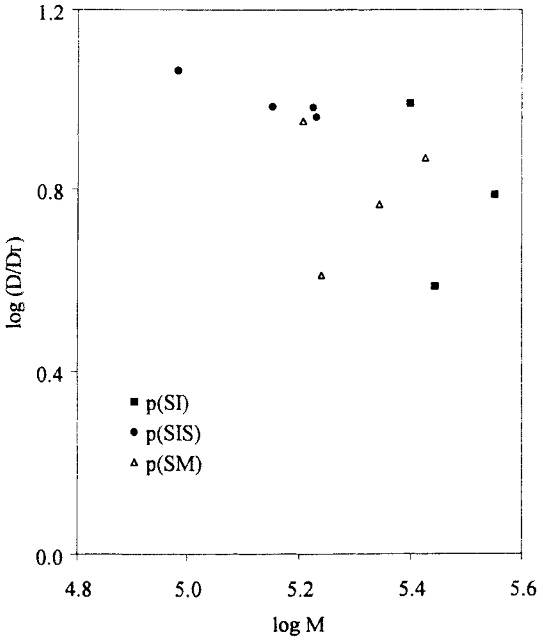

Figure 2. Plot of log (D/D_T) vs. log M for various copolymers.

In 1990, Schimpf et al.[15] used copolymers to study the effect of bonding arrangement and the shape of copolymer on the thermal diffusion coefficient. Jeon et al.[16] studied the variation of D_T with copolymer composition in ThFFF system. In this work, D_T of copolymers is studied using copolymers of various compositions and structures. ThFFF results are compared to those obtained from GPC.

MATERIALS AND METHODS

Thermal Field-Flow Fractionation (ThFFF)

ThFFF system used in this study is a model T100 polymer fractionator from FFFractionation, LLC (Salt Lake City, UT). The channel is 0.0127 cm thick, 1.9 cm wide, and the tip-to-tip length is 45.6 cm. The channel void volume (V_0) was measured to be 1.03 mL from injection of methanol.

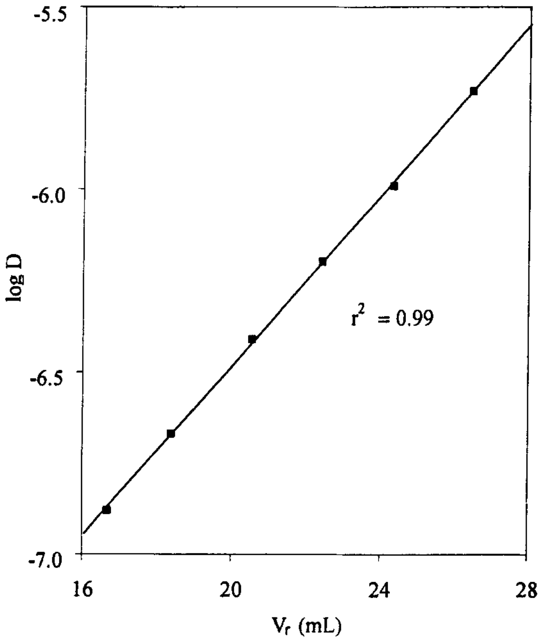

Figure 3. GPC Calibration curve of PS for determination of diffusion coefficient (D) of polymers.

A flow restrictor (Spectra-physics, San Jose, CA) was used to reduce the pulse from the pump. A model 6000A pump (Waters Associates, Milford, MA) was used for solvent delivery. An R401 Refractive Index detector (Waters Associates, Milford, MA) was used to monitor the sample elution and a Bromma 2210 recorder was used to display detector response.

Results were collected and processed using the data analysis software version 2.0 from FFFractionation, LLC. Flow rate was measured with a stopwatch and a buret.

Gel Permeation Chromatography (GPC)

Three μ-styragel GPC columns (7.8 x 300 mm, Waters Associates, Milford, MA) having pore sizes of 10^3, 10^4, and 10^5 Å were used.

Table 3

ThFFF Retention Data of Various Copolymers in THF

Polymer	PS (mol %)	$V_r{}^a$ (mL)	R	λ
p(SI) 1	26	1.34	0.77	0.25
2	49	1.69	0.61	0.16
3	66	2.34	0.44	0.10
p(SIS) 1	31	1.35	0.76	0.24
2	50	1.34	0.77	0.25
3	59	1.38	0.75	0.23
4	72	1.26	0.82	0.29
p(SM) 1	29	1.94[b]	0.53	0.17
2	48	1.39[b]	0.74	0.30
3	49	2.30[b]	0.45	0.13
4	66	1.18[b]	0.84	0.45

[a] Calculated from the peak maximum; [b] Calculated from the center of gravity of the peak.

Samples and Experimental Conditions

The cold wall temperature was kept at 30-32°C. The temperature difference, ΔT was varied from 20 to 60°C. Carrier solvent was tetrahydrofuran (THF, Burdick and Jackson, Muskegon, MI). Flow rate of carrier solvent was between 0.08 to 0.34 mL/min. Following the injection, carrier flow was stopped for 1min. for sample relaxation. Samples were random poly(styrene-co-methylmethacrylate) (p(SM)), diblock poly(styrene-co-isoprene) (p(SI)), and triblock poly(styrene-co-isoprene-co-styrene) (p(SIS)) copolymers ranging from 10^4 to 10^5 molecular weight. All their shapes are linear. NMR was used to determine the composition of p(SM) random copolymers. Polymer samples used in this study are summarized in Table 1. All samples were dissolved in THF and then filtered through a 0.45μm disposable syringe filter for the removal of impurities. The homopolymer samples were diluted to a concentration of 0.3% and the copolymer samples were diluted to a concentration of 0.5-1% prior to injection. Samples were introduced into the channel via sample injection valve fitted with a 20mL sample loop. In most cases, each run was repeated 3 or 4 times.

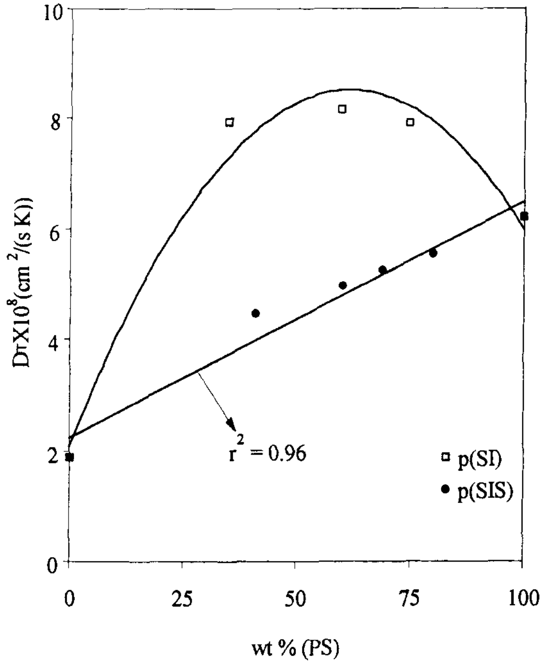

Figure 4. Dependence of D_T on the wt % of PS for p(SI) and p(SIS) block copolymers in THF.

RESULTS AND DISCUSSION

Measurement of MW

Table 2 shows measured molecular weights and intrinsic viscosities of samples. Molecular weights were determined by GPC using a calibration curve constructed with polystyrene (PS) standards.

Viscosities were measured at sample concentrations of 0.5-2.5 mg/mL by measuring the flow time of a certain volume of solution through a capillary of fixed length. Flow time is recorded in seconds as the time for the meniscus to pass between two designated marks in the viscometer. To establish similar condition as in ThFFF, viscosities were measured at 30°C which is the same as the cold wall temperature. Intrinsic viscosity was determined as the reduced specific viscosity extrapolated to c = 0.

Table 4

D and D_T Values of Homopolymers and Copolymers in THF

Polymer		D x 10^7 [a] (cm^2/s)	D/D_T	D_T x 10^8 ($cm^2/(s \cdot K)$)
PS	1	10.30	18.50	5.58
	2	6.35	10.30	6.19, 6.22[b]
	3	3.91	6.04	6.47
	4	2.13	3.21	6.63
PI	1	4.57	24.20	1.89
PMMA	1	16.10	13.20	12.2
	2	10.50	8.43	12.5
	3	7.50	6.06	12.4
	4	5.38	4.32	12.5, 12.4[c]
	5	3.63	3.13	11.6
	6	2.90	2.27	12.8
	7	2.43	1.86	13.1
p(SI)	1	7.76	9.77	7.94
	2	5.01	6.14	8.16
	3	3.09	3.90	7.92
p(SIS)	1	4.27	9.56	4.47
	2	4.79	9.64	4.97
	3	4.79	9.09	5.27
	4	6.46	11.60	5.57
p(SM)	1	3.98	4.11	9.68
	2	5.57	7.42	7.75
	3	4.27	5.83	7.32
	4	5.89	8.93	6.60

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[a] Determined from plot of V_r vs. log D in GPC;
[b] Average [Standard deviation = 0.40 (0.18 except PS1)];
[c] Average [Standard deviation = 0.40].

Measured molecular weights of copolymers are different from reported values as they were determined using a PS calibration. Intrinsic viscosity increases with molecular weight for homopolymers, while it changes with the composition and molecular weight for copolymers. These values were used to investigate the hydrodynamic volumes of samples.

Retention in ThFFF

To examine the retention of copolymers of various chemical compositions (or structures), appropriate experimental conditions were chosen through preliminary experiments. The cold wall temperature, T_C, was kept constant in the range of 30-32°C as the retention varies with T_C. D_T and flow rate were in the range of 20 - 60 °C and 0.08 - 0.34 mL/min., respectively.

As explained earlier, solute retention depends on the ratio (D/D_T) in a given polymer-solvent system and a given D_T (see eqn.3). For PS and PMMA standards, retention time increases with the increase of molecular weight as shown in Fig. 1. This is expected, as D_T remains constant for homopolymers in a given solvent, and D decreases with increasing molecular weight (see eqn.4). Thus, for homopolymers, ThFFF separation is obtained based on the solute molecular weight.

Contrarily for copolymers, no linear relationship between molecular weight and retention was found (see Table 3 and Fig. 2). This result indicated that there is an additional factor (or factors) besides molecular weight affecting the retention of copolymers. This additional factor is related to chemical composition of copolymers. That is, change of chemical composition affects the D and D_T.

Since the retention of copolymer is influenced by two independent variables (composition and molecular weight), measurement of molecular weight of copolymer is not straightforward. A new calibration method accounting both composition and molecular weight effect is needed to measure molecular weights of copolymers.

Measurement of Thermal Diffusion Coefficient

From experimentally observed V_r, λ can be calculated using eqn. (2). D_T is then calculated using eqn.(3), provided D is known. D can be obtained by measuring intrinsic viscosity and molecular weight and then, by using eqn. (4)

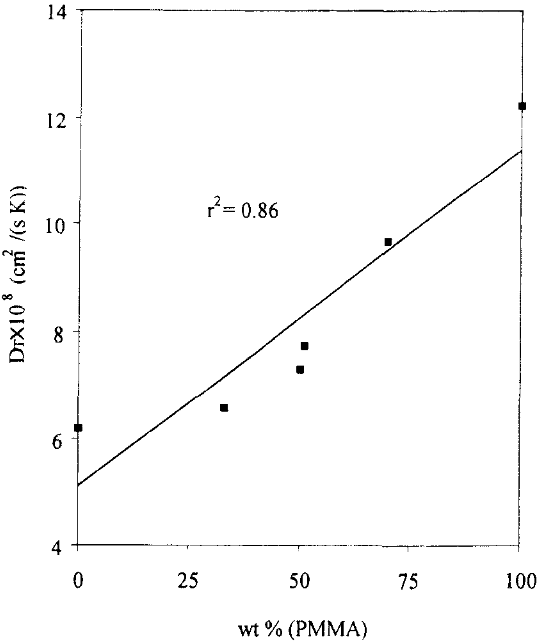

Figure 5. Dependence of D_T on the wt % of PMMA for p(SM) random copolymers in THF.

or by using a plot of retention volume (V_r) versus log D obtained from GPC data. In this study, we used the latter method with polystyrene standards. Fig. 3 illustrates the plot obtained from PS standards. Results are shown in Table 3. Values of D and D_T are shown in Table 4.

As previously reported,[11] D_T of homopolymer increases in the order of PI < PS < PMMA. Fig. 4 illustrates the dependence of D_T on the wt % of PS for p(SI) and p(SIS) block copolymers. It is shown that D_T changes with copolymer composition. In case of p(SI) block copolymers, D_T values are roughly the sum of D values of PS and PI constituents. A linearity exists for p(SIS) triblock copolymers, that is, D_T increases with the increase of wt % of PS. This linearity is similar to that of random copolymers.

This is illustrated in Fig. 4. The correlation coefficient (r^2) is 0.96. This result indicates that D_T of p(SIS) triblock copolymer is affected mostly polystyrene constituent. Fig. 5 shows a plot of D_T versus wt % of PMMA for p(SM) random copolymers. D_T increases with the increase of wt % of

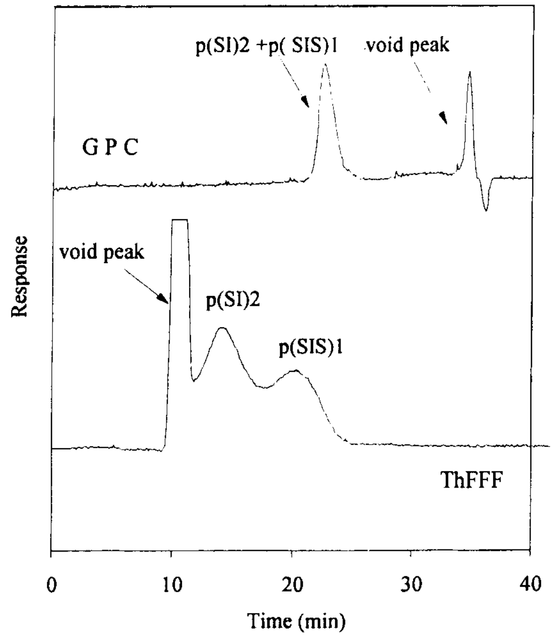

Figure 6. Comparison of separation efficiency of GPC and ThFFF for p(SI)2 and p(SIS)1 mixture.

methymethacrylate with the correlation coefficient (r^2) of 0.93. Results shown in Fig. 4 and 5 indicate D_T varies with structure of copolymer. These results suggests D_T of copolymer is affected, not only by the chemical composition, but also by the effect of structural change.

Comparison of Separation in ThFFF and GPC

Comparative studies on separation of homopolymers in ThFFF and GPC were previously reported,[8,17,18] but that of copolymers has not yet been reported. In this study, two techniques are compared for separation of copolymers.

Figure 6 shows results obtained for two copolymers; hydrodynamic size of p(SI)2 is 22,400 and that of p(SIS)1 is about 37,000. Retention in GPC depends only on the hydrodynamic size. The difference in hydrodynamic size between two copolymers is apparently too small for GPC to separate. ThFFF, however, provided good separation for the copolymers, probably due to the

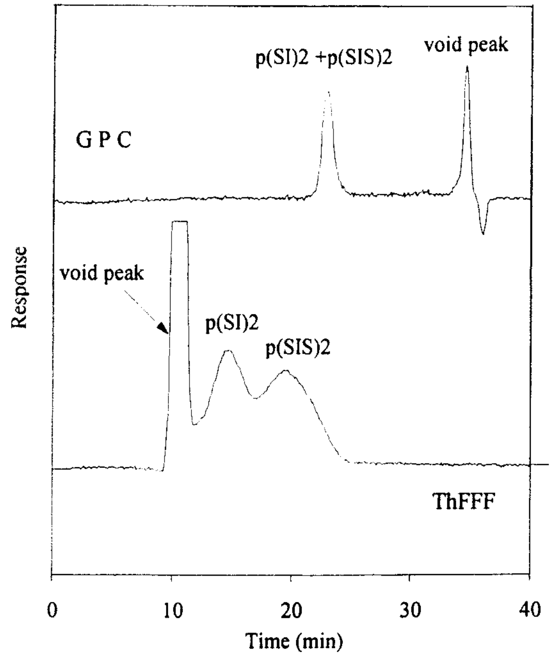

Figure 7. Comparison of separation efficiency of GPC and ThFFF for p(SI)2 and p(SIS)2 mixture.

difference in D_T. There are structural differences and 20% differences in styrene% between two copolymers. There are two factors causing the difference in D_T between two copolymers. First, the higher the composition of styrene is the larger then D_T. Second, D_T of triblock copolymer is higher than that of diblock copolymer.

Figure 7 shows results obtained for copolymers having similar chemical composition and hydrodynamic volume but different structures. Separation in this case is primarily due to the difference in D_T caused by the structural difference of copolymers.

In summary, separation mechanisms of GPC and ThFFF are different. In GPC, separation is based only on the hydrodynamic size of solute molecules. The hydrodynamic size of polymer is influenced by its composition and structure. Still, polymers having different compositions or structures may have similar hydrodynamic sizes, and they may not be separated by GPC. For ThFFF, separation is based on the thermal diffusion as well as the size. For polymers (or copolymers) having similar hydrodynamic sizes, ThFFF may provide separations based on the difference in composition or structure and, thus, a tool for the analysis of such samples.

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