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Characterization of Thermal Diffusion in Polymer Solutions by Thermal Field-Flow Fractionation: Effects of Molecular Weight and Branching

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ABSTRACT: Thermal field-flow fractionation has been applied to 29 linear and branched polystyrene samples dissolved in ethylbenzene. The samples varied widely in chain length and branching configuration. The dependence of retention on the molecular weight and the ordinary diffusion coefficient was established. It is shown from these results that the thermal diffusion coefficient is essentially constant, independent of both molecular weight and the form of branching. This result is consistent with the theoretical conclusions of Brochard and de Gennes.

Introduction

The thermal diffusion of polymers in solution is an intrinsically interesting transport phenomenon, but it is poorly understood and infrequently studied. However, thermal diffusion has gained in practical importance recently because it underlies the technique of thermal field-flow fractionation (thermal FFF or ThFFF). Fortunately, every ThFFF experiment is capable of producing thermal diffusion data. In this way ThFFF has become the best technique for the systematic study of thermal diffusion and thus of its own foundations.

ThFFF is a technique applicable to the separation and characterization of polymeric materials.[1-3] In this technique a thin pulse of dilute polymer sample is carried by flow along a narrow ribbonlike channel across which an external "field" in the form of a thermal gradient is applied. The velocity profile of the carrier liquid in the channel is near parabolic, with a higher flow velocity in the channel center than near the walls. The polymer, under the influence of the temperature gradient, is forced toward the cold wall. The resulting buildup of concentration at the cold wall is opposed by ordinary diffusion, and a dynamic steady-state condition is reached in which the field-induced motion is balanced against back-diffusion.

The spatial distribution of polymer formed at the cold wall under this steady-state condition is exponential in form and can be characterized by the effective thickness l, the distance from the cold wall to the center of gravity of the polymer zone. The parameter l is typically expressed in the dimensionless form $\lambda = l/w$, where w is the channel thickness or distance between hot and cold walls. The constant λ is termed the retention parameter and can be related, by considering the flow profile, to the experimental retention volume V_r, the volume of carrier solvent required to transport the polymer through the length of the channel. For parabolic flow[3]

$$R = V^0/V_r = 6\lambda(\coth(1/2\lambda) - 2\lambda) \qquad (1)$$

where R is the retention ratio and V^0 is the channel void volume. Clearly, each experimental measurement of V_r yields a unique value of λ. Equation 1 must be corrected somewhat to account for the departure from parabolic flow induced by the temperature gradient and attendant viscosity changes in the channel.[4]

The variation of retention parameter λ among different polymers can be attributed to changes both in thermal diffusion and in ordinary diffusion. The relationship of λ to the corresponding transport coefficients is given by[3]

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$$\frac{1}{\lambda} = \frac{wD_T}{D}\frac{dT}{dx} \tag{2}$$

where D_T and D are the thermal and ordinary (concentration) diffusion coefficients for the polymer–solvent system, respectively, and dT/dx is the temperature gradient applied across the channel.

Equations 1 and 2 show that the separation of polymer samples into components, represented by increments in V_r and thus in λ, results from differences both in D_T and D. It is important to sort out the contributions of the two factors.

Differences in D are governed by effective molecular size according to the Stokes–Einstein equation

$$D = kT/6\pi\eta R_h \tag{3}$$

where k is Boltzmann's constant, η is the carrier viscosity, and R_h is the hydrodynamic radius. The dependence, through D and R_h, of ThFFF retention on molecular size is a feature shared with size-exclusion chromatography (SEC). The size-based separating power of ThFFF is comparable to or in some cases greater than that of SEC.[5] However, the concurrent influence of the thermal diffusion coefficient D_T on retention imparts an additional factor to be manipulated for polymer separation by ThFFF.

Previous studies have shown that D_T, in contrast to D, is independent of molecular weight (size) for linear chains in a given solvent.[6] However, more recent ThFFF studies have shown that D_T is influenced by the chemical properties of the polymer–solvent system,[5] making ThFFF applicable to the separation of polymers according to chemical composition and to molecular weight. We have proposed combining ThFFF and SEC to examine simultaneously size and compositional variations. However, the chemical composition effects are not yet well characterized.

None of the previous studies have dealt with the effects of chain branching on D_T. In this work we investigate a number of linear and branched chain polymers (both star and comb) of various molecular weights and arm numbers to see if any systematic relationships can be found between branching and D_T.

Molecular Weight Dependence

The retention of a variety of linear chain polymers has been observed in earlier studies.[3,4,7,8] The relationship between λ and molecular weight M in each case can be described by the general equation

$$\lambda = \lambda'/M^{S_m} \tag{4}$$

where λ' and S_m are constants for a given polymer–solvent system. The parameter S_m is termed the mass selectivity and falls between 0.5 and 0.6 for ThFFF systems examined thus far.

An analogous equation can be used for the variation of D with molecular weight[9]

$$D = A/M^b \tag{5}$$

where the exponent b also commonly falls in the range 0.5–0.6. Substituting eq 4 and 5 into eq 2 and rearranging, we get

$$D_T = \frac{A}{\lambda'}\left(w\frac{dT}{dx}\right)^{-1}\frac{M^{S_m}}{M^b} \tag{6}$$

where to a good approximation dT/dx can be approximated as $\Delta T/w$, where ΔT is the temperature difference between hot and cold walls. The independence of D_T and molecular weight M is manifested in the fact that $S_m \simeq b$ for all polymer–solvent systems so far examined. According to Brochard and de Gennes[10] this independence is explained by an absence of long-range coupling between monomers undergoing thermal diffusion. As a result, a polymer chain is expected to move in a thermal gradient with the same velocity that would be seen with separated monomers.

Table I
Summary of Molecular Weight Information

sample code	conformation	M_W	no. of arms	arm M	Backbone M
S310	linear	97 200			
4b	linear	110 000			
NBS705	linear	179 000			
50124	linear	233 000			
00507	linear	300 000			
5a	linear	498 000			
60914	linear	600 000			
S121	star	93 000	4	23 000	
2161	star	351 000	4	87 800	
S141	star	521 000	4	130 300	
S181	star	1 030 000	4	257 500	
HS101	star	317 000	6	52 800	
HS041	star	509 000	6	84 800	
HS051	star	1 090 000	6	181 700	
PS9-12	star	55 000	12	4 600	
PS6-12	star	149 000	12	12 400	
PS4-12	star	467 000	12	38 900	
PS10-12	star	1 690 000	12	140 800	
12-PS1	star	5 700 000	12	475 000	
C612	comb	475 000	31	6 500	275 000
C622	comb	624 000	30	11 700	275 000
C632	comb	913 000	25	25 700	275 000
C642	comb	1 630 000	29	47 000	275 000
C652	comb	3 130 000	29	98 000	275 000
C712	comb	1 055 000	30	6 500	860 000
C722	comb	1 190 000	28	11 700	860 000
C732	comb	1 530 000	26	25 700	860 000
C732	comb	1 530 000	26	25 700	860 000
C742	comb	2 230 000	29	47 000	860 000
C752	comb	3 620 000	28	98 000	860 000

In order to examine the relationship between D_T and branching, accurate values for the polymer diffusion coefficients must be available. For the linear chains these were taken from empirical curves established by Schaefer and Han[11] using quasi-elastic light scattering; the results can be expressed by eq 5. Diffusion coefficients for the branched polymers, where eq 5 is no longer applicable, were calculated with Einstein's relation $D = kT/f$, where the friction coefficient f was determined by Roovers and Toporowski[12] using sedimentation velocity measurements.

Experimental Section

The ThFFF system used is identical with that described earlier.[13] The channel thickness is 76 μm, the breadth is 2.3 cm, and the tip-to-tip length is 34 cm. A ΔT value of 30 °C was used throughout the study. Injection was performed by a Valco (Houston, TX) valve with a 3-μL cell volume. Polymer concentrations were typically 2.0 mg/mL and the carrier solvent used was ethylbenzene. Peak detection was obtained with a Waters Associates (Amherst, MA), R401 refractive index monitor. The channel void volume was determined to be 0.65 mL from injections of cyclohexane, which is unretained. A minimum of four repetitive runs was made in determining values of retention volume V_r for each sample. These values were determined by measuring the distance to the maximum of the sample peak.

In addition to linear polystyrenes, our samples consisted of several series of star polymers[14,15] of increasing molecular weight with constant arm number. These include 4-, 6-, and 12-arm series. We also utilized two independent series of comb-shaped polymers,[16] where the molecular weight of the backbone chain and the number of branches is approximately constant but the molecular weight of the branches is varied. Details on branching and molecular weight are summarized in Table I.

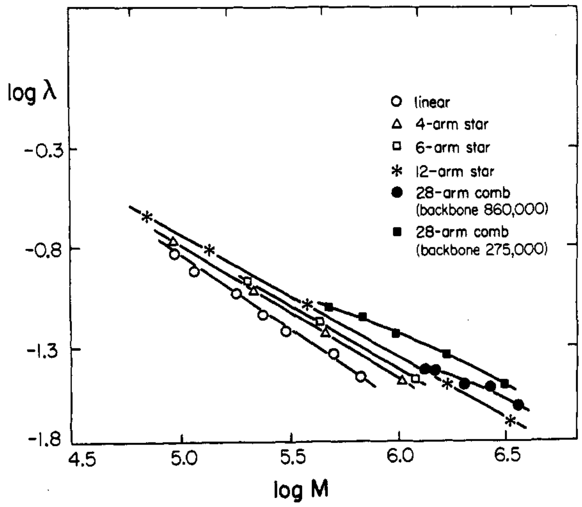

Figure 1. Logarithmic plots of $\lambda = l/w$ vs. M for different polymer families.

The samples were obtained from a variety of sources. The linear polymers are Pressure Chemical Co. (Pittsburgh, PA) standards. The 12-arm star series was obtained from Lewis Fetters (Exxon Corp., Clinton, NJ), and the remaining branched polymers were obtained from Jacques Roovers (National Research Council of Canada, Ottawa, Ontario, Canada).

Results and Discussion

The relationship between retention volume (expressed in terms of $\lambda = l/w$) and molecular weight M for the various families of linear and branched polymers is illustrated in Figure 1. (The λs are obtained from a modification to eq 1 that allows for small departures from parabolic flow caused by the temperature gradient.) It is apparent that molecular weight is not the sole criterion for retention in this polymer–solvent system, which would require all points to lie on a single line. Instead there is a systematic increase in λ with the number of arms at a given M.

Fetters and Roovers have demonstrated[15,17] that as the number of arms increases in the star polymers the effective size of the polymer molecule of a given molecular weight decreases. Thus the common trend in which λ decreases with size *within* all the polymer families of Figure 1 is equally applicable for comparisons *between* families. Figure 1 therefore suggests that size rather than molecular weight may be the fundamental factor governing the retention of polymer samples in ThFFF.

The availability of diffusion coefficients, which depend entirely on size, allows us to examine the possibility of a D_T–size correlation. Specifically, we look for a unique relationship between retention parameter λ and D. Figure 2 illustrates that such a relationship exists and that it is a linear one. According to eq 2 the slope of such a plot equals $(wD_T\ \mathrm{d}T/\mathrm{d}x)^{-1}$. Since the temperature gradient $\mathrm{d}T/\mathrm{d}x$ and the channel thickness w are constant for all runs, the observation of a linear relationship between λ and D for polymers of widely varying sizes and structures demonstrates that D_T is independent of either polymer size or the type of branching for polystyrene in ethylbenzene.

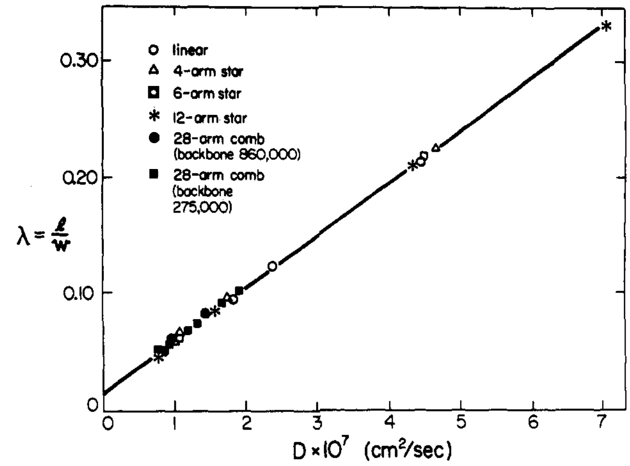

Figure 2. Plot of λ vs. diffusion coefficient D in which all polymer families fall on same line.

Conclusion

This study shows that the thermal diffusion coefficient D_T is independent of branching configuration and molecular weight or size for polystyrene in ethylbenzene. This is consistent with the theoretical deductions of Brochard and de Gennes.[10] Further studies are under way on a wide variety of polymer–solvent systems to examine the dependence of D_T on the chemical composition of the polymer and solvent.

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