

Thermal Field-Flow Fractionation for Characterization of Architecture in Hyperbranched Aromatic-Aliphatic Polyesters with Controlled Branching

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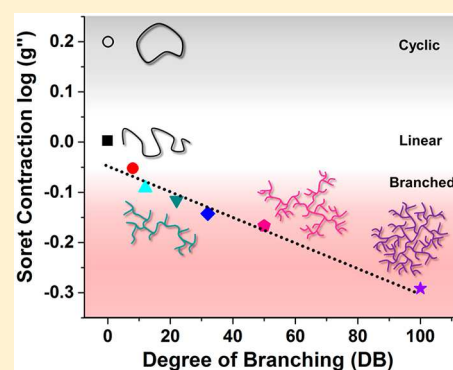
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Supporting Information

ABSTRACT: Thermal field-flow fractionation (ThFFF) was used to characterize the architecture of aromatic–aliphatic polyesters with varying degrees of branching. Thermal diffusion and Soret coefficients (D_T and S_T , respectively) provide a novel route to polymer architecture analysis. This paper demonstrates an innovative strategy to extract architecture information from the physicochemical separation parameters embedded in ThFFF retention times without explicit separation of linear and branched samples. A Soret contraction factor (g''), defined as the ratio of the S_T of a branched polymer to the S_T of a molecular weight equivalent linear analogue, is introduced as a metric to indicate degree of branching (DB). This approach circumvents several challenges associated with the analysis of high molar mass polymers with a high degree of branching. The g'' value is shown to be proportional to the degree of branching for linear (DB, 0%), gradually branched (DB, <50%), hyperbranched (DB, 50%), and pseudodendritic (DB, 100%) polyesters allowing the establishment of architecture calibration curves. Furthermore, positive $\log(g'')$ values (~ 0.2) at low molar mass are attributed to cyclic subpopulations. This work demonstrates the usefulness of the Soret contraction factor for statistically and hyperbranched polymer systems and its sensitivity to cyclic polymers.



Hyperbranched (hb) polymers are a class of branched polymers where the branching repeat units have a possibility of secondary branching leading to random and highly dense polymer structures. The commercialization of hb polyesters is driven by the low production cost, the industrial scalability, and relatively easy “one-pot” synthesis.¹ However, this process often leads to polymers which have distributions both in molecular weight (M_w) and degree of branching (DB), both of which strongly influence the polymer’s rheological and solution behavior, processability, and end product performance.^{2–4} Measurement of hb polymer molecular weight is typically done by a combination of size exclusion chromatography (SEC) with online viscometry or multiangle light scattering (MALS) detection.⁵ While this approach works for low M_w hb polymers, in some cases, hb polymers with high M_w can experience enthalpic and physical interactions with the stationary phase that may cause abnormal elution behavior leading to inaccuracy in the measured M_w and dispersity.⁶ Ideal separations in SEC are based solely on entropic considerations; therefore, the solvent and column chemistries are chosen explicitly to mitigate any complications from undesirable analyte–column interactions. Adsorption phenomena have however been exploited for branching characterization and separations using solvent gradient interaction chromatography

(SGIC), liquid chromatography at critical conditions (LCCC), and temperature gradient interaction chromatography (TGIC),⁷ where conditions and columns are chosen specifically to tune the strength of analyte–column interactions. In this regard, LCCC has proven to be useful in the separation of branched, linear, and cyclic polymers, though there is some discrepancy between theoretical prediction and experimental retention behavior.⁸ High-resolution 2D-SGIC-SEC has also been used to determine both branching and molar mass for linear and branched polymer blends.⁹ However, strong enthalpic interactions of hyperbranched polyesters with high molar masses (>50 kDa) can lead to significant adsorption causing poor sample recovery and can convolute retention volume branching correlations.¹⁰ The average degree of branching is commonly determined using ensemble techniques like NMR.¹¹ Similarly, the rheological properties of polymers can be correlated to the overall average branching in a polymer sample allowing linear and branched architectures to be differentiated.^{12,13} While these ensemble techniques provide an average value for the degree of branching, they do

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not yield the distribution.¹⁴ A method able to identify the degree of branching, number of branches or chain ends, and their distributions is imperative to understanding the structure–function relationships and behavior of these complex polymers.

Typical analyses of macromolecules emphasize the measurement of properties like molar mass and “size”, and the latter is given by an equivalent spherical radius. Correlation of the volume a polymer occupies in dilute solution with the mass and/or geometric radius can provide valuable information on polymer conformation. Further comparison of the conformational state with that of a molar mass equivalent linear analogue helps to illuminate polymer architecture. One of the foremost of these relations is the light scattering contraction factor (g) whose definition is shown in eq 1:

$$g = \frac{(R_g \text{ Branched})^2}{(R_g \text{ Linear})^2} \quad (1)$$

where R_g is the radius of gyration.¹⁵ From this proportion, a reasonable estimate of branching can be made using the Zimm–Stockmayer formalism.¹⁶ Determination of g requires a polymer to have a sufficiently large size (larger than $\frac{\text{MALS wavelength}}{\sim 50}$) so that R_g can be determined from the light scattering angular dependence with reasonable accuracy.¹⁷ For this reason, hb polymers of low molar mass have been carried out via the coupling of separations methods to viscometry.¹⁸ Following a similar process as above, a viscometric contraction factor (g') can be determined and has been shown to be effective for determining branching in polymers with regular architecture.¹⁹ Recent studies have looked into the universality of the relation^{20,21} between g' and g in order to understand the difficulty of this method for quantifying random or statistical branching.²² In order to address the problems associated with column-based chromatography techniques and light scattering detection limits, an additional technique for branching analysis must be introduced.

Thermal field-flow fractionation (ThFFF) is a separation technique that has been developed for the characterization of both polymer molar mass and composition.²³ Thermal FFF utilizes a temperature gradient to induce the migration of molecules (usually) toward regions of lower temperature. The magnitude of this thermal diffusion is dependent on the chemistry of the polymer–solvent interface; this flux is balanced by molecules undergoing translational diffusion in the opposite direction. The ratio of the thermal diffusion coefficient D_T to the translational diffusion coefficient D is termed the Soret coefficient or S_T .²⁴ The S_T is conveniently directly proportional to the measured ThFFF retention time (as discussed further in the [Experimental Section](#)). As an alternative to traditional chromatography, ThFFF provides several benefits due to its open channel design and absence of packing material. These benefits include a high molar mass range as well as limited sample loss and degradation. These problems are especially relevant in the architecture characterization of high molar mass polymer where chromatography stationary-phase induced shear degradation and adsorption are commonplace. Recently, a new approach to architecture characterization has been introduced based on first-principles of the ThFFF separation mechanism.²⁵ This work compared experimentally measured Soret coefficients (S_T) for regularly branched star and miktoarm star polymers with theoretical

Soret coefficients of the corresponding linear polymer based on a predictive model of thermal diffusion. A ratio of S_T values defines the Soret contraction factor (g'').²⁵

$$g'' = \frac{S_T \text{ Branched}}{S_T \text{ Linear}} \quad (2)$$

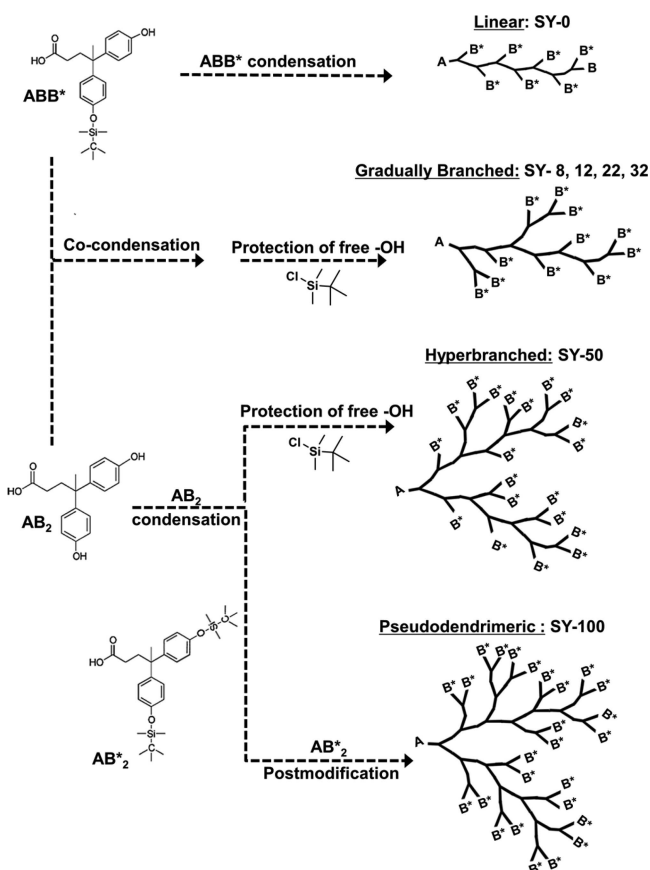
As S_T contains information about the hydrodynamic size of a polymer, via D , a ratio of branched and linear polymer S_T values can perform a similar function to viscometric- and light scattering-based contraction factors. The original work investigated polymers with regular branching (linear, star, pom-pom) and demonstrated that the number of chain ends could be determined via the construction of a calibration curve which was independent of polymer chemical composition. This principle was later applied to investigate bottle-brush polymers with variations in backbone and side-chain lengths.²⁶ Recent application of this analysis to linear and star polystyrene illustrated how the thermodynamic quality of the solvent may cause deviation in the estimation of chain ends.²⁷ It should be noted that g'' is an empirical relationship and a fully quantitative relation to various types of branching has yet to be established. To the best of our knowledge, this approach has only been applied to polymers with regular branching topologies.

The objective of this current study is to investigate the potential of the Soret contraction (g'') to characterize hyperbranched polymers with random or statistical branching and not to develop an architecture-based separation. This study focuses on the determination of S_T values from ThFFF retention times and their use in conjunction with MALS and dynamic light scattering (DLS) to simultaneously determine distributions in M_w and DB for hyperbranched and pseudodendrimeric polymers. Accordingly, the ThFFF retention behavior of a series of aromatic-aliphatic polyesters with controlled DB of 100, 50, 32, 22, 12, 8, and 0% was investigated. Three approaches that utilized thermal diffusion coefficients D_T , hydrodynamic conformation plots, and Soret contraction factors for architecture characterization were evaluated and compared.

■ EXPERIMENTAL SECTION

Materials. Polyesters with DB from 0 to 50% were prepared via an ABB*/AB₂ polycondensation of 4,4-bis(4'-hydroxyphenyl) valeric acid (AB₂) with a *tert*-butyldimethylsilyl protected version of the monomer (ABB*) as previously described.²⁸ The ABB*/AB₂ ratio dictates the degree of branching of the resultant polymer. These samples are referred to as SY-0, -8, -12, -22, -32, and -50 to denote the presence of the silyl group (SY) and the nominal DB. The SY-100 sample was produced following a postmodification process where the OH-50 (analogue to SY-50 but with OH end groups for further modification) sample was reacted with additional AB*₂ monomer with two silyl groups.²⁹ This replaced any remaining linear regions that are statistically present in the hyperbranched sample with an AB*₂ terminal chain creating a pseudodendrimer. The final structure had two distinct chemistries, polar ester groups providing linear or dendritic linkage and nonpolar silyl pendant groups ([Scheme 1](#)). Molecular weights and PDI from SEC-MALS analysis are summarized in [Table 1](#). Experimental details to the SEC analysis are given in the [Supporting Information](#). Solubility of the polymers was investigated in several solvents. Tetrahydrofuran (THF) and

**Scheme 1. Scheme of Polyester Synthesis Following ABB*/
AB₂ Condensation Process for DB 0–50%^a**



^aThe DB 100% is produced by postmodification of linear units on the SY-50 hyperbranched sample with AB₂* monomers producing a pseudodendrimer.

Table 1. Degree of Branching, Molecular Mass, and $\bar{D} = M_w/M_n$ for Aliphatic-Aromatic Polyester Samples

sample	topology	degree of branching (%) ^a	M_w (g/mol) ^b	$\bar{D}$
SY-0	linear	0	73300 ± 200	2.28
SY-8	gradually branched	8	30300 ± 200	2.42
SY-12	gradually branched	12	53700 ± 100	2.14
SY-22	gradually branched	22	60700 ± 300	2.56
SY-32	gradually branched	32	44700 ± 200	2.38
SY-50	hyperbranched	50	42400 ± 200	1.86
SY-100	pseudodendritic	100	153100 ± 300	2.42

^aDetermined by ¹³C NMR according to ref 28. ^bUncertainties represent one standard deviation.

cyclohexane (CH) (Sigma-Aldrich, St. Louis, MO) were used in the subsequent study representing polar and nonpolar solvents, respectively.

Thermal Field-Flow Fractionation (ThFFF) and Light Scattering. Fractionation was conducted using a TF2000 model ThFFF system coupled online to a model PN 3621 multiangle light scattering (MALS) and a PN 3150 dRI (Postnova Analytics, Salt Lake City, UT). The refractive index increment (dn/dc) for the polyester samples was determined

to be 0.1550 mL/g in THF (in agreement to previous studies^{20,28}) and 0.1435 in CH following a standard batch method (Figure S1). No significant dependence of dn/dc on degree of branching had been observed; therefore, average values were used for all samples. The ThFFF channel had dimensions of 250 μ m in thickness, 2.0 cm in breadth, and 45.6 cm in length. The carrier liquid in all experiments was CH or THF pumped through the channel at 0.2 mL/min. Samples were introduced into the system by a PN 5300 autosampler (Postnova Analytics) with a 102.5 μ L sample loop. All SY samples were prepared at ~3–5 mg/mL, and the injected volume was ~50 μ L; the total mass of sample was below the average sample overloading mass of 400 μ g as determined by an overloading study.³⁰ The void time was 11.04 min. Temperature dependent dynamic light scattering (DLS) studies were performed using a Wyatt DynaPro Nanostar (Wyatt Technology Corporation, Santa Barbara, CA) at 5 °C intervals from 20 to 50 °C for THF and from 20 to 60 °C in CH (Figure S2). Each temperature step was 17 min to ensure adequate equilibration time; data was taken for a 5 min period after the temperature stabilized with an acquisition time interval of 5 s. Attenuation and laser power were automatically adjusted for each sample. All samples were filtered through a 0.2 μ m PTFE filter prior to analysis, and 1 mL was added and the cuvette sealed securely. Values were calculated with the Dynamics software version 7.6.0.48 using the cumulant autocorrelation fit method.

Calculation of S_T and D_T . In a normal mode separation, ThFFF analytes elute according to the balance of thermal (D_T) and translational diffusion (D) coefficients also known as the Soret coefficient (S_T). An approximation of the ThFFF retention equation is given in eq 3:

$$t_r \cong \frac{D_T \Delta T t^0}{6D} \quad \text{or} \quad \frac{S_T \Delta T t^0}{6} \quad (3)$$

where t^0 is the void time (the travel time through the ThFFF channel of an unretained solute) and ΔT is the temperature drop across the spacer. The value of ΔT is known, D is measured by batch and/or online DLS, and t^0 and t_r (the retention time at peak maximum) are determined from ThFFF fractograms. Therefore, S_T and D_T can be calculated for any given ThFFF retention time resulting in continuous values across a sample peak. Equation 3 holds only for highly retained analytes ($t_r \geq 5$ times the void time).³¹ A deeper look at ThFFF retention theory at high temperatures and considerations for D values and actual equations used in calculation of D_T values from retention time can be found in the Supporting Information section 2.

RESULTS AND DISCUSSION

The ThFFF retention behavior of a series of linear, gradually branched, hyperbranched, and pseudodendritic polyester was investigated, and the fractograms obtained in THF and CH are shown in Figure 1a–g. All samples exhibited higher retention in THF due to a larger hydrodynamic size (Figure S3). The thermal diffusion coefficient (D_T) can also impact retention time and these values were calculated according to eqs S1 and S2 and plotted in Figure 2. Two distinct trends are observed in CH and THF. Branching did not influence the D_T of polymers dissolved in CH with all values falling within one standard deviation about the mean. In THF, a different behavior is observed with polymer D_T decreasing with

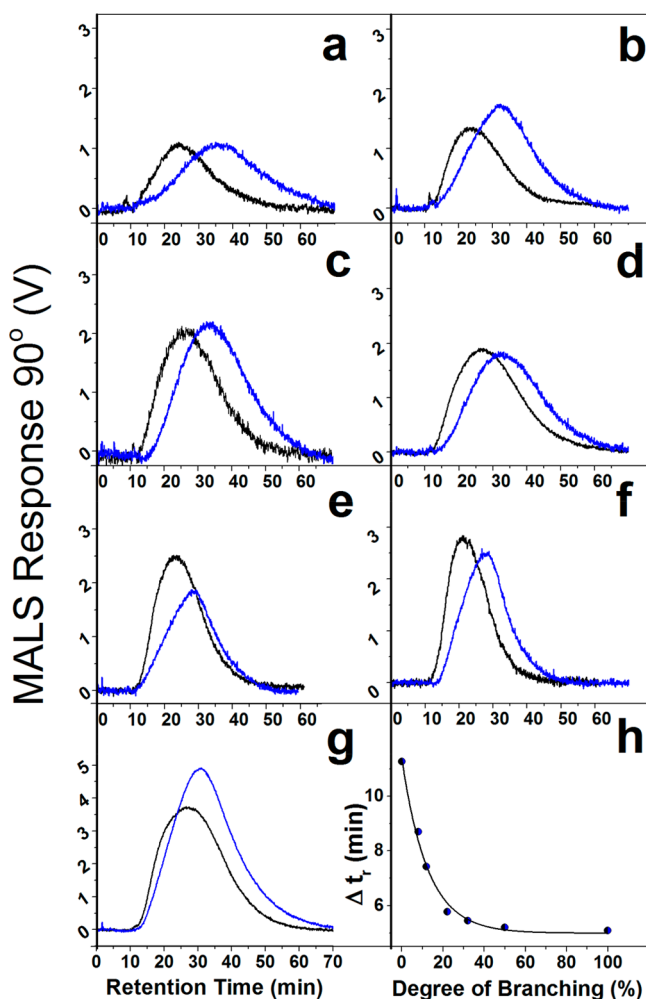


Figure 1. Overlay of MALS fractograms of polyester samples in THF (blue) and CH (black) for (a) SY-0, (b) SY-8, (c) SY-12, (d) SY-22, (e) SY-32, (f) SY-50, (g) SY-100, and (h) the difference in retention time for each sample between solvents.

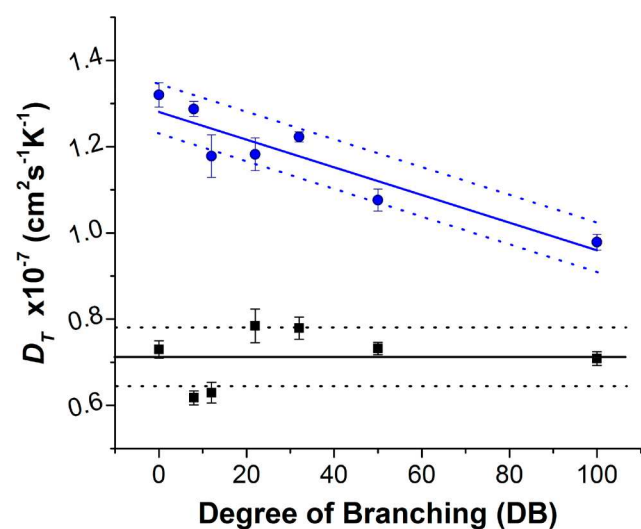


Figure 2. Polymer D_T dependence on DB and solvent (THF blue, CH black). The solid line represents the fit for trend in THF and mean value in CH. Dotted lines represent one standard deviation.

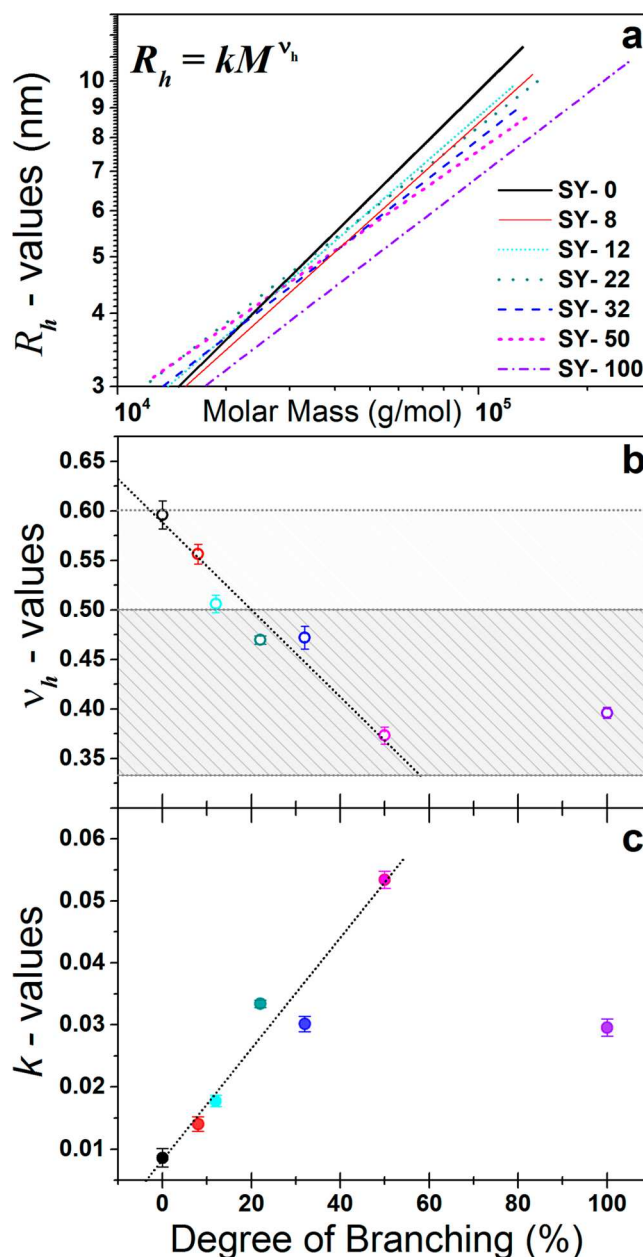


Figure 3. (a) Conformation plots of R_h and M_w from ThFFF-DLS for all samples in THF, (b) plot of conformation slope (ν_h), and (c) conformation plot intercept (k) with respect to the degree of branching.

increasing DB. D_T has been shown to be sensitive to the polymer chemistry, and this sensitivity was exploited for determining composition distributions.³² Furthermore, architecture and branching is not expected to influence the D_T of a homopolymer in a good solvent.³³ The observed trend in THF could be due to copolymer-like thermal diffusion behavior. As polymer D_T is based on polymer–solvent interactions at the interface, copolymer D_T will be a combination of the behavior of both blocks.³⁴ The presence of the silyl and ester groups present two distinct chemistries at the polymer–solvent interface. The D_T in THF decreases as the ratio of terminal silyl-groups to dendritic ester groups at the solvent interface increases. Conversely, a copolymer in a selective solvent for one of the blocks exhibits D_T behavior that is dominated by the solvated block.³⁵ In CH, polar ester sites are sequestered in the

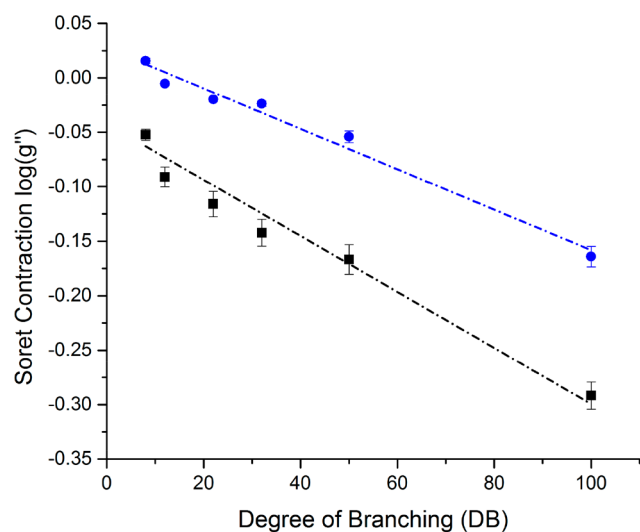


Figure 4. Dependence of Soret contraction (g'') on degree of branching in THF (blue) and CH (black).

polymer excluded volume with the silyl groups in the solvent accessible region. Therefore, the D_T of the polyesters in CH is driven by silyl–CH interactions at the interface. Thus, no trend in D_T with respect to DB is observed in CH. The absence of a trend in D_T with respect to DB prevents determination of branching based on thermal diffusion when using CH as a carrier fluid. Although D_T can readily differentiate SY-0 and SY-50 in THF, discerning the gradually branched (SY-8 to SY-32) from the linear SY-0 is difficult, as the error bars for these points do not show a significant difference.

A second method by which architecture information can be obtained is through the construction of conformation plots. The scaling of the polymers size with respect to the molar mass is expressed in eq 4:

$$R_h = kM^{\nu_h} \quad (4)$$

where R_h is the hydrodynamic radius, M is the molar mass, and k and ν_h are scaling parameters. In Figure 3a, fits for hydrodynamic radius (R_h) versus molar mass from online ThFFF-MALS-DLS for each of the SY samples are overlaid. Overlays of R_h vs M_w raw data can be seen in Figure S4. The linear SY-0 displays the highest slope with the hyperbranched SY-100 exhibiting the lowest slope. The other SY samples fits fall in an expected manner between these bounds. The slopes (ν_h) of these Figure 3 plots offer an indication of both, polymer architecture and the thermodynamic quality of the

solvent system.¹⁹ In Figure 3b, the slope of the conformation plots (ν_h) is seen to decrease with increased DB. Branched species therefore exhibit smaller changes in size with respect to changes in molar mass, suggestive of an increase in apparent density of the polymer with increased DB. A decrease in ν_h is indicative of the presence of long chain branching in the polymer.³⁶ Alternately, fits that are shifted to higher molar masses while maintaining similar slopes can reveal the presence of both short-chain branching³⁷ and changes in monomer functionality.³⁸ This trend is easily visualized as a decrease in the conformation plot intercept (k). This is illustrated by comparing SY-50 and SY-100 in Figure 3c. Although both samples exhibit similar ν_h values, the fit of SY-100 is shifted to higher molar masses and lower k value compared to SY-50 indicating additional “short chain” branching. This is expected as the SY-100 sample is produced via the addition of monomer to the statistically branched OH-50 sample producing terminal short chains at any of the remaining linear positions (see Scheme 1).

As mentioned above, ν_h also provides a means to describe solvent quality. In Figure 3b, the upper shaded region represents slope values for a linear random coil in a “good” solvent ($\nu_h \approx 0.6$) to theta solvent ($\nu_h \approx 0.5$), while the lower region represents more compact polymer conformations approaching the slope value for a hard sphere ($\nu_h \approx 0.33$). THF is believed to be a good solvent for both chemistries present in the SY polyesters, which is confirmed from the conformation slope of the linear SY-0 ($\nu_h = 0.59 \pm 0.01$). Solvent quality was also investigated via measurement of the second virial coefficient (A_2) from MALS (data not shown) and SANS which was positive in both solvents, with A_2 in THF being greater than in CH.^{20,39} Because of poor light scattering in CH, a comparative conformation analysis was not possible with MALS online. Although the construction of conformation plots yields useful complementary information about the polymer architecture, it does not provide a quantitative method for distinguishing the degree of branching for hyperbranched (SY-50) and pseudodendrimer species (SY-100).

We are therefore introducing a third method to extract architecture information from ThFFF retention data. Treatment of ThFFF data to create Soret contraction relations is possible if the S_T of a compositionally analogous linear polymer can be determined either theoretically or via experiment. In the initial work on Soret contraction,²⁵ a predictive model of thermal diffusion developed by Mes et al.⁴⁰ was used to calculate the Soret coefficient of a linear polymer (polystyrene and polyacrylates) at any molar mass. This enabled determination of architecture from g'' without the

Table 2. Summary of Hydrodynamic Radius and Translational and Thermal Diffusion Coefficients^a

sample	tetrahydrofuran			cyclohexane		
	R_h (nm)	$D \times 10^{-7}$ (cm ² s ⁻¹)	$D_T \times 10^{-8}$ (cm ² K ⁻¹ s ⁻¹)	R_h (nm)	$D \times 10^{-7}$ (cm ² s ⁻¹)	$D_T \times 10^{-8}$ (cm ² K ⁻¹ s ⁻¹)
SY-0	6.9 ± 0.1	7.9 ± 0.2	13.2 ± 0.3	4.9 ± 0.2	6.5 ± 0.2	7.3 ± 0.2
SY-8	5.5 ± 0.1	10.1 ± 0.1	12.8 ± 0.2	5.5 ± 0.2	5.7 ± 0.2	6.2 ± 0.2
SY-12	6.8 ± 0.4	8.1 ± 0.3	11.7 ± 0.5	5.9 ± 0.2	5.3 ± 0.2	6.3 ± 0.2
SY-22	6.5 ± 0.1	8.4 ± 0.3	11.8 ± 0.4	5.0 ± 0.3	6.2 ± 0.3	7.8 ± 0.4
SY-32	5.3 ± 0.1	10.6 ± 0.1	12.2 ± 0.1	4.3 ± 0.1	7.5 ± 0.3	7.8 ± 0.3
SY-50	5.4 ± 0.1	10.3 ± 0.2	10.8 ± 0.3	4.1 ± 0.1	7.9 ± 0.2	7.3 ± 0.1
SY-100	7.4 ± 0.2	7.4 ± 0.1	9.8 ± 0.2	5.4 ± 0.1	5.9 ± 0.1	7.1 ± 0.2

^aUncertainties represent one standard deviation (instrumental).

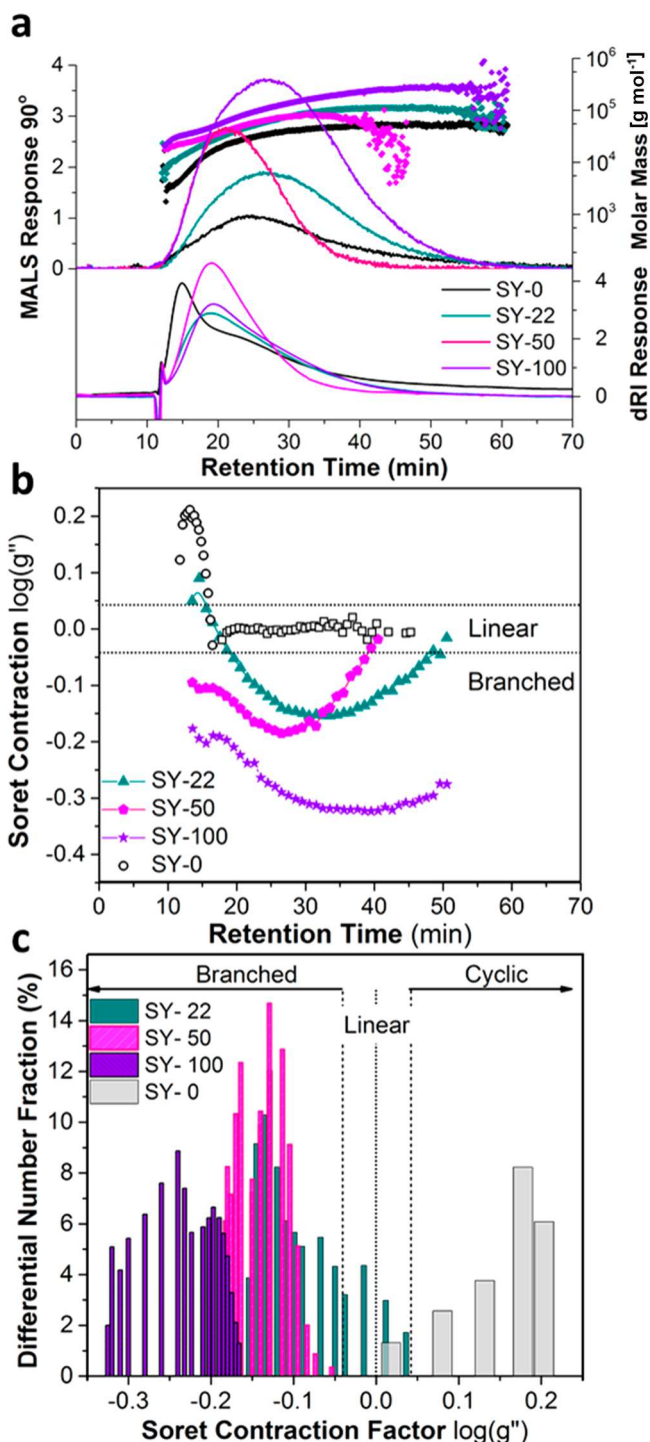


Figure 5. (a) Fractograms of linear SY-0 (black), SY-22 (green), SY-50 (pink), and SY-100 (purple) in CH. MALS and molar mass (top) overlaid with dRI signal (bottom). (b) Overlay of $\log(g'')$ calculated at 1 min intervals. (c) Distribution of g'' within each sample. For parts b and c, the linear region ($\log(g'') = 0$) is bounded by dotted lines based on error of fit from Figure S4.

need to experimentally measure a linear analogue. This method is effective for common polymers, where tables of solution properties are readily available. For novel polymers, the temperature dependence of solubility and interaction parameters in the necessary solvents systems would need to be determined. Alternatively, a linear analogue can be used if one exists. Ideally a linear analogue with the equivalent M_w of each

DB sample would be analyzed when calculating g'' . If this is not possible, the ThFFF can be calibrated with either a series of narrowly distributed M_w of linear standards or a single high dispersity standard.⁴¹ In this work, the chemically analogous linear polyester (SY-0) was used for this purpose. The resulting calibration plot of S_T versus molecular weight is shown in Figure S5b. Values of g'' are then calculated according to eq 2 using M_w equivalent $S_{T \text{ Linear}}$ values from the calibration plot and average values of $S_{T \text{ Branched}}$ from the retention times of the peak maximum in Figure 1a–g. The relation of Soret contraction g'' and DB in both CH and THF is shown in Figure 4. This relation enables the construction of architecture-based calibration curves. The magnitude of contraction is higher in CH than in THF, and this translates to the difference in R_h as seen by DLS (Table 2). The sensitivity of the g'' calibration is greater in CH than in THF by ~30%. The lower sensitivity in THF can be attributed to the inverse relation of DB and D_T shown in Figure 2. The relation of DB to $\log(g'')$ provides a metric to determine the distribution of DB within a polymer sample based on ThFFF retention time. Fractograms of SY-0, -22, -50, and -100 in cyclohexane are shown in Figure 5a. Soret contraction factors are calculated from M_w and $S_{T \text{ Branched}}$ as a continuous function of retention time, following the same process for calculating the average g'' in Figure 3. This is shown in Figure 5b where the SY-0 linear region is bounded by the dotted lines and the branched samples falling below (in the region where $\log(g'')$ is negative). Within a sample, the higher DB subpopulations are expected to elute earlier while the more “linear-like” polymers are expected to elute at higher retention times. This is indeed observed for the SY-22 and SY-50 (Figure 5b), which showed an initial decrease in g'' followed by an increase toward the linear region. Using the dRI (Figure 5a) to determine the concentration of each g'' subpopulation (Figure 5b) within a sample, a corresponding differential distribution can be constructed. The three branched samples SY-22, -50, -100 exhibited different amounts of dispersity with respect to g'' and thus to DB. Figure 5c shows three distinct regions where (i) $\log(g'') < 0$ represents polymers in a “contracted” state with lower S_T when compared to a linear polymer of analogous molecular weight; (ii) $\log(g'') \cong 0 \pm 0.04$ signifies the presence of linear polymers; and (iii) a region with positive $\log(g'')$ values, discussed below.

Interestingly, the linear polyester SY-0 showed the presence of a low M_w subpopulation eluting at ~14 min (Figure 5a). This subpopulation exhibited a Soret contraction factor above unity (Figure 5b), which means it is more retained than the M_w equivalent linear polymer. A low M_w subpopulation was also noted in SEC-MALS of the as-synthesized samples (Figure S6) and was identified as 2–5 kDa cyclic polyesters by MALDI-TOF MS.²⁸ The low M_w subpopulation in SY-0 was collected as it eluted from ThFFF and further analyzed by MALDI-TOF MS (Figure S8). The presence of subpopulations with positive $\log(g'')$ were also identified in both the SY-8 and SY-12 samples. These subpopulations were also collected for analysis by MALDI-TOF and confirmed the presence of cyclic polyester (Figure S8a,b). The Soret contraction methodology suggests the presence of a different architecture, e.g., the cyclic subpopulation, (Figure 5) as compared to SEC (Figure S6) that only indicates the presence of a low-molecular weight population. The Soret contraction ($g'' > 1$) for cyclic polymers is in opposition to traditional g -values from light scattering which have contracted conformations ($g \cong 0.5$).⁴² We hypothesize that these cyclic oligomeric species exhibit

different thermal diffusion than the corresponding linear species leading to higher retention than expected at this molecular weight. This first report of the thermal diffusion behavior of cyclic polymers is an exciting development and could lead to advancements in their analyses, particularly in mixtures.

CONCLUSIONS

An innovative approach founded in Soret contraction factors derived from ThFFF retention times is shown to provide insights into distributions in the degree of branching in complex random and statistical branched polymer systems. This analysis was possible despite separations based on size and composition (as evidenced by MALS M_w measurements and changes in D_T as a function of retention time when THF was used as the separation solvent). Aromatic-aliphatic polyesters with controlled DB of 100, 50, 32, 22, 12, 8, and 0% were used as a model system. The extension of the Soret contraction to statistically and randomly branched systems showed that $\log(g'')$ is linearly correlated to the degree of branching enabling identification of the average polymer DB as well as online determination of architecture distributions. Care must be taken when using this method for copolymers and functionalized polymers as the solvent quality may influence the selectivity of the architecture calibration. The unexpected enhanced retention of cyclic subpopulations requires further study; their distinct thermophoretic behavior opens a new avenue of analysis for these difficult polymeric species.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.9b02664.

Increment of refraction (dn/dc) determination, temperature-programmed dynamic light scattering, R_h versus M_w conformation plots data and fits, molecular weight versus Soret calibration using ThFFF-MALS, polyester room temperature SEC, isolation and characterization of cyclic polyester subpopulations, and thermal FFF multiangle light scattering overlays (PDF)

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Notes

The authors declare no competing financial interest.

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are those of the author(s) and do not necessarily reflect those of the NSF.

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