

COMPARISON OF GPC AND THERMAL FIELD-FLOW FRACTIONATION METHODS FOR LINEAR AND STAR BRANCHED POLYSTYRENE SAMPLES*

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ABSTRACT

The Thermal Field-Flow Fractionation (TFFF) method was used to determine the elution volume of a series of star branched polystyrene having different number of arms but the same arm molecular weight and polystyrene standards with narrow distribution whose molecular weight ranged from 5.0×10^4 to 8.6×10^6 . Results were obtained by measuring at two temperature difference ($\Delta T = 30^\circ\text{C}$ and $\Delta T = 50^\circ\text{C}$) in THF. The same star branched samples were measured by means of GPC method. Comparison of V_r - M relationships obtained from TFFF and GPC showed that the displacement of V_r - M curves for star and linear polystyrene is larger than that in GPC. This difference is caused by the entirely different mechanism of separation for these two methods. As the controlling factor is hydrodynamic volume of the polymer chain in solution for GPC, it is the diffusion coefficient of polymer molecules for TFFF. The experimental results indicate that the influence of variance of chain structure on diffusion coefficient is stronger than that on the hydrodynamic volume and that TFFF technique may be used as a method for characterizing branching of polymer molecules. For this purpose a proper theoretical model and more accurate experiments are needed.

INTRODUCTION

Thermal Field-Flow Fractionation (TFFF) was developed by Giddings and co-workers^[1,2]. Several applications of TFFF were oriented toward the separation of extra-high molecular weight polystyrene sample^[3] and determination of molecular weight distribution of PS^[4,5,6].

TFFF is similar to chromatography in many aspects. However, all of the processes with the separation take place in fluid phase and there is no stationary phase which would play an active role in GPC.

TFFF column is made by clamping two polished chrome plated copper bars together over a thin thermal insulating spacer. The metal bars form the top (hot) and bottom (cold) faces of the channel. The external field (thermal field) is formed by temperature drop ΔT across the channel. As soon as a solute species enters the channel, the external field begins to force it toward the far wall of the channel. In the case of TFFF the solute molecules are forced by the thermal diffusion phenomenon toward the cold wall (Figure 1. a).

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As solute molecules begin to concentrate at the wall, however, diffusion counteracts additional concentration. Soon a thin steady state layer is established next to the wall. The distribution of the solute species in this layer is exponential and can be expressed by (2)

$$C = C_0 \exp(-x/l) \quad (1)$$

where C is the concentration of solute at distance x from the cold wall, C_0 is the concentration at the wall (where $x = 0$), and l is a characteristic distance and is approximately the mean thickness of the solute layer. When l is small compared to the channel width, w , the zone becomes almost entirely attenuated before reaching the upper wall ($x=w$). This condition, $l \ll w$, is applicable to most practical cases of TFFF.

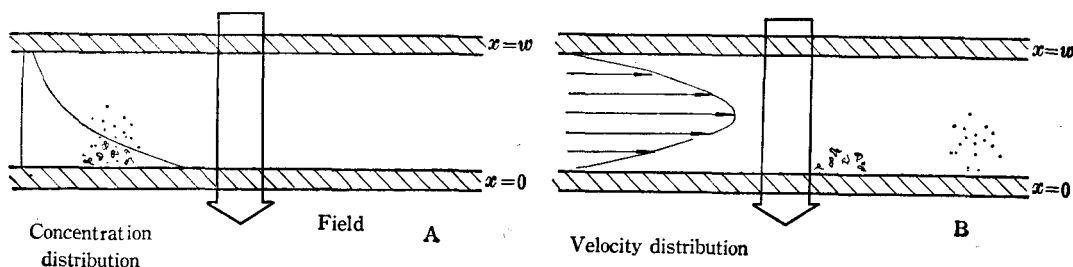


Fig. 1 The basic steps of Thermal Field-Flow Fractionation

- The solute zone is compressed into a narrow layer against cold wall by the thermal field
- Flow profile and solute layer distribution in channel

As the thermal diffusion coefficient, D , is essentially independent of molecular weight, the thickness of solute species of different molecular weight is solely dependent on diffusion coefficient D , which can be expressed by

$$D = K \times M^{-\beta} \quad (2)$$

where K is constant depending on system and β is approximately equal to 0.5 [7,8]. Therefore, sample species with different molecular weight have different concentration distribution under the same field strength (ΔT).

Once the steady state layer has been formed solvent flow along the channel displaces the solute downstream. When the channel breadth b is large enough ($b > 40w$) the flow profile between the two parallel plates of the channel is parabolic (Figure 1. b)

$$v = 6 \langle v \rangle \left(\frac{x}{w} - \frac{x^2}{w^2} \right) \quad (3)$$

where $\langle v \rangle$ is the mean velocity. Fluid velocity v is the greatest at the center of the channel and zero at the walls. Solutes whose layers extend well into rapid streamlines will be swept out first, and species compressed into the relatively slow regions near the wall will elute later. This is the basis for selective retention. In general it produces a spectrum in which the smaller species appear at first and then the larger species.

According to Giddings' theory retention volume, V_r , can be expressed by

$$V_r = V_0 \left\{ 6\lambda \left[\coth \left(\frac{1}{2\lambda} \right) - 2\lambda \right] \right\}^{-1} \quad (4)$$

$$\lambda = 1/w \quad (5)$$

where V_0 is the channel volume (void volume), dimensionless parameter λ is the most important fundamental parameter of TFFF. For TFFF the value of λ is expressed by

$$\lambda = \left[\left(\frac{\alpha}{T} + \gamma \right) w \frac{dT}{dx} \right]^{-1} \quad (6)$$

where α is the dimensionless thermal diffusion factor

$$\alpha = D_t \times T/D \quad (7)$$

T is absolute temperature and γ is the coefficient of thermal expansion.

Although both TFFF and GPC can separate solute species according to their molecular weight, however, the mechanism of separation is entirely different. The elution order is contrary. The smaller molecular weight solute is eluted first in TFFF but last in GPC.

In the papers published by Giddings and co-workers the retention ratio, R ($= V_0 / V_r$), or retention parameter, λ , was used for dealing with experimental results and theoretical calculation. The main aim of this work is to extend the TFFF method to branched polystyrene samples and to compare the results obtained from TFFF with GPC. So we still use retention volume as the fundamental parameter.

EXPERIMENTAL

Apparatus

TFFF: Figure 2 presents a generalized apparatus scheme of TFFF. The principal TFFF column used in this work consisted of two chrome plated copper bars with highly polished clamped together over a 0.25 mm Mylar spacer. A flow channel of the desired dimensions was out of the spacer. The channel dimension were 2 cm in breadth by 47 cm long with tapered ends. Samples were injected into the flowing solvent by a six port valve. Peak detection was obtained by a UV monitor (Waters Associates R 404, 254 nm).

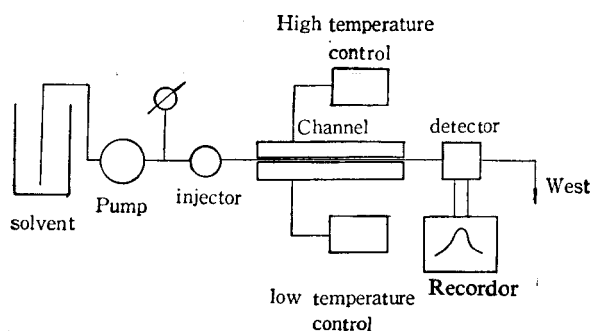


Fig. 2 Schematic illustration of TFFF apparatus

GPC: A Shimadzu LC-4A chromatogram was used in this work. High performance GPC column were packed with J- μ crosslinked polystyrene gel produced by Jilin University. Column length was 50 cm. Column efficiency was 22000/m.

Samples

Branched polystyrene of the star type was polymerized in high vacuum system by anionic

polymerization. The active polystyrene-lithium reacted with multichloro-coupling agent quantitatively. The number of chlorine atoms of the multichloro-coupling agent is the number of the arms of the branched molecule.



Excess polystyrene prepolymers were removed by fractional precipitation. The final product was dried to constant weight in vacuum oven. The data are listed in Table 1.

PS standards (Jilin University) with narrow molecular weight distribution were used for this study. M_w/M_n was less than 1.06 in the majority of cases. The data on average molecular weight for these PS are presented in Table 2.

Carrier

The carrier solvent was tetrahydrofuran (THF) for both GPC and TFFF measurements. The flow rate was 1.0 ml/min for GPC and 10 ml/h for TFFF.

Table 1 Number of arms, molecular weight, and TFFF data of star branched polystyrene

Sample	Number of arms	M ($\times 10^{-4}$)	V_r (ml)	
			$\Delta T=50^\circ\text{C}$	$\Delta T=30^\circ\text{C}$
5501	1	7.19	3.73	2.88
5502	3	21.2	4.95	3.91
5503	4	31.5	6.41	4.32
5504	6	41.0	7.61	4.78
5505	8	55.9	8.64	5.19
5506	12	83.3	8.64	5.55

Table 2 Molecular weight and TFFF data of PS standards

Sample	M ($\times 10^{-4}$)	V_r (ml)	
		$\Delta T=50^\circ\text{C}$	$\Delta T=30^\circ\text{C}$
PS1	5.0	3.64	2.67
PS2	10.0	4.10	3.09
PS3	16.0	5.13	3.58
PS4	20.0	5.53	3.73
PS5	30.0	9.19	5.26
PS6	49.8	7.75	6.26
PS7	60.0	10.98	7.54
PS8	86.0	13.70	8.60

RESULTS AND DISCUSSION

TFFF chromatograms of star branched PS samples (5503, 5506) and linear PS standard (PS 4) are shown in Figure 3. Figure 4 shows the GPC chromatogram of branched samples.

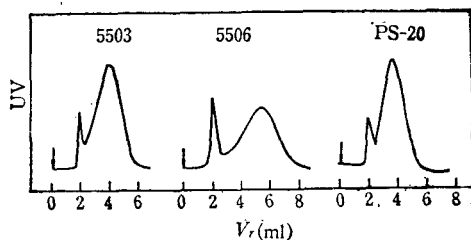


Fig. 3 TFFF fractogram of star branched PS and PS standard

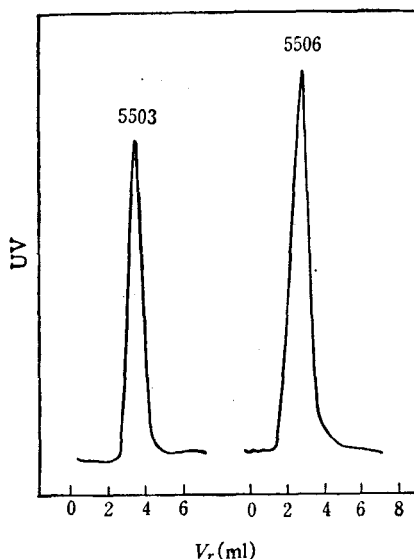


Fig. 4 GPC chromatogram of star branched PS

It is seen that the molecular weight distribution of star branched polymers are narrow except the sample 5506.

The GPC calibration curve obtained by linear PS standards and curve representing the relationship between the retention volume, V_r , and molecular weight of branched polymer are shown in Figure 5.

The molecular structure of branched polymer is more compact. Therefore the volume of branched polymer in solution is smaller than that of linear polymer with the same molecular weight. It can be seen in GPC chromatogram and it is the base for GPC as a method of studying branched polymer. According to a specific model one can obtain some information about degree of branching from GPC data in conjunction with other method, such as viscosity measurement^[9].

The principle of TFFF is diffusion phenomenon of solute molecules in solution. Diffusion coefficient depends on the structure of molecular chain. But the quantitative relationship between them has not been studied extensively so far. The branched polystyrene samples used in this work are star in shape and have different number of arms whose molecular weight are the same. Therefore it can be used for describing the relationship between some physical

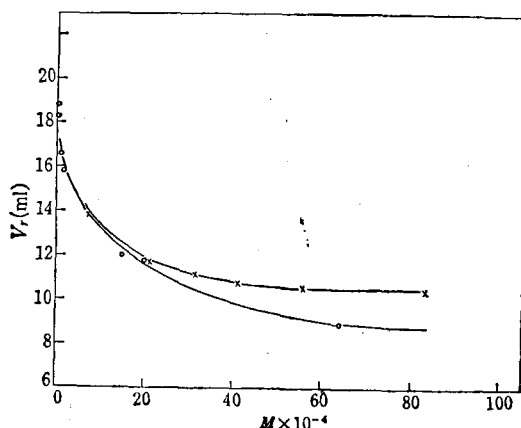


Fig. 5 Dependence of retention volume V_r on molecular weight in GPC for PS standard (O) and star branched PS (x)

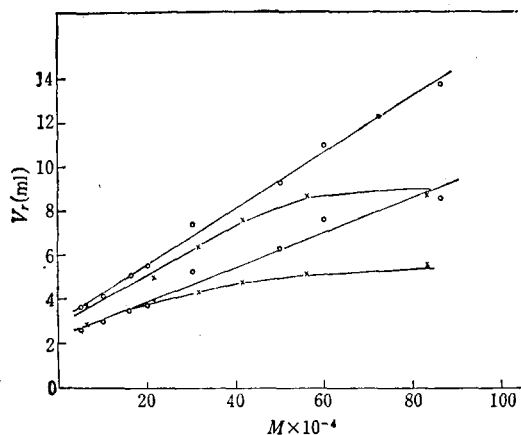


Fig. 6 Dependence of retention volume V_r on molecular weight in TFFF for PS standard (O) and star branched PS (x) at $\Delta T = 30^\circ\text{C}$ (bottom) and $\Delta T = 50^\circ\text{C}$ (top)

property and the chain structure. Figure 6 shows the dependence of V_r on molecular weight for both star branched and linear polystyrene samples obtained TFFF column. In the range of low degree of branching the V_r - M curves for branched and linear PS are relatively close to each other. But the departure between them is increasing with the degree of branching (molecular weight). Comparing Figure 6 with Figure 5, it is seen that the difference between V_r - M curves obtained from TFFF is considerably larger than that obtained from GPC. The two groups of curves of Figure 6 show that the departure between V_r - M dependence of branched and linear PS obtained at high field strength ($\Delta T = 50^\circ\text{C}$) is larger than that obtained at low field strength ($\Delta T = 30^\circ\text{C}$). Regulating and even programming field strength is one of the characteristics of TFFF. For this reason one can obtain more information by regulating field strength. Characterization of branching is a rather complicated problem. This work just quasiquantitatively shows that TFFF provides a new method for studying branched molecules. However a proper theoretical model and more accurate experiments are needed for a satisfactory

solution.

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