Second Virial Coefficient of Arborescent Polystyrenes and Its Temperature Dependence

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The solution behavior of arborescent (highly branched) polymers was examined in terms of A_2 variation with polymer structure, solvent type, and temperature. Two series of graft polymers in three successive generations were examined, with side chains of either 5000 (S05 series) or 30 000 (S30 series). Scaling relationships $A_2 \propto M_w{}^a$ were found for both series, with $a = -0.94$ or -0.97, consistent with rigid-sphere behavior. Temperature-dependent measurements were carried out in cyclohexane and in toluene, to allow decomposition of A_2 into its enthalpy ($A_{2,H}$) and entropy ($A_{2,S}$) components. In cyclohexane, the magnitudes of $A_{2,H}$ and $A_{2,S}$ were mainly affected by the branching functionality of the polymers, and less significantly by the molecular weight of the side chains. Furthermore, the temperature dependence of A_2 in both solvents was found to be more strongly influenced by branching functionality than by the molecular weight of the polymers. Variations in the Θ temperature for polymers of low branching functionality in cyclohexane are consistent with the trends observed in star-branched polymers. However, no measurable Θ temperature was observed for a polymer with a branching functionality $f_w = 180$.

Introduction

Arborescent polymers are a class of dendritic macromolecules obtained by anionic polymerization and grafting. Styrene-based arborescent polymers can be prepared by partial chloromethylation of a linear polystyrene sample and subsequent reaction with polystyryl anions under appropriate conditions. Repetition of chloromethylation and grafting reaction cycles leads to successive generations $G = 0, 1, 2$, etc., of increasing molecular weight and branching functionality (Figure 1). Polymers with molecular weights ranging from ca. 5×10^4 to over 10^8 have thus been obtained, with branching functionalities from 10 to over 10^4, while maintaining a narrow molecular weight distribution.[1,2] Arborescent polymers incorporate structural features common to both dendrimers and star-branched polymers:[3] Molecules with high branching functionalities can be obtained according to a generation scheme typical of dendrimers but using fewer reaction cycles. Very high molecular weight materials are obtained, similarly to star-branched polymers, but with considerably higher branching functionalities than are normally attainable in these systems.[4]

The second virial coefficient (A_2) of polymers in solution, a measure of solvent quality, not only varies according to the nature of solvent−polymer interactions but also is sensitive to molecular weight and to polymer architecture.[5] The relation between structure and A_2 has been explored in some detail in star-branched polymers, particularly in terms of the variation of the Θ temperature in poor solvents, albeit only for branching functionalities up to 22.[3] Arborescent polymers provide an interesting opportunity to extend these studies to higher branching functionalities. The variation of A_2 with temperature has been studied extensively in linear polymer solutions, but only a very limited amount of data is available for star-branched polymers. Detailed analysis of A_2 in terms of enthalpy and
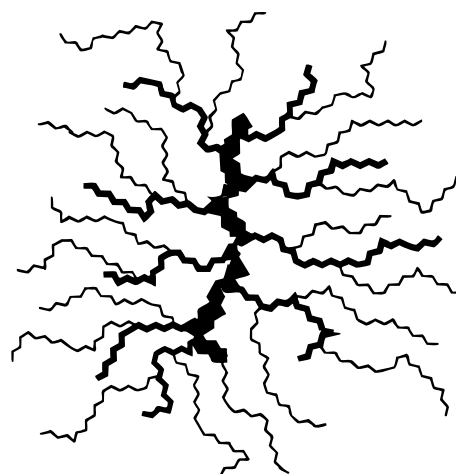
Figure 1. Simplified representation of a first-generation arborescent polymer molecule. The lines of decreasing thickness indicate side chains added in two successive grafting reactions, starting from the core.

entropy contributions according to a proposed scheme[6] can provide useful insight into thermodynamic factors affecting the solubility behavior of polymers. This type of analysis has, to our knowledge, only been applied to linear polymers so far. We propose using this approach to get some insight into the relationships between the structure and the solution behavior of arborescent polymers. The variation of A_2 in these systems will now be examined as a function of branching functionality, branch molecular weight, solvent type, and temperature.

Experimental Procedures

Materials. The arborescent polystyrenes used in the measurements were prepared by successive cycles of chloromethylation and anionic grafting reactions.[1] Two series of branched polymers were investigated. Series S05 was synthesized from

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a backbone polymer with a weight-average molecular weight $M_w = 4.7 \times 10^3$ and a polydispersity index $M_w/M_n = 1.08$. The grafting reactions used side chains with $M_w \approx 5 \times 10^3$ for each generation. The S30 series was prepared from the same linear polymer core but incorporated side chains with $M_w \approx 3 \times 10^4$ for each generation. Residual ungrafted side chains were removed from the samples by precipitation fractionation in toluene/methanol mixtures. Polymers up to generation $G = 2$ (three times grafted) were investigated in each series. The solvents used in the light scattering measurements, cyclohexane (BDH, ACS reagent), and toluene (Caledon, reagent) were purified by distillation. The absolute M_w of the arborescent polymers was determined by light scattering, as described below. The molecular weight distribution of the branches (characterized by M_w and M_w/M_n) was determined by removing a sample of the side chains from the reactor before the grafting reaction and deactivating the anions with degassed methanol. The side chain samples were analyzed by size exclusion chromatography in tetrahydrofuran (THF) using a linear polystyrene standards calibration curve.

Measurements. The refractive index increment (dn/dc) of the polymer solutions was determined as a function of temperature using a Brice-Phoenix differential refractometer equipped with a 510 nm band-pass interference filter. A linear polystyrene sample ($M_w = 7.3 \times 10^4$, $M_w/M_n = 1.05$), $G = 0$ and $G = 1$ samples in the S05 series (S05-0 and S05-1, respectively), and a $G = 0$ sample in the S30 series (S30-0) were investigated. The measurements were carried out in cyclohexane and in toluene, using eight solutions in a concentration range of 0.1–0.7% (w/v) (cyclohexane) or 0.2–1.4% (w/v) (toluene) and a temperature range of 25–65 °C. Corrections were made for the concentration of the solutions, to account for thermal expansion, and the temperature in the cell was controlled to ±0.1 °C throughout the measurements.

Light scattering experiments were done on a Brookhaven Instruments BI-200 SM goniometer equipped with a 2 W Lexel Model 95 argon ion laser. In all measurements, eight solutions with concentrations similar to those in the dn/dc determinations were used. The solutions were clarified by successive filtrations using polytetrafluoroethylene (PTFE) membrane filters with a pore size of either 0.2 or 0.47 μm, depending on the sample. The concentrations of the solutions were corrected for thermal expansion. One series of measurements on all polymers was done in toluene at 25 °C, at angles ranging from 30 to 150°. The Zimm extrapolation technique was used to determine M_w and A_2. Samples of linear polystyrene, S05-0, S05-1, and S30-0 were also investigated as a function of temperature (25–65 °C) in cyclohexane and in toluene. The temperature-dependent measurements were carried out at an angle of 90°, and Debye plots served to determine A_2 from the scattering data. The temperature coefficients ($\partial A_2/\partial T)_p$ were determined by regression analysis of the data collected over the whole temperature range investigated.

Results and Discussion

Molecular Weight Dependence of A_2. The characterization results obtained in toluene at 25 °C are summarized in Table 1. The nomenclature system specifies the composition, side chain molecular weight, and generation number of a sample. For example, S05-0 refers to a styrene-based arborescent polymer with $M_w \approx 5000$ side chains, of generation $G = 0$. The total branching functionality f_w of an arborescent polymer of genera-

TABLE 1: Characterization Results for the Arborescent Polystyrene Samples Investigated

	branches[a]		graft polymers	
sample	M_w^{br}	$(M_w/M_n)^{br}$	$M_w{}^b$	f_w
S05-0	4.3×10^3	1.03	6.7×10^4	14
S05-1	4.6×10^3	1.03	8.7×10^5	180
S05-2	4.2×10^3	1.04	1.3×10^7	3100
S30-0	2.8×10^4	1.15	5.1×10^5	18
S30-1	2.7×10^4	1.09	9.0×10^6	330
S30-2	2.7×10^4	1.09	1×10^8	3700

[a] From SEC analysis in THF. [b] From light scattering measurements in toluene at 25 °C.
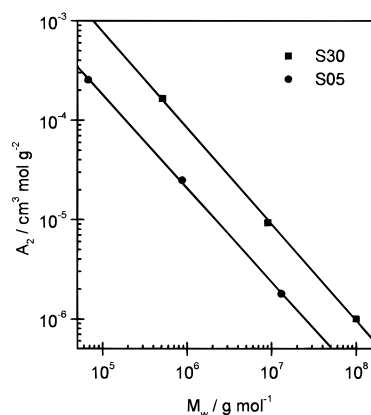
Figure 2. Molecular weight-scaling behavior of A_2 in two series of arborescent polymers with either 5000 (S05) or 30 000 (S30) side chains. Each series of points is for successive arborescent polymer generations, starting from $G = 0$. Measurements performed in toluene at 25 °C.

tion G was calculated from

$$f_w = \sum_{i=0}^{G} \frac{M_w(i) - M_w(i-1)}{M_w(i)^{br}} \tag{1}$$

where $M_w(i)$ and $M_w(i - 1)$ represent the absolute weight-average molecular weights (from light scattering) of the graft polymers of generation i and of the preceding generation, respectively, and $M_w(i)^{br}$ is the weight-average molecular weight of the branches (from SEC analysis). The molecular weight and the branching functionality of arborescent polymers in each series increases roughly exponentially for successive generations, confirming the success of the synthetic procedures used. The SEC data also show that the branches are of uniform size, as expected from anionic polymerization techniques.

The variation of A_2 as a function of molecular weight for each series of arborescent polymers is depicted in Figure 2. While the amount of data is limited (three samples in each series), the second virial coefficient of arborescent polymers clearly scales with molecular weight according to a relation of the type

$$A_2 = kM_w{}^a \tag{2}$$

where k is a constant and the exponent a can be obtained from the slope of the log–log plot. For the S05 series, $a = -0.94 \pm 0.02$ ($r^2 = 0.9996$), and for the S30 series, $a = -0.97 \pm 0.02$ ($r^2 = 0.9995$). For linear polymers, the effects of molecular weight and solvent quality on A_2 can be expressed over the whole molecular weight range as[7]

$$A_2 = A_2^{\infty} + \sigma M^{-(1-\alpha)} \tag{3}$$

where A_2^∞ is for a polymer with an infinitely high molecular weight, σ is a parameter describing the relaxation of polymer coils in the presence of the solvent, and α is the Mark–Houwink–Sakurada exponent relating intrinsic viscosity to molecular weight. For linear polystyrene solutions in toluene, $\alpha \approx 0.70$[8] and an exponent $a \approx -0.3$ is expected in eq 2, leading to a slow decrease in A_2 with increasing molecular weight. For molecules behaving like rigid spheres, in contrast, $a = -1.00$ is predicted.[5] The exponents obtained from light scattering measurements for the S05- and S30-series arborescent polystyrenes clearly demonstrate that these polymers behave like rigid spheres in dilute solution. This is consistent with previous results obtained using viscometry,[9] in which the intrinsic viscosities of arborescent polystyrenes in toluene were found to be almost independent of molecular weight over five generations. Such an effect is expected for rigid sphere molecules, as long as their average densities remain constant over successive generations. The intrinsic viscosity of a dispersion of rigid spheres is given by the Einstein equation,

$$[\eta] = \frac{5}{2} N_A \frac{V_H}{M} \tag{4}$$

where V_H and M are the hydrodynamic volume and the mass of the spheres, respectively, and N_A is Avogadro's number. The ratio V_H/M is the reciprocal of the so-called "hydrodynamic density" of the molecules in solution. As long as the hydrodynamic density of the spheres remains constant, $[\eta]$ should remain constant and independent of their size.

Temperature dependence of A_2. The temperature dependence of A_2 becomes obvious when it is expressed in terms of the excess Gibbs free energy of the solvent ΔG_1^E, according to a scheme proposed by Schulz et al.[6]

$$A_2 = -\Delta G_1^E/RTc_2^2 V_1 \tag{5}$$

where R is the ideal gas constant, c_2 is the polymer concentration, and V_1 is the molar volume of the solvent. The excess Gibbs free energy of the solvent represents the portion of ΔG due to nonideal behavior of the solution:

$$\Delta G_1^E = \Delta G_1(\text{real solution}) - \Delta G_1(\text{ideal solution}) \tag{6}$$

The excess Gibbs free energy of the solvent can be split up into an enthalpy term and an entropy term, leading to a modified form of eq 5,

$$A_2 = A_{2,H} + A_{2,S} = \frac{-\Delta H_1}{RTc_2^2 V_1} + \frac{\Delta S_1^E}{Rc_2^2 V_1} \tag{7}$$

where ΔH_1 is the heat of mixing of the solvent and ΔS_1^E is the excess entropy of the solvent. Differentiating eq 7 with respect to temperature, the two components of A_2 can be rewritten

$$A_{2,H} = T\alpha_1 A_2 - T\left(\frac{\partial A_2}{\partial T}\right)_P \tag{8}$$

$$A_{2,S} = A_2 - A_{2,H} = A_2(1 - \alpha_1 T) + T\left(\frac{\partial A_2}{\partial T}\right)_P \tag{9}$$

where α_1 is the thermal expansion coefficient of the solvent and $(\partial A_2/\partial T)_P$ represents the temperature dependence of A_2 at constant pressure. According to eqs 8 and 9, the contributions of enthalpy and entropy effects to A_2 and the solvation process can be evaluated by examining the temperature dependence of
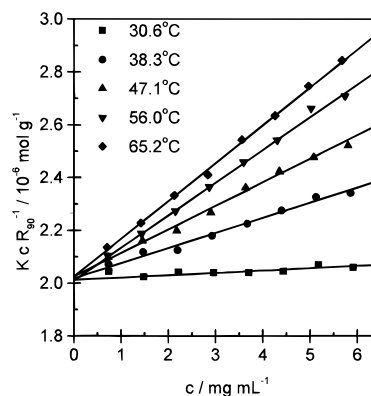

Figure 3. Debye plot for sample S30-0 in cyclohexane at an angle of 90°. The temperatures are as indicated for the individual curves.

A_2. This is the approach selected to investigate the solution behavior of arborescent polymers. The investigation was limited to a few samples, because arborescent polymers have a branched structure and a high molecular weight and correspondingly small virial coefficients. As discussed subsequently, not only A_2 but also its temperature dependence become very small with increasing branching functionality and molecular weight, making it difficult to produce reliable results using light scattering measurements on higher generation arborescent polymers. Therefore, the study was limited to samples S05-0 and S05-1 in the short-branch series and to S30-0 in the long-branch series. A linear polystyrene sample with a molecular weight comparable to that of S05-0 was also investigated for comparison purposes.

The intrinsic viscosity of arborescent polystyrenes in solution was already examined in cyclohexane and in toluene, typical poor and good solvents for polystyrene, respectively, to explore the influence of structure and of solvent quality on molecular expansion of the branched polymers.[9] Arborescent polystyrenes with short (5000) side chains displayed very little expansion in toluene relative to cyclohexane. Molecular expansion was much more noticeable in the case of polymers with long side chains (30 000). Cyclohexane and toluene were also selected for the light scattering measurements reported in this work, to provide further insight into the effect of branching functionality and branch length on polymer–solvent interactions. While star-branched polymers have been the object of many investigations,[3] arborescent polymers provide an interesting opportunity in that higher branching functionalities can be attained than in most star-branched polymer systems (e.g., $f_w = 180$ for S05-1). Also, star-branched polymers have been studied mostly in terms of variation in the Θ temperature and A_2 as a function of structure, but not in terms of the more detailed enthalpy and entropy effect analysis discussed here. Because of the very distinct character of cyclohexane and toluene as solvents for polystyrene, the results obtained in each case will be presented separately.

Cyclohexane Solutions. An example of raw scattering data for the temperature-dependent measurements in cyclohexane is provided in Figure 3 for sample S30-0 over a temperature range of 30–65 °C. The slopes of the plots ($2A_2$) increase with temperature as expected, due to increasing solvent quality. The good linearity of the plots confirms that the data do not have significant A_3 contributions in the concentration range used for the measurements.

The variation of A_2 with temperature for the linear sample and three arborescent polymers in cyclohexane is compared in Figure 4. The magnitude of A_2 for all polymers is lower in cyclohexane than in toluene, since it is a poorer solvent. The relative variation of A_2 (and solvent quality) with temperature,

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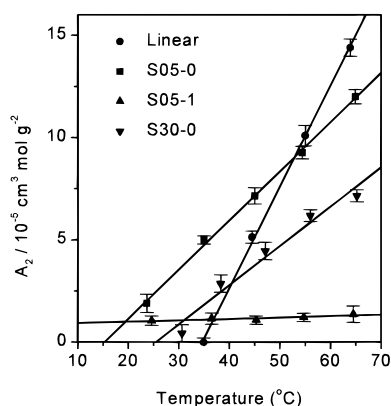
Figure 4. Temperature dependence of A_2 for linear and arborescent polystyrene samples in a poor solvent (cyclohexane).

TABLE 2: Temperature Coefficient of A_2 and Θ-Temperature Determined from Light Scattering Measurements at an Angle of 90°

	cyclohexane		toluene
sample	$(\partial A_2/\partial T)_P/$ $(10^{-6}\ cm^3 \cdot mol \cdot g^{-2} \cdot K^{-1})$	$\Theta_+/°C$	$(\partial A_2/\partial T)_P/$ $(10^{-6}\ cm^3 \cdot mol \cdot g^{-2} \cdot K^{-1})$
linear	5.0 ± 0.1	34.6	1.3 ± 0.3
S05-0	2.40 ± 0.06	15.3	0.9 ± 0.2
S05-1	0.07 ± 0.02		0.03 ± 0.07
S30-0	1.9 ± 0.2	25.4	0.0 ± 0.5

however, is quite pronounced. Cyclohexane is a known Θ solvent for polystyrene, with an endothermal Θ temperature $\Theta_+ = 34.5$ °C for high molecular weight polymers. The effect of branching on Θ_+ is well-characterized for star-branched polymers.[3] An increased branching functionality at constant total molecular weight leads to a decrease in Θ_+, and an increase in arm length at constant branching functionality results in Θ_+ moving closer to the limiting (34.5 °C) value. The Θ temperatures determined for the polymers investigated in this study are given in Table 2. The trends observed are mainly as expected, the linear polymer having $\Theta_+ = 34.6$ °C, followed by S30-0 ($\Theta_+ = 25.4$ °C) and S05-0 ($\Theta_+ = 15.3$ °C). Interestingly, sample S05-1, with a branching functionality $f_w = 180$, has no detectable Θ temperature. This suggests that solvent quality is invariant with temperature for polymers incorporating a large number of arms. The temperature dependence of A_2 in cyclohexane has been examined for six-arm star-branched polystyrenes.[11] A lower temperature coefficient was observed as a function of increasing arm molecular weight at constant branching functionality. No similar data were reported in terms of the influence of branching functionality at constant arm molecular weight.

The temperature coefficients $(\partial A_2/\partial T)_P$ of the polymers investigated, determined from the slope of the curves in Figure 4, are summarized in Table 2. The relations observed between arborescent polymer structure and $(\partial A_2/\partial T)_P$ are consistent with the trends mentioned for star-branched polymers. Sample S30-0

has a branching functionality comparable to S05-0, but a side chain molecular weight about six times higher. The temperature coefficient of S30-0 is correspondingly smaller. Furthermore, the effect of branching functionality becomes apparent when comparing the results obtained for samples S30-0 and S05-1. The two samples have comparable molecular weights, but S05-1 ($M_w = 8.7 \times 10^5$, $f_w = 180$) has a branching functionality 10 times higher than S30-0 ($M_w = 5.1 \times 10^5$, $f_w = 18$). The $(\partial A_2/\partial T)_P$ value is 27 times lower for S05-1 than for S30-0. This clearly indicates that the branching functionality of arborescent polymers has more influence on the temperature dependence of polymer–solvent interactions than the side chain (or overall) molecular weight.

Decomposition of A_2 into its components $A_{2,H}$ and $A_{2,S}$ (Table 3) reveals major differences in comparison with the toluene solutions, as well as among the branched polymer samples. The enthalpy and entropy components for linear polystyrene in cyclohexane at 35 °C are large, of equal magnitude and opposite in sign, since it is very close to $\Theta_+ = 34.6$ °C. Likewise for S05-0 and S30-0, $A_{2,H}$ and $A_{2,S}$ are 16–33 times larger than the global values. This effect was also observed in previous studies of linear polymer solutions such as polystyrene in cyclohexane[12] and poly(methyl methacrylate) in various solvents[6] close to Θ conditions. While the global A_2 values are very small, leading to "pseudoideal" solution behavior, enthalpy and entropy effects are still important.

The effect of polymer structure on solution thermodynamics can be deducted by comparing the trends observed within the series of polymers characterized. For polymers of comparable molecular weight (linear sample and S05-0), $A_{2,H}$ and $A_{2,S}$ both decrease by about 50% as a result of branching. For polymers with a similar branching functionality but different side chain lengths (S05-0 and S30-0), a less pronounced decrease in these parameters, and similar to what would be expected for linear polymers, is also observed. This suggests that branching functionality has somewhat more influence on $A_{2,H}$ and $A_{2,S}$ than the side chain molecular weight. Sample S05-1 has a 13-fold higher branching functionality than S05-0 and a molecular weight only 70% higher than S30-0, but it also has by far the smallest $A_{2,H}$ and $A_{2,S}$ values observed. Once again, this result is consistent with a stronger influence of branching functionality over side chain molecular weight on the magnitude of $A_{2,H}$ and $A_{2,S}$. Based on these results, branching functionality seems to influence the magnitude of $A_{2,H}$ and $A_{2,S}$ similarly in a *poor solvent*, and in a more pronounced fashion than either the side chain or overall molecular weight of the polymers. A drop in $A_{2,S}$ as a result of branching intuitively seems reasonable, since a higher branching functionality is expected to lead to increased molecular rigidity and correspondingly to a lower excess entropy of mixing. Comparing the linear polymer and the branched polymers in the S05 series, $A_{2,H}$ decreases about 100-fold as a result of increased branching functionality and molecular weight, corresponding to a strong trend toward increasingly athermal solution behavior. The entropy parameter, likewise, decreases

TABLE 3: Enthalpic and Entropic Contributions to A_2 Calculated at 35 °C in Toluene and Cyclohexane Solutions

	cyclohexane			toluene		
sample	$A_2/$ $(cm^3 \cdot mol \cdot g^{-2})$	$A_{2,H}/$ $(10^{-4}\ cm^3 \cdot mol \cdot g^{-2})$	$A_{2,S}/$ $(10^{-4}\ cm^3 \cdot mol \cdot g^{-2})$	$A_2/$ $(cm^3 \cdot mol \cdot g^{-2})$	$A_{2,H}/$ $(10^{-4}\ cm^3 \cdot mol \cdot g^{-2})$	$A_{2,S}/$ $(10^{-4}\ cm^3 \cdot mol \cdot g^{-2})$
linear	0	-15.3 ± 0.3	15.3 ± 0.3	7.2×10^{-4}	-2 ± 1	9 ± 1
S05-0	4.8×10^{-5}	-7.2 ± 0.2	7.7 ± 0.2	2.7×10^{-4}	-1.8 ± 0.7	4.5 ± 0.7
S05-1	1.1×10^{-5}	-0.17 ± 0.07	0.28 ± 0.07	2.7×10^{-5}	a	a
S30-0	1.8×10^{-5}	-5.8 ± 0.6	-6.0 ± 0.6	1.5×10^{-4}	a	a

^{a} Calculation not attempted, because of the large error on $(\partial A_2/\partial T)_P$.
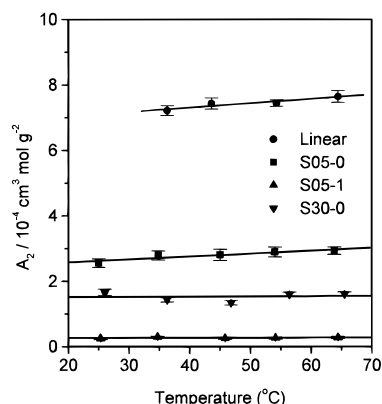
Figure 5. Temperature dependence of A_2 for linear and arborescent polystyrene samples in a good solvent (toluene).

50-fold. It therefore seems impossible to change $A_{2,H}$ and $A_{2,S}$ completely independently from each other simply by varying the structure of the polymers.

Toluene Solutions. The variation of A_2 with temperature in toluene is compared in Figure 5 for the linear and three arborescent polystyrenes investigated. For linear polystyrene, a decrease in $(\partial A_2/\partial T)_P$ with increasing molecular weight has been reported in toluene solutions.[10] The slope values determined for each of the curves in Figure 5, $(\partial A_2/\partial T)_P$, are summarized in Table 2. Solvent quality does not vary widely in toluene (a good solvent) over the temperature range examined (25−65 °C), and the temperature coefficients are correspondingly small. The linear sample and S05-0 have a comparable M_w, and the branched polymer has a somewhat smaller temperature coefficient in toluene, although the effect is not clearcut since the error domains of the two parameters overlap. For the higher molecular weight samples (S05-1 and S30-0), on the other hand, $(\partial A_2/\partial T)_P$ is zero within experimental error limits. This suggests that the nature of solvent−solute interactions of branched polymers with a good solvent become less sensitive to temperature, not only as a function of increasing molecular weight (as with linear polymers) but also with increasing branching functionality.

The enthalpic ($A_{2,H}$) and entropic ($A_{2,S}$) components calculated at 35 °C according to the procedure outlined above for linear polystyrene and S05-0 are compared in Table 3. No calculations were attempted for S05-1 and S30-0, because of the large errors on the $(\partial A_2/\partial T)_P$ values. The two components are of comparable magnitude to A_2 and opposite in sign. The entropy component is larger than $A_{2,H}$ and positive, indicating that the dissolution process is entropy-driven for the linear polymer and S05-0. Since $A_{2,H}$ is small compared with $A_{2,S}$ and negative, the solutions are only slightly endothermal according to eq 7, in agreement with previous findings for high molecular weight linear polystyrene solutions in toluene.[10] The limited results in Table 3 suggest that, for polymers of comparable molecular weight in a *good solvent*, branching has little influence on the enthalpic component of A_2, while the magnitude of the entropic component (or ΔS_1^E) decreases. As discussed for the cyclohexane solutions, this seems reasonable since branching necessarily implies increased molecular rigidity and fewer arrangements possible for the solvent molecules, and therefore a decreased importance of entropy effects in the dissolution process.

Conclusions

The light scattering results obtained illustrate some of the unusual properties of arborescent polymers. The well-defined

structure of these molecules may also be useful in terms of predicting the solution properties of star-branched polymers with high branching functionalities and of branched polymers in general. Some of the properties observed such as hard-sphere behavior are reminiscent of condensation-type dendritic polymers. The structure−property relations established in terms of A_2 variation with branching functionality and side chain dimensions are consistent with what is known for star-branched polymers. The variation of A_2 with temperature in good and poor solvents alike became negligible not only as a function of increasing molecular weight but also with increasing branching functionality. This temperature invariance led to no measurable Θ temperature for sample S05-1 in cyclohexane. The more detailed thermodynamic analysis used in terms of enthalpy and entropy components, not previously applied to branched polymer systems, revealed interesting additional features. The entropy component ($A_{2,S}$) consistently decreased in good and poor solvents alike as a result of branching, in addition to the contribution from increased molecular weight observed in linear polymers. This effect is attributed to increased molecular stiffness leading to a less pronounced contribution of entropy effects in the dissolution process. The enthalpy component ($A_{2,H}$) in a good solvent, on the other hand, did not seem to vary strongly with branching but was affected similarly to $A_{2,S}$ in a poor solvent. Due to problems inherent to their high molecular weight and branching functionality, temperature-dependent measurements could only be carried out on three of the arborescent polymer samples available. Even though these results are limited, they form an interesting basis for a systematic investigation of the effect of branching functionality and branch size on the solution properties of arborescent polymers. It is hoped that, in the future, a wider range of arborescent polymer samples of related structure with A_2 values within a range readily accessible experimentally will be investigated.

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