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Polymer 42 (2001) 2579–2584

polymer

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# Dilute-solution properties of arborescent polystyrenes: further evidence for perturbed-hard-sphere behavior

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Received 14 February 2000; received in revised form 11 August 2000; accepted 15 August 2000

## Abstract

Toward improved understanding of the dilute-solution properties of arborescent polystyrenes, new measurements are reported for osmotic second virial coefficients and for intrinsic viscosities in three common organic solvents. As observed for other branched polymers, branching decreases the second virial coefficient in good solvents and lowers the theta temperature for a polymer–solvent system. For generation-zero arborescent polystyrene in methylcyclohexane, the theta temperature is 36 ± 2°C.

A correspondence between intrinsic viscosity and second virial coefficient, valid for hard-spheres solutions, holds in good solvents; this correspondence improves with decreasing branch molecular weight.

The osmotic-pressure data are interpreted with a colloid-like thermodynamic framework using a van der Waals-type equation of state. The reference state is the hard sphere and the perturbation is given by an attraction decaying with the sixth power of the center-to-center distance between polymers. The hard-sphere diameter is obtained from intrinsic-viscosity data. Predicted and observed osmotic pressures are in good agreement. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords*: Arborescent polystyrene; Osmotic second virial coefficient; Intrinsic viscosity

## 1. Introduction

Dendritic polymers are a class of highly branched polymers with controllable architecture. Using convergent or divergent synthetic schemes [1,2], it is possible to build dendrimers with ‘ad-hoc’ functionalized surfaces. In general, because dendrimer building blocks are small molecules, many steps are required to produce a high-molecular-weight material. Gauthier and coworkers developed a synthetic ‘graft-on-graft’ technique using polymers as building blocks [3–5]. Through this technique, arborescent polymers of ultra-high molecular weight can be obtained in fewer steps than those required by traditional dendrimer syntheses [6,7]. Melt rheology [8] and dilute-solution properties [3] suggest that upon developing generation-one into generation-two arborescent polymers, a transformation from flexible, branched polymers to rigid, spherically-shaped macromolecules occurs [8]. The spherical shape of arborescent polymers allows the production of ultra-thin films [6].

Several experimental studies suggest that arborescent polymers behave like hard spheres in dilute solution. Static and dynamic light-scattering experiments in toluene give the molecular-weight dependence of the translational diffusion coefficient, radius of gyration, and second virial coefficient; these dependence follow the behavior typical of hard spheres [4]. The molecular-weight independence of intrinsic-viscosity at fixed temperature in toluene and cyclohexane is also a typical feature of solutions of hard spheres [7]. In the same solvents, the hydrodynamic radius varies with the molecular weight raised to the 1/3 power, a typical characteristic of hard-sphere behavior [7]. Measurements in the semidilute regime, however, showed a progressive structural stiffening effect as the branching density increases [4].

In concentrated polymer solutions, branching increases the sorption of poor solvents [9] but the effect upon sorption of good solvents is negligible.

In dilute solutions, arborescent polymers present peculiar characteristics. The theta temperature (the temperature where the osmotic second virial coefficient is zero [10])

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PII: S0032-3861(00)00625-X

Table 1
Polymer characterization data

| Polymer | Side chains | | Whole sample | | |
|---|---|---|---|---|---|
| | $M_w$ (g/mol) | $M_w/M_n$ | $M$ (g/mol) | $M_w/M_n$ [a] | Number of branches |
| Linear[b] | – | – | 53,100[c] | 1.06 | – |
| G0 | 5220 | 1.07 | 66,700[d] | 1.18 | 12 |
| G1 | 6160 | 1.06 | 727,000[d] | 1.18 | 108 |
| G2 | 5210 | 1.07 | 5,030,000[d] | 1.11 | 826 |
| G3 | 5960 | 1.06 | 22,300,000[d] | 1.15 | 2900 |

[a] By size-exclusion chromatography, using a linear polystyrene standards calibration curve.

[b] Sample purchased from Polysciences Inc., lot # 480592.

[c] Number-average molecular weight by membrane osmometry.

[d] Weight-average molecular weight by light scattering.

for arborescent polystyrenes in cyclohexane is lower than that for the linear homolog [11]. There is evidence that the difference between the theta temperatures for linear and for arborescent polymers increases with decreasing branch molecular weight [11], in agreement with experimental evidence for other kinds of branched polymers [12].

The purpose of this work is to investigate further the influence of polymer architecture on intermolecular interactions in dilute solutions. With a membrane osmometer, osmotic second virial coefficients were measured for generation-zero and for generation-one arborescent polystyrenes in toluene (good solvent) and in cyclohexane (theta solvent), and for generation-zero arborescent polystyrene in methylcyclohexane (poor solvent). Intrinsic viscosity measurements, reported here, in cyclohexane and methylcyclohexane provide information on the ‘coil-to-globule’ transition [13,14]. These measurements also provide the hydrodynamic radii for the polymers studied here.

As suggested by previous studies [3,4,7], a perturbed-hard-sphere model is suitable for calculating osmotic pressures. In the McMillan–Mayer [15] framework, the osmotic-pressure data were correlated with a colloid-like potential of mean force, using a hard sphere as reference [16], and a perturbation described by an attractive potential decaying with the sixth power of the center-to-center distance between polymer molecules.

## 2. Materials and experimental results

Arborescent polystyrenes of generations zero, one, two and three were studied, together with a linear polystyrene. Polymers characteristics are shown in Table 1. Solvents used were toluene (from Fisher Sc.), a good solvent for polystyrene, cyclohexane (from Fisher Sc.), a theta solvent, and methylcyclohexane (from Aldrich), a poor solvent. Solvent purity was at least 99%. Solvents were used as received, while polymers were kept under vacuum for a few days before the osmotic-pressure measurements to ensure the absence of low-molecular-weight impurities.

From the customary virial expansion of the osmotic pressure $\Pi$ as a function of polymer concentration, we obtain the osmotic second virial coefficient $B_{22}$ [10,17]. $B_{22}$ is positive for a polymer in a good solvent, negative for a polymer in a poor solvent and zero at the theta temperature [10].

Osmotic pressures of polymer solutions were measured with a Jupiter Inst. Co. Membrane Osmometer model 231 (Jupiter, FL, USA) for several low concentrations. The cellulose-acetate membrane has a molecular-weight cutoff

Table 2
Number-average molecular weight $M_n$ and second osmotic virial coefficient $B_{22}$ from osmometry. Radii, $R$, from intrinsic viscosity and energetic parameter $H$ used to fit Eq. (4) to the experimental osmotic-pressure data

| Polymer | Solvent | $T$ (°C) | $M_n$ ($10^3$ g/mol) | $B_{22}$ ($10^{-4}$ cm$^3$ mol/g$^2$) | $R$ (Å) | $H$ ($k_BT$) |
|---|---|---|---|---|---|---|
| Linear | Toluene | 49.2 | 59.5 ± 1.4 | 2.6 ± 0.2 | – | – |
| G0 | Toluene | 38.6 | 68.1 ± 0.2 | 2.15 ± 0.03 | 48 | 0.526 |
| G0 | Toluene | 47.7 | 64.5 ± 1.2 | 2.16 ± 0.17 | 48 | 0.314 |
| G1[a] | Toluene | 38.5 | 940 ± 60 | 0.148 ± 0.03 | 112 | 0.949 |
| G1[a] | Toluene | 47.8 | 800 ± 20 | 0.15 ± 0.03 | 112 | 0.547 |
| G0 | Cyclohexane | 32.2 | 61.8 ± 0.8 | 0.32 ± 0.10 | 47.4 | 0.835 |
| G1[a] | Cyclohexane | 32.2 | 592 ± 4 | 0.060 ± 0.003 | 102.6 | 0.045 |
| G1[a] | Cyclohexane | 43.0 | 787 ± 3 | 0.20 ± 0.04 | 103.3 | 0.270 |
| G0 | Methylcyclohexane | 32.6 | 65.7 ± 1.2 | −0.68 ± 0.10 | 45 | 1.227 |
| G0 | Methylcyclohexane | 41.6 | 67.6 ± 0.8 | 0.49 ± 0.08 | 46 | 0.961 |

[a] Molecular weight too high to be determined accurately by membrane osmometry.

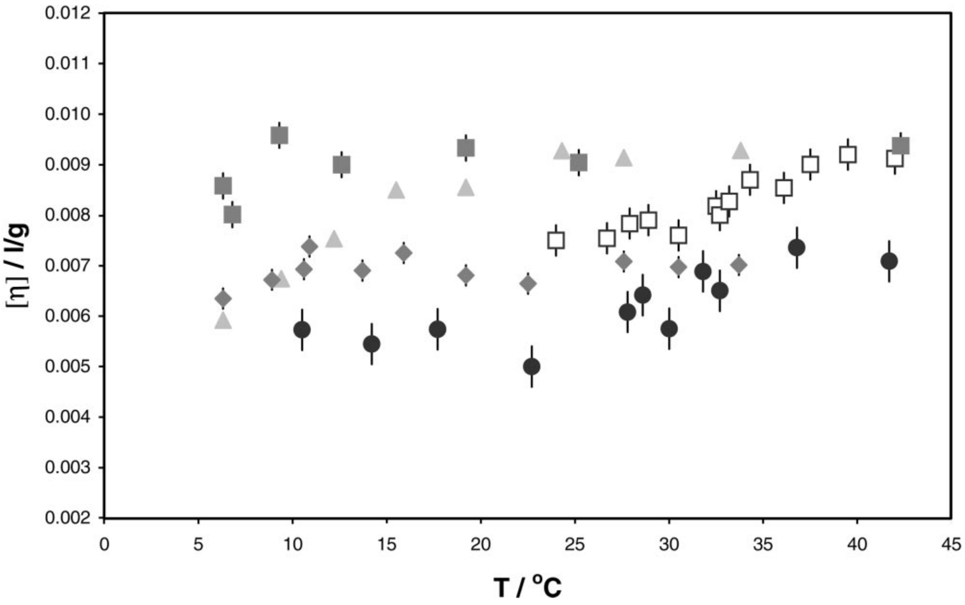

Fig. 1. Intrinsic viscosity as a function of temperature for arborescent polystyrenes, different generations, in methylcyclohexane (empty symbols) and in cyclohexane (full symbols). Squares represent G0 arborescent polymer, triangles G1, diamonds G2 and circles G3.

at 20,000 g/mol. $B_{22}$ for generation-zero (sample G0) and generation-one (sample G1) polymers were measured in toluene and in cyclohexane. $B_{22}$ for G0 were also measured in methylcyclohexane at different temperatures. Because osmotic pressure is a colligative property, a function of the number of molecules in solution, dilute solutions (10–20 g/l) of high-molecular-weight generation-two (G2) and generation-three (G3) arborescent polymers give osmotic pressures that are too low for accurate measurement with our instrument. Osmotic-pressure measurements for polymeric solutions with higher concentrations are not feasible because the solution viscosity becomes too large.

Results for $B_{22}$ are listed in Table 2. The results observed in toluene and cyclohexane generally agree with those obtained with light scattering [11]; because those data are for slightly different polymers, they are not reported here. The observed differences may be due to the higher concentrations required to measure osmotic pressures: small contributions from three-body interactions may be reflected in the data from osmometry. The experimental number-average molecular weights from membrane osmometry are in good agreement with the polymer specifications given in Table 1 for the arborescent polymer of generation-zero, when sample polydispersity is taken into account. G1 arborescent polymer has a molecular weight too high to be determined with accuracy by membrane osmometry.

In a good solvent, $B_{22}$ is lower for arborescent polymers than that for linear homologs. Branching lowers the theta temperature for a branched polymer in a solvent, when compared to that of the linear homolog.

By interpolation, osmotic-pressure data for G0 polystyrene in methylcyclohexane at two different temperatures yield a theta temperature of 36 ± 2°C. The theta temperature for linear polystyrene in methylcyclohexane lies between 60 and 70°C [18].

At 32.2°C, the osmotic second virial coefficient for G0 in cyclohexane is positive, indicating that the theta temperature for G0 arborescent polystyrene in cyclohexane is lower than that for the linear homolog (34.5°C) [19]. No additional experiments were performed to determine the theta temperature, already known for a similar polymer–solvent system [11].

The intrinsic viscosity, $[\eta]$, for sufficiently long polymer chains [14] is a function of the radius of gyration according to:

$$[\eta] = \frac{\Phi \langle S^2 \rangle^{3/2}}{M_v} \tag{1}$$

where $\Phi$, $\langle S^2 \rangle$, $M_v$ are, respectively, Flory's viscosity factor [20], the average radius of gyration squared, and the polymer viscosity-average molecular weight [19]. The factor $\Phi$ is essentially constant for a given polymer architecture [21]. A linear polymer contracts to a compact form when the solvent quality decreases as, for example, when lowering the temperature [22,23]. For high-molecular-weight linear chains, the hydrodynamic-radius contraction associated with a coil-to-globule transition is significant. Contraction is due to a collapse to very small dimensions within a narrow temperature region below the theta temperature, and a slight expansion at higher temperatures [24–26]. However, for low-molecular-weight chains, the coil-to-globule transition does not imply a significant collapse [26]. Because of the compact structure that characterizes arborescent polymers made by low-molecular-weight

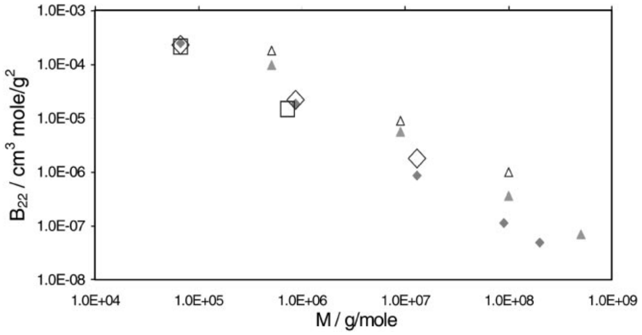

Fig. 2. $B_{22}$ for arborescent polystyrenes in toluene as a function of molecular weight. Comparison between experimental data (empty symbols) and predictions from Eq. (3) using intrinsic-viscosity data (full symbols). $[\eta]$ from Gauthier et al. [7]. Triangles are for arborescent polymers obtained from a linear polystyrene core and side chains with a molecular weight of 30,000 g/mol [11]. Diamonds are for arborescent polymers obtained from a linear core and side chains of 5000 g/mol [11]. Squares represent $B_{22}$ measured in this work.

branches [7], their coil-to-globule transition likely resembles that of low-molecular-weight chains.

Intrinsic-viscosity measurements were performed with a standard viscometer of the Ubbelohde type. The temperature was maintained constant within ±0.2°C using a water bath. $[\eta]$ for G0, G1, G2, and G3 polymers in cyclohexane, and for G0 in methylcyclohexane, were measured at different temperatures, to observe the coil-to-globule transition near the theta temperature [13,14,26,27]. Our measurements for the molecular weight of G0 arborescent polystyrene in methylcyclohexane at 32.6 and at 41.6°C exclude molecular aggregation in this temperature range. Molecular-weight data for arborescent polymers, obtained by light-scattering experiments in cyclohexane, exclude intra-chain association [28].

Fig. 1 shows $[\eta]$ as a function of temperature. For the G0 sample, $[\eta]$ does not depend significantly on temperature in cyclohexane, while in methylcyclohexane there is a strong dependence. The data suggest that the G0 sample does not display a coil-to-globule transition in cyclohexane, although $[\eta]$ seems to decrease below 10–15°C, in agreement with a theta temperature lower than that for linear polystyrene in the same solvent. For a polymer similar to G0, Gauthier and coworkers found a theta temperature near 15°C [11]. Because the coil-to-globule transition occurs at temperatures close to the theta temperature, the intrinsic-viscosity data in methylcyclohexane agree with the theta temperature determined by membrane osmometry for this polymer–solvent system.

For the G1 sample in cyclohexane, $[\eta]$ decreases at temperatures below 25°C, suggesting a coil-to-globule transition.

For the G2 polymer, $[\eta]$ is almost constant with temperature; therefore, there is no evidence of a coil-to-globule transition, possibly because of the globular structure developed upon building the G2 molecules from the G1 homologs [8]. This polymer may present a compact, globular, very dense morphology at every temperature in the range studied. Further shrinking becomes unfeasible due to steric effects.

For the G3 sample, $[\eta]$ decreases below 33°C, suggesting a transition in cyclohexane very close to the theta temperature of linear polystyrene in the same solvent. Because G3 polymers should present a denser structure than G2, this experimental evidence is contrary to the general observation that branching lowers the theta temperature for a given polymer–solvent system. G3 polymers with branch molecular weight comparable to the one used here shows differences when compared to other arborescent polymers also in diffusion studies [29] and in the production of mononuclear films [6]. Further experimental work is required to understand the thermodynamic properties of G3 arborescent polymers.

While additional experimental determination of $B_{22}$ for G2 and G3 polymers in the solvents here considered will be useful, membrane osmometry is not adequate for such experiments. Additional information might be obtained by dynamic light-scattering techniques. It was not possible to prepare solutions with G1 arborescent polymer in methylcyclohexane of concentrations suitable for osmotic-pressure measurements.

## 3. Discussion

For a dispersion of hard spheres, the Einstein equation relates intrinsic viscosity to hydrodynamic radius $R_H$ according to

$$[\eta] = \frac{10\pi}{3} \times N_A \times \frac{R_H^3}{M} \tag{2}$$

where $N_A$ and $M$ are Avogadro's number and the mass of the sphere.

For rigid-sphere molecules with negligible attractive interactions, it is possible to obtain an 'effective' radius $R_T$ from $B_{22}$ [30] using

$$B_{22} = \frac{16\pi}{3} \times N_A \times \frac{R_T^3}{M^2} \tag{3}$$

For monodisperse spheres of uniform density, the hydrodynamic radius is equal to the effective radius [12]. The morphology of a hyperbranched polymer, like an arborescent polymer, is similar to that of a hard sphere [4,7]. Fig. 2 shows $B_{22}$ measured by membrane osmometry (this work) or by light scattering [11] as a function of molecular weight, together with $B_{22}$ calculated from intrinsic-viscosity data in toluene. Data for $[\eta]$ are from Gauthier et al. [7]. The polymer weight-average molecular weight was used for $M$. The symbols are larger than the experimental uncertainty. Because intermolecular attractions are neglected, we cannot expect to obtain a good estimate of $B_{22}$ by combining Eqs. (2) and (3). However, for arborescent polymers of the same generation in a good solvent, the correspondence is reasonable and improves with decreasing branch molecular

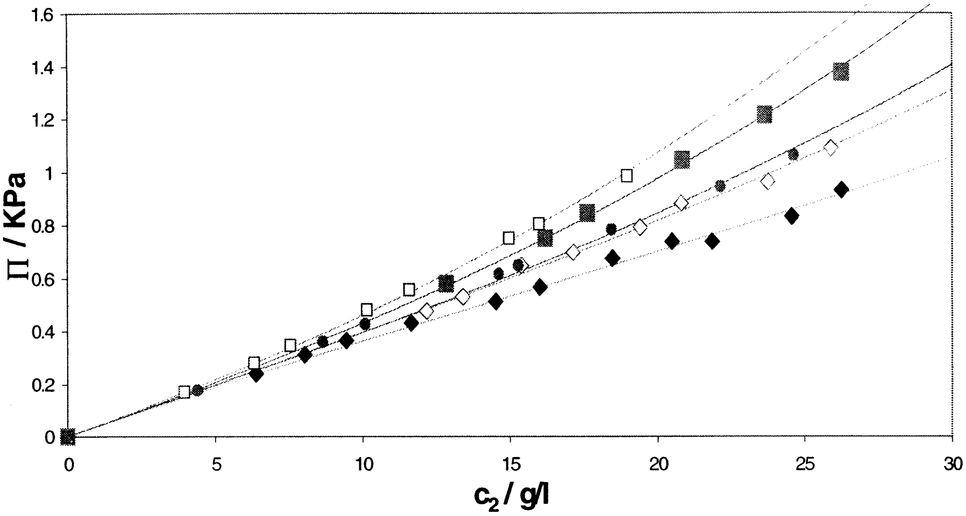

Fig. 3. Osmotic pressures for generation-zero arborescent polystyrene in different solvents. Symbols are experimental data; lines are calculated from Eq. (4). Squares are for data in toluene (filled at 38.6°C, empty at 47.7°C); circles are for data in cyclohexane at 32.2°C, and diamonds are for data in methylcyclohexane (filled at 32.6°C, empty at 41.6°C).

weight; in other words, correspondence improves with increasing spherical morphology of the polymer in solution. In cyclohexane, a poor solvent, the correspondence remains generally valid, but only at temperatures higher than the theta temperature, because the relation between $[\eta]$ and $B_{22}$ fails at the theta temperature and Eq. (3) holds only for positive second virial coefficients.

## 4. Osmotic pressure from a theoretical equation of state

Static and dynamic light-scattering experiments [4,11], intrinsic-viscosity measurements at constant temperature [7], and other experimental evidence [6,8], suggest that arborescent polymers in dilute solutions can be viewed as essentially spherical macromolecules. Therefore their thermodynamic properties in solution may be described with a colloid-like framework.

The osmotic-pressure data are readily reproduced with a van der Waals-type equation of state. The reference state is the hard-sphere system [16]; the perturbation is given by an attractive potential energy that scales with the sixth power of the inverse distance between polymers $r$

$$\frac{\Pi}{\rho kT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} + 2\pi\rho \times \int_{\sigma}^{\infty} \left\{ 1 - \exp\left[ -\frac{H}{kT}\left(\frac{\sigma}{r}\right)^6 \right] \right\} r^2 \, dr \qquad (4)$$

In Eq. (4), $\Pi$, $\rho$, $\eta$, and $\sigma$, are respectively, the osmotic

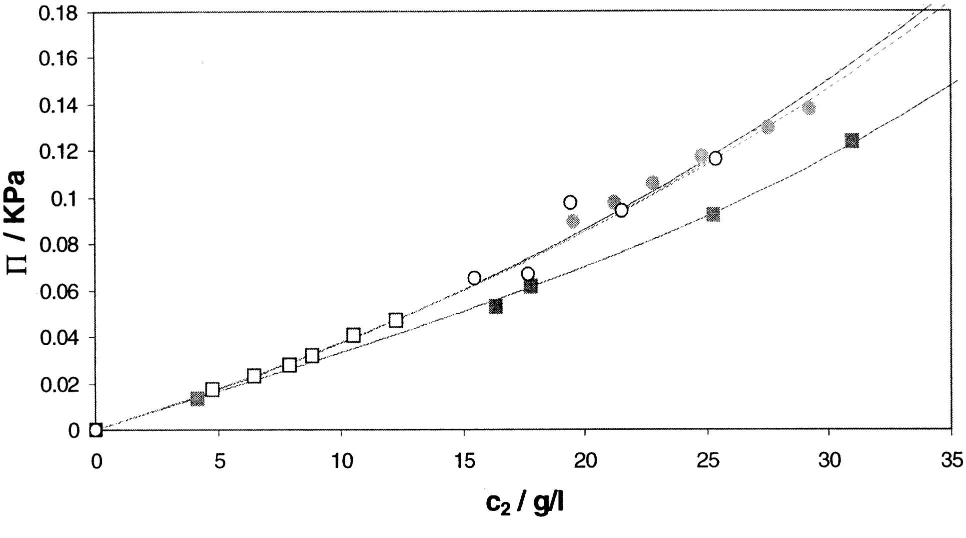

Fig. 4. Osmotic pressures for generation-one arborescent polystyrene in different solvents. Symbols are experimental data; lines are calculated from Eq. (4). Squares are for data in toluene (filled at 38.5°C, empty at 47.8°C); circles are for data in cyclohexane (filled at 32.2°C, empty at 43.0°C).

pressure, the polymer number density, the packing fraction ($\eta = (\pi/6)\rho\sigma^3$), and the hard-sphere diameter; $H$ represents the long-range attractive energy parameter. The parameters used to fit Eq. (4) to the experimental data are listed in Table 2. Because the hydrodynamic radius is obtained from $[\eta]$, the only adjustable parameter is $H$; our results for $H$ are similar to Hamaker constants reported for polymer solutions [31,32]. The fitted osmotic pressures are compared for the G0 (Fig. 3) and G1 (Fig. 4) polymers in different solvents. In all cases fits are reasonable, confirming the colloid-like nature of these dissolved polymers.

## 5. Conclusions

New osmotic second virial coefficients $B_{22}$ are reported for solutions of arborescent polystyrenes in toluene, cyclohexane and methylcyclohexane. In a good solvent, due to the smaller radius of gyration, $B_{22}$ for a branched polymer is always lower than that for the homologous linear polymer. In a theta solvent, branching tends to increase solubility, lowering the theta temperature. For generation-zero arborescent polystyrene in methylcyclohexane, the theta temperature is $36 \pm 2$°C.

Intrinsic-viscosity data were used to obtain polymer size and to estimate osmotic second virial coefficients. In good solvents, predicted and observed second virial coefficients agree well. Agreement improves with decreasing branch molecular weight.

Because these polymers are considered to be essentially spherical macromolecules, the experimental osmotic pressures have been fitted with a molecular-thermodynamic equation suitable for colloids. The good fits obtained provide further evidence for the perturbed-hard-sphere behavior of arborescent polymers in dilute solutions.

## Acknowledgements

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Science Division of the US Department of Energy under Contract Number DE-AC03-76SF00098. For financial support, A.S. thanks Fondazione ‘Ing. Aldo Gini’ and M.G. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors are grateful to Prof. S.J. Muller for use of her viscometer and for valuable discussions, and to S. Sackmann, A. Calabria, D. Wong, J. Ward and C.-J. Lee for assistance in data acquisition.

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