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Chemical Sciences Division

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**Dilute-Solution Properties of Arborescent
Polystyrenes: Further Evidence for
Perturbed-Hard-Sphere Behavior**

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Dilute-Solution Properties of Arborescent Polystyrenes: Further Evidence for Perturbed-Hard-Sphere Behavior

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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 $36\pm 2^\circ\text{C}$.

The spherical topology of these polymers allows a correspondence between intrinsic viscosity and second virial coefficient that holds in good solvents; this correspondence improves with decreasing branch molecular weight.

The osmotic-pressure data are interpreted using 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 second virial coefficients are in good agreement.

Key words: Arborescent Polystyrene, Osmotic Second Virial Coefficient, Intrinsic Viscosity, van der Waals-type Equation of State

Introduction

Dendritic polymers are a class of highly branched polymers with a controllable architecture. The structure of these polymers can be approximated by a set of concentric layers derived from a central core, and terminating in an external surface. Using convergent or divergent synthetic schemes [1]-[3], it is possible to build polymers 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. However, Gauthier and coworkers developed a synthetic 'graft-on-graft' technique using polymers as building blocks [4]-[6]. Through this technique, arborescent polymers of

ultra-high molecular weight with a compact, spherical topology [7], [8] can be obtained in fewer steps than those required by traditional dendrimer syntheses.

Figure 1 is a schematic representation of the structure of a generation-one arborescent polymer. The transformation from flexible, branched polymers to rigid, spherically-shaped macromolecules occurs upon developing generation one into generation two [9]. Arborescent graft polymers are similar to colloidal particles because the large molecules possess a well-defined spherical surface [7]. Their shape allows the production of ultra-thin films [7]. Their high molecular weight, compared to traditional dendrimers, allows investigation through osmotic measurements of the effect of polymer architecture on intermolecular interactions in solution.

In concentrated polymer solutions, branching increases the sorption of poor solvents [10] but the effect upon the sorption of good solvents is negligible. However, in dilute solutions, arborescent polymers present peculiar characteristics. The theta temperature (the temperature where the osmotic second virial coefficient is zero [11]) for arborescent polystyrenes in cyclohexane is lower than that for the homologous linear polymer [12]. There is evidence that the difference between the theta temperatures for linear and for arborescent polymers increases with decreasing branch molecular weight [12], in agreement with experimental evidence for other kinds of branched polymers [13].

The purpose of this work is to study 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-globule' transition [14], [15]. These measurements also provide the hydrodynamic radii of the polymers studied here.

As suggested by previous studies [8], a perturbed-hard-sphere model is suitable for calculating osmotic second virial coefficients. In the McMillan-Mayer [16] framework, the osmotic-pressure data were correlated with a colloid-like potential of mean force, using a hard sphere as reference [17] and a perturbation described by an attractive

potential decaying with the sixth power of the center-to-center distance between polymer molecules.

This report is organized in three sections. New osmotic second virial coefficient and intrinsic viscosity measurements are first presented. This is followed by a discussion of the perturbed-hard-sphere behavior of arborescent polymers, relating the second virial coefficients to the intrinsic viscosity. The osmotic-pressure data are finally interpreted within a colloid-like thermodynamic framework.

Materials and Experimental Results

Arborescent polystyrenes of generations zero, one, two and three were studied, together with a linear polystyrene. The characteristics of the polymers are shown in Table 1. Different common organic solvents were used in the measurements: toluene, a good solvent for polystyrene, cyclohexane, a theta solvent, and methylcyclohexane, a poor solvent. Table 2 summarizes the characteristics of each solvent. The solvents were used as received, while the polymers were kept under vacuum for a few days before the osmotic-pressure measurements to ensure the absence of low-molecular-weight impurities.

The osmotic pressure of dilute and semidilute polymer solutions is widely utilized for probing molecular interactions (see for example Merkle et al., [18]; Higo et al., [19]; Berry, [20]). Deviation from the Van't Hoff law gives the second virial coefficient; where determined as a function of temperature, that coefficient provides information on the nature of the force law between dissolved molecules [21]. Statistical mechanics links the osmotic second virial coefficient with the potential of mean force between two polymer molecules in solution [16]. The investigation of osmotic second virial coefficients for linear and branched polymers yields an understanding of the effect of branching upon intermolecular interactions [18], [22].

The osmotic pressure Π of a polymer solution can be expressed in a virial expansion [23]:

$$\frac{\Pi}{R \cdot T} = \frac{1}{M_n} \cdot c_2 + B_{22} \cdot c_2^2 + B_{222} \cdot c_2^3 + \dots \quad (1)$$

where R , T , M_n , B_{22} , B_{222} and c_2 are, respectively, the gas constant, the absolute temperature, the number-average molecular weight of the polymer [24], the osmotic

second and third virial coefficients, and the polymer mass concentration. At low polymer concentration, terms of order higher than second can be neglected, and Equation 1 reduces to:

$$\frac{\Pi}{R \cdot T} \cdot \frac{1}{c_2} = \frac{1}{M_n} + B_{22} \cdot c_2 \quad (2)$$

The results reported here are obtained fitting Equation 2 to the experimental data. Coefficient B_{22} is positive for a polymer in a good solvent, negative for a polymer in a poor solvent and equal to zero at the theta temperature.

Osmotic pressures of polymer solutions at different low concentrations were measured with a Jupiter Instrument Company Recording Membrane Osmometer model 231 (Jupiter, Florida, USA). The cellulose-acetate membrane has a molecular-weight cutoff of 20,000 g/mole. Osmotic second virial coefficients for generation-zero (sample G0) and generation-one (sample G1) polymers were measured in toluene and in cyclohexane. The osmotic second virial coefficient of G0 was also measured in methylcyclohexane at different temperatures. Osmotic pressure is a colligative property, a function of the number of molecules in solution; therefore, 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. Higher concentrations cannot be used to determine the osmotic second virial coefficient, because the solution viscosity becomes too large.

The osmotic second virial coefficients obtained in all experiments are listed in Table 3. The results observed in toluene and cyclohexane generally agree with those obtained with light scattering [12]. Since those data were collected for slightly different polymers, they are not here reported. The differences observed might be due to the higher concentrations required to measure osmotic pressures: small contributions from three-body interactions may be present. The experimental number-average molecular weight values determined by membrane osmometry are in good agreement with the polymer specifications given in Table 1 for the arborescent polymer of generation zero, if sample polydispersity is taken into account. The arborescent polymer of generation one has a molecular weight too high to be determined with accuracy by membrane osmometry.

In agreement with previous studies for branched structures relative to a chemically similar linear polymer of the same molecular weight, the osmotic second virial coefficient in a good solvent is lower for arborescent polymers. Branching lowers the theta temperature for a branched polymer in a solvent, when compared to that of the linear homologue.

Figure 2 shows osmotic-pressure data measured for G0 in methylcyclohexane at two different temperatures. These are experimental data used to determine B_{22} by Equation 2. Interpolation of the data obtained at two temperatures yields a theta temperature of $36 \pm 2^\circ\text{C}$. The theta temperature for linear polystyrene in methylcyclohexane lies between 60 and 70°C [25].

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 homologue (34.5°C [24]).

The intrinsic viscosity, $[\eta]$, for sufficiently long polymer chains [15] is a function of the radius of gyration according to:

$$[\eta] = \frac{\Phi \cdot \langle S^2 \rangle^{3/2}}{M_v}, \quad (3)$$

where Φ , $\langle S^2 \rangle$, M_v are, respectively, Flory's viscosity factor [26], the average radius of gyration squared, and the polymer viscosity-average molecular weight [24]. The factor Φ is essentially constant for a given polymer architecture [27]. A linear polymer contracts to a compact form when the solvent quality decreases, for example when lowering the temperature [28], [29]; at very low temperatures, the polymer molecules may aggregate. It is possible to observe the coil-globule transition by measuring the intrinsic viscosity at different temperatures [14], [30], [31]. The expansion factor α is defined by

$$\alpha = \left(\frac{\langle S^2 \rangle}{\langle S^2 \rangle_0} \right)^{1/2} \quad (4)$$

where the subscript 0 indicates the unperturbed dimensions; α characterizes the extent to which polymer-solvent interactions expand or contract the chain dimensions relative to

their unperturbed values. The expansion factor is unity at theta conditions [15]. It is also possible to define the ‘viscosity’ expansion factor [14] as

$$\alpha_{\eta} = \left(\frac{[\eta]}{[\eta]_0} \right)^{1/3} \quad (5)$$

In what follows, the expansion factor is assumed equal to the viscosity expansion factor. The renormalization-group theory [29] suggests that the expansion factor near the theta temperature obeys the scaling law

$$\alpha \propto (N \cdot \tau^2)^k, \quad (6)$$

where N is the degree of polymerization and τ is the reduced temperature defined as

$$\tau = \frac{\theta - T}{T} \quad (7)$$

Here θ is the theta temperature [14]. In Equation 6, the exponent k is a parameter that assumes different values for temperatures higher or lower than θ .

Intrinsic-viscosity measurements were performed with a standard viscometer of the Ubbelohde type. The temperature was maintained constant within $\pm 0.2^\circ\text{C}$ using a water bath. For the G0, G1, G2, and G3 polymers in cyclohexane, and for the G0 sample in methylcyclohexane, the intrinsic viscosity was measured at different temperatures to observe the coil-globule transition near the theta temperature [14], [15].

Figure 3 shows all intrinsic viscosity results as a function of temperature for all systems considered. For the G0 sample, $[\eta]$ does not depend significantly upon temperature in cyclohexane, while in methylcyclohexane there is a strong dependence. This behavior suggests that the G0 sample does not display a coil-globule transition in cyclohexane, even though $[\eta]$ seems to decrease below 10-15 $^\circ\text{C}$, 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 [12] found a theta temperature near 15 $^\circ\text{C}$. For the G1 sample in cyclohexane, $[\eta]$ decreases for temperatures below 25 $^\circ\text{C}$, thereby suggesting a coil-globule transition. For the G2 polymer, $[\eta]$ is almost constant with temperature; therefore there is no evidence of a coil-globule transition, possibly because of the globular structure developed upon building the G2 molecules from the G1 homologues [9]. 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. This experimental evidence is contrary to the general observation that branching lowers the theta temperature for a given polymer-solvent system. Generation 3 arborescent polymers with branch molecular weight comparable to the one used here shows differences when compared to other arborescent polymers in other studies, for example, in diffusion studies [32] and in the production of mononuclear films [7].

In Figure 4, the expansion factor is plotted as a function of the reduced temperature multiplied by the square root of the molecular weight for the G1 and G3 polymers in cyclohexane, and for sample G0 in methylcyclohexane. To compute the reduced temperature, assumed theta temperatures are 32°C (G0 in methylcyclohexane), 24°C (G1 in cyclohexane) and 33°C (G3 in cyclohexane). Since this plot suggests a sort of universal behavior at temperatures below θ , the assumed theta temperatures are probably nearly correct. Therefore, Figure 4 suggests a theta temperature for G0 in methylcyclohexane that agrees, within experimental uncertainty, with the membrane-osmometry results.

For arborescent polystyrenes with branches of the same molecular weight, a Mark-Houwink-Sakurada dependence between intrinsic viscosity and molecular weight

$$[\eta] = A \cdot M_v^\zeta \quad , \quad (8)$$

where A and ζ are constants, is not observed, as previously pointed out [8], probably because of variations in the architecture of arborescent polymers of different generations. A dependence of the Mark-Houwink-Sakurada type should be observed for polymers characterized by the same number of branches, that is, by considering arborescent polymers of the same generation but with different molecular weights. However, insufficient data are available to test this conjecture.

Discussion

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

$$[\eta] = \frac{10 \cdot \pi}{3} \cdot N_A \cdot \frac{R_H^3}{M}, \quad (9)$$

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

For rigid-sphere molecules with negligible attractive interactions, it is possible to obtain an 'effective' radius R_T from the second virial coefficient using the equation [33]:

$$B_{22} = \frac{16 \cdot \pi}{3} \cdot N_A \cdot \frac{R_T^3}{M^2}. \quad (10)$$

For a hard sphere, the hydrodynamic radius is equal to the effective radius [13]. Figures 5 and 6 show the second virial coefficients measured by membrane osmometry (this work) or by light scattering [12] as a function of molecular weight, together with the second virial coefficients calculated from intrinsic-viscosity data in toluene (Figure 5) and in cyclohexane (Figure 6). The viscosity data used are either from this work or from Gauthier et al. [8]. The polymer weight-average molecular weight was used as M . The symbols are larger than the experimental uncertainty. Generally, because intermolecular attractions are neglected, we cannot obtain a good estimate of B_{22} by combining Equations 9 and 10. However, for arborescent polymers of the same generation in a good solvent (Figure 5), the correspondence is reasonable and improves with decreasing branch molecular weight; in other words, correspondence improves with increasing spherical morphology of the polymer in solution. In a poor solvent (Figure 6), the correspondence remains generally valid, but only at temperatures higher than the theta temperature, because Equation 10 holds only for positive second virial coefficients. These observations provide evidence for the perturbed-hard-sphere behavior of arborescent polymers in dilute solution.

Osmotic Pressure from a Theoretical Equation of State

The experimental data presented here, as well as those reported previously [8], [9] support the concept that arborescent polymers have an essentially spherical morphology in solution. Because these dissolved macromolecules can be viewed as colloids, their thermodynamic properties in solution can be described with a colloid-like framework [34]-[37].

The osmotic pressure data are readily reproduced with a van der Waals-type equation of state. The reference state is the hard-sphere system [17]; the perturbation is given by an attractive potential energy that scales with the sixth power of the inverse distance between polymers r :

$$\frac{\Pi}{\rho \cdot k \cdot T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} + 2 \cdot \pi \cdot \rho \cdot \int_{\sigma}^{\infty} \left\{ 1 - \exp \left[-\frac{H}{k \cdot T} \cdot \left(\frac{\sigma}{r} \right)^6 \right] \right\} \cdot r^2 dr \quad (11)$$

In Equation 11, Π , ρ , η , and σ are, respectively, the osmotic pressure, the density of the polymer, the packing fraction ($\eta = \frac{\pi}{6} \cdot \rho \cdot \sigma^3$), and the hard-sphere diameter. The symbol H represents the long-range attractive energy parameter. The parameters used to fit Equation 11 to the experimental data are listed in Table 4. Because the hydrodynamic radius is obtained from intrinsic-viscosity measurements, the only adjustable parameter is H ; our results for H are similar to Hamaker constants reported for polymer solutions [38], [39]. The fitted osmotic pressures for are compared for the G0 (Figure 7) and G1 (Figure 8) polymers in different solvents. In all cases the fit is reasonable, confirming the colloid-like nature of these dissolved polymers.

Conclusions

New osmotic second virial coefficient data are reported for solutions of arborescent polystyrenes in toluene, cyclohexane and methylcyclohexane. In a good solvent, due to the smaller radius of gyration, the second virial coefficient 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 $36 \pm 2^\circ\text{C}$.

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

Because these polymers have an essentially spherical morphology, 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.

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Table 1 Polymer characterization data

Side Chains			Whole sample		
Polymer	M_w (g/mol)	M_w / M_n	M (g/mol)	M_w / M_n ^a	Number of Branches
Linear ^c	-	-	53,100 ^d	1.06	-
G0	5,220	1.07	66,700 ^b	1.18	12
G1	6,160	1.06	727,000 ^b	1.18	108
G2	5,210	1.07	5,030,000 ^b	1.11	826
G3	5,960	1.06	22,300,000 ^b	1.15	2900

^a by size-exclusion chromatography, using a linear polystyrene standards calibration curve

^b weight-average molecular weight by light scattering

^c sample purchased from Polysciences, Inc., lot # 480592

^d number-average molecular weight by membrane osmometry

Table 2 Solvent characteristics

Solvent	Supplier	Lot number	Purity %
Toluene	Fisher Scientific	982728	99.8
Cyclohexane	Fisher Scientific	992006	99.7
Methylcyclohexane	Aldrich	LR08119KR	99

Table 3 Number-average molecular weight M_n and second virial coefficient B_{22} from osmometry

Polymer	Solvent	Temperature (° C)	M_n (10^3 g/mol)	B_{22} (10^{-4} cm ³ mol/g ²)
Linear	toluene	49.2	59.5 ± 1.4	2.6 ± 0.2
G0	toluene	38.6	68.1 ± 0.2	2.15 ± 0.03
G0	toluene	47.7	64.5 ± 1.2	2.16 ± 0.17
G1 ^a	toluene	38.5	940 ± 60	0.148 ± 0.03
G1 ^a	toluene	47.8	800 ± 20	0.15 ± 0.03
G0	cyclohexane	32.2	61.8 ± 0.8	0.32 ± 0.10
G1 ^a	cyclohexane	32.2	592 ± 4	0.060 ± 0.003
G1 ^a	cyclohexane	43.0	787 ± 3	0.20 ± 0.04
G0	methylcyclohexane	32.6	65.7 ± 1.2	-0.68 ± 0.10
G0	methylcyclohexane	41.6	67.6 ± 0.8	0.49 ± 0.08

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

Table 4 Parameters used to fit Equation 11 to the experimental data

Polymer	Solvent	Temperature (°C)	Radius (Å)^a	H (k T)
G0	Toluene	38.6	48	0.526
G0	Toluene	47.7	48	0.314
G1	Toluene	38.5	112	0.949
G1	Toluene	47.8	112	0.547
G0	Cyclohexane	32.2	47.4	0.835
G1	Cyclohexane	32.2	102.6	0.045
G1	Cyclohexane	43.0	103.3	0.270
G0	Methylcyclohexane	32.6	45	1.227
G0	Methylcyclohexane	41.6	46	0.961

^a Radii obtained from intrinsic-viscosity measurements. The only adjustable parameter is H.

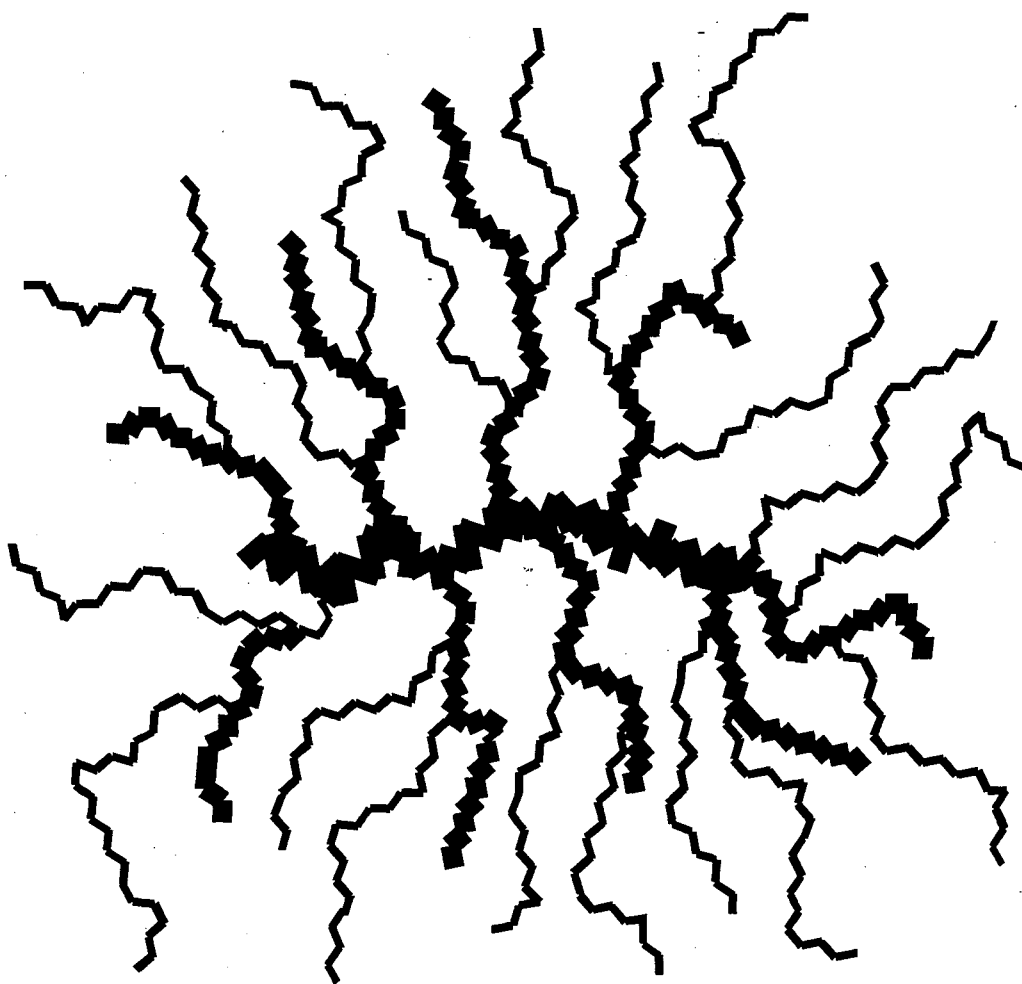


Fig. 1 Schematic representation of a generation-one arborescent polymer.

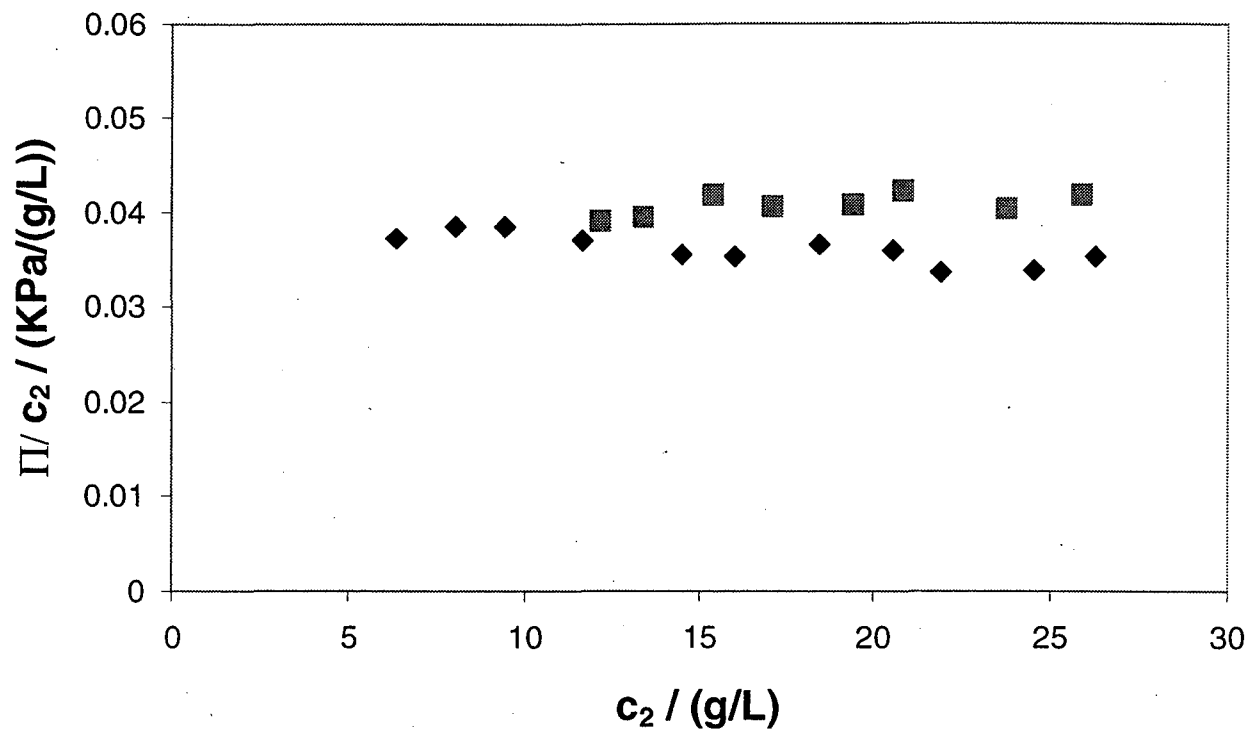


Fig. 2 Osmotic pressure divided by polymer concentration versus polymer concentration for generation-zero arborescent polystyrene in methylcyclohexane at different temperatures (diamonds at 32.6°C, squares at 41.6°C).

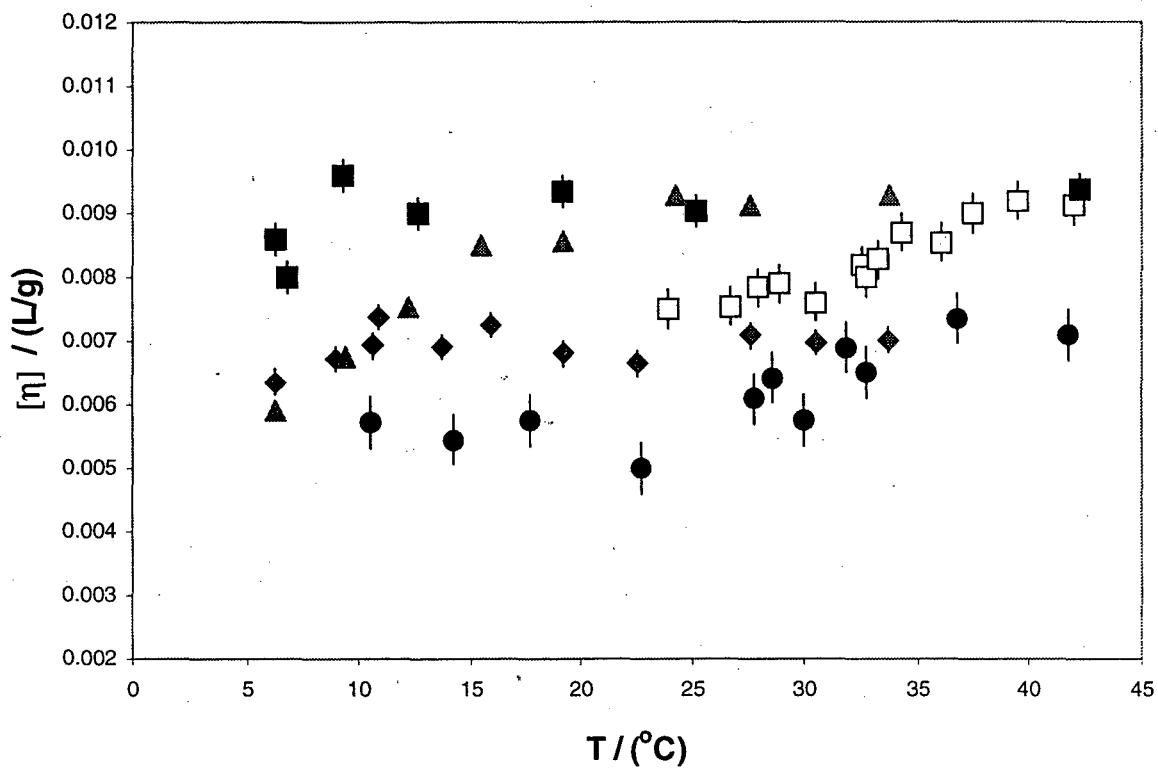


Fig. 3 Intrinsic viscosity as a function of temperature for arborescent polystyrenes, different generations, in methylcyclohexane (empty symbols) and in cyclohexane (full symbols). Squares represent G0 arborescent polymer, triangles G1, diamonds G2 and circles G3.

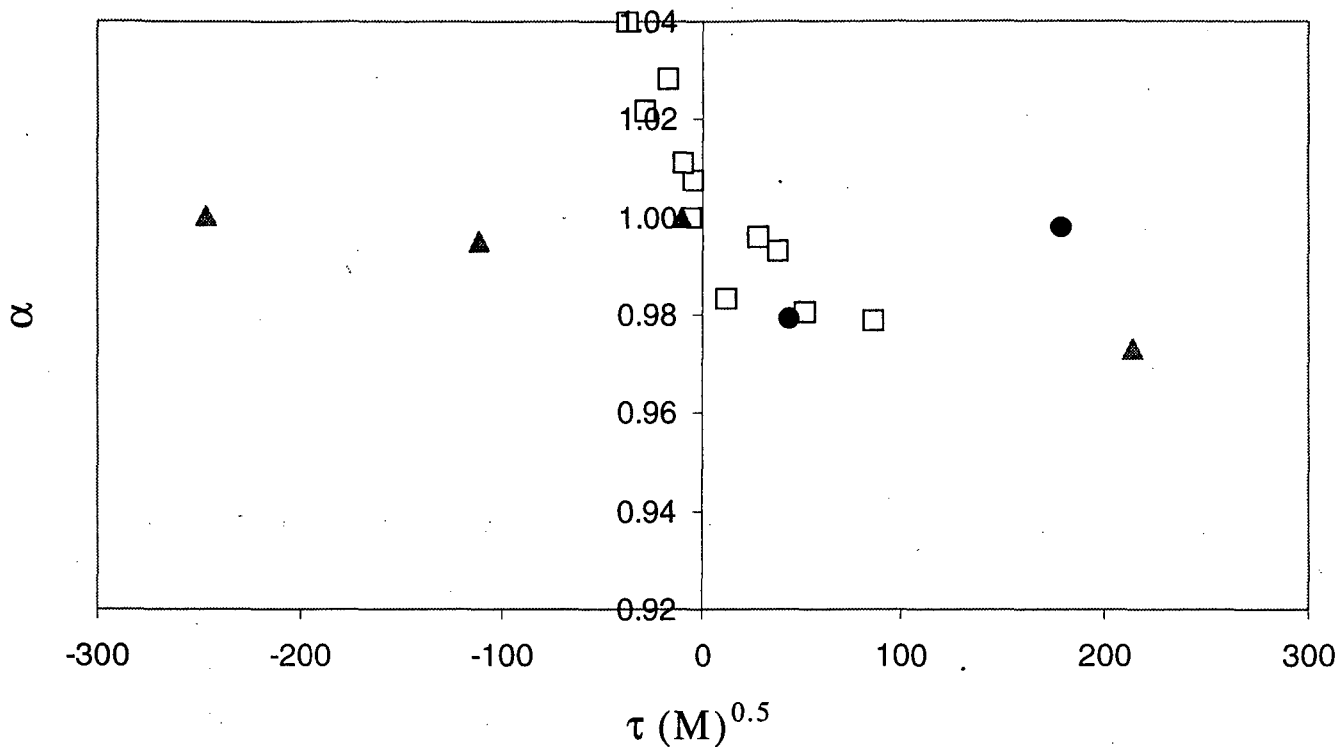


Fig. 4 Expansion factor as a function of the reduced temperature multiplied by the square root of the molecular weight for arborescent polystyrenes in different solvents. Squares represent G1 in methylcyclohexane, triangles G1 in cyclohexane, circles G3 in cyclohexane. To compute the reduced temperature, assumed theta temperatures are 32°C (G0 in methylcyclohexane), 24°C (G1 in cyclohexane) and 33°C (G3 in cyclohexane).

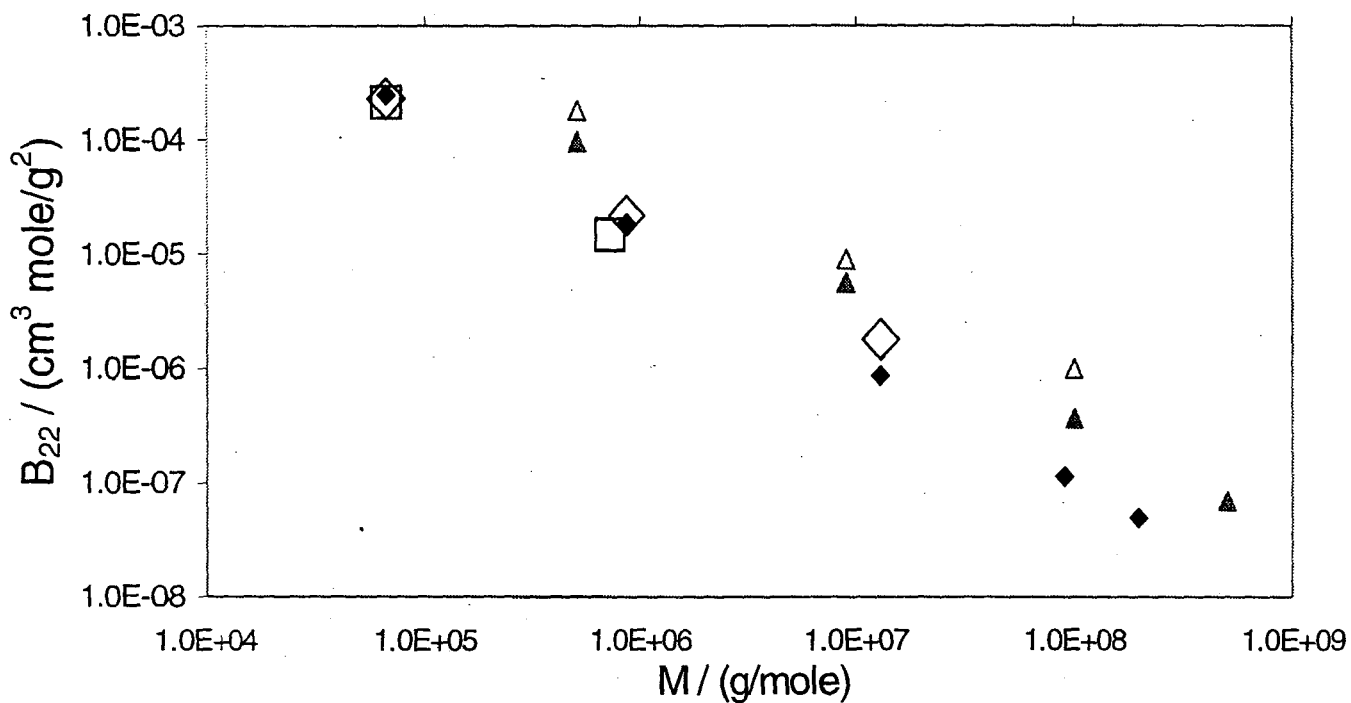


Fig. 5 Osmotic second virial coefficients for arborescent polystyrenes in toluene as a function of molecular weight. Comparison between experimental data (empty symbols) and predictions from Equation 10 using intrinsic-viscosity data (full symbols). Viscosity data are from Gauthier et al., [8]. Triangles are for arborescent polymers obtained from a linear polystyrene core and side chains with a molecular weight of 30,000 g/mole [12]. Diamonds are for arborescent polymers obtained from a linear core and side chains of 5,000 g/mole [12]. Squares represent second osmotic virial coefficients measured in this work.

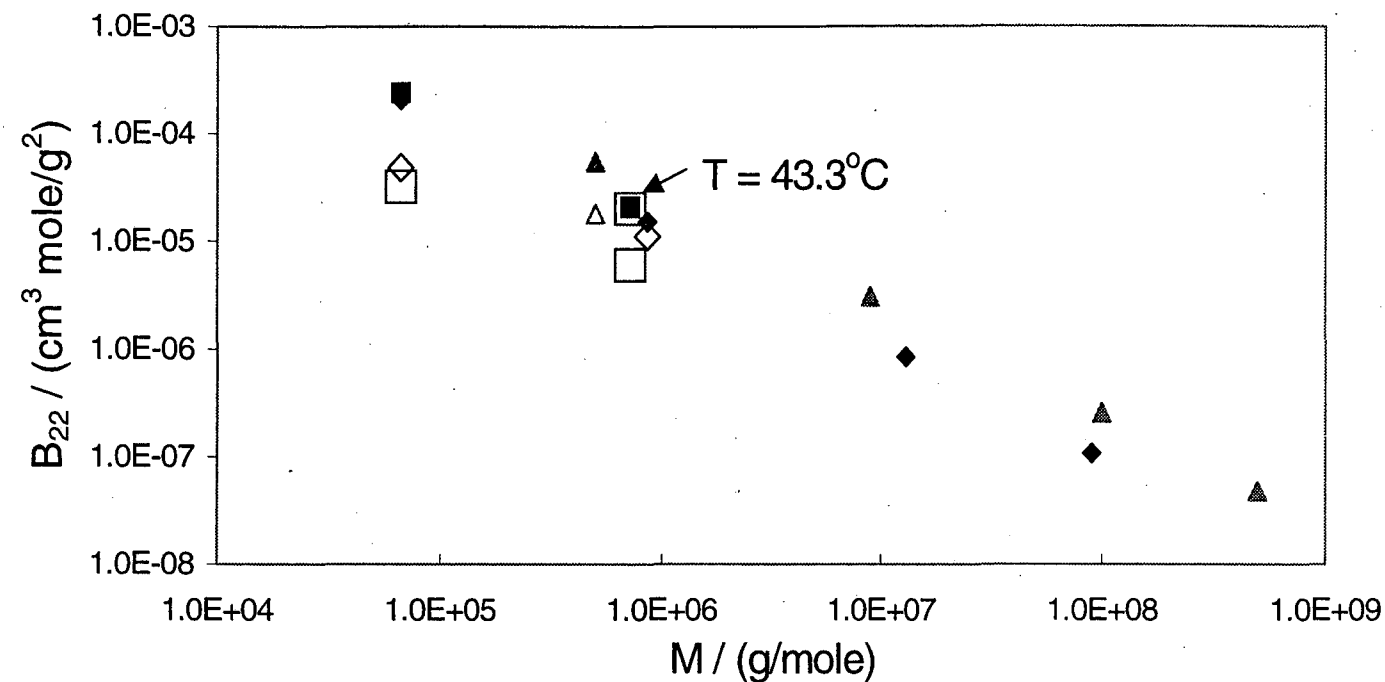


Fig. 6 Osmotic second virial coefficients for arborescent polystyrenes in cyclohexane as a function of molecular weight. Comparison between experimental data (empty symbols) and predictions from equation 10 using intrinsic-viscosity data (viscosity data either from this work or from Gauthier et al., [8]). Triangles are for arborescent polymers obtained from a linear polystyrene core with molecular weight 30,000 g/mole [12]. Diamonds are for arborescent polymers obtained from a linear core of 5,000 g/mole [12]. Squares represent second osmotic virial coefficients measured in this work.

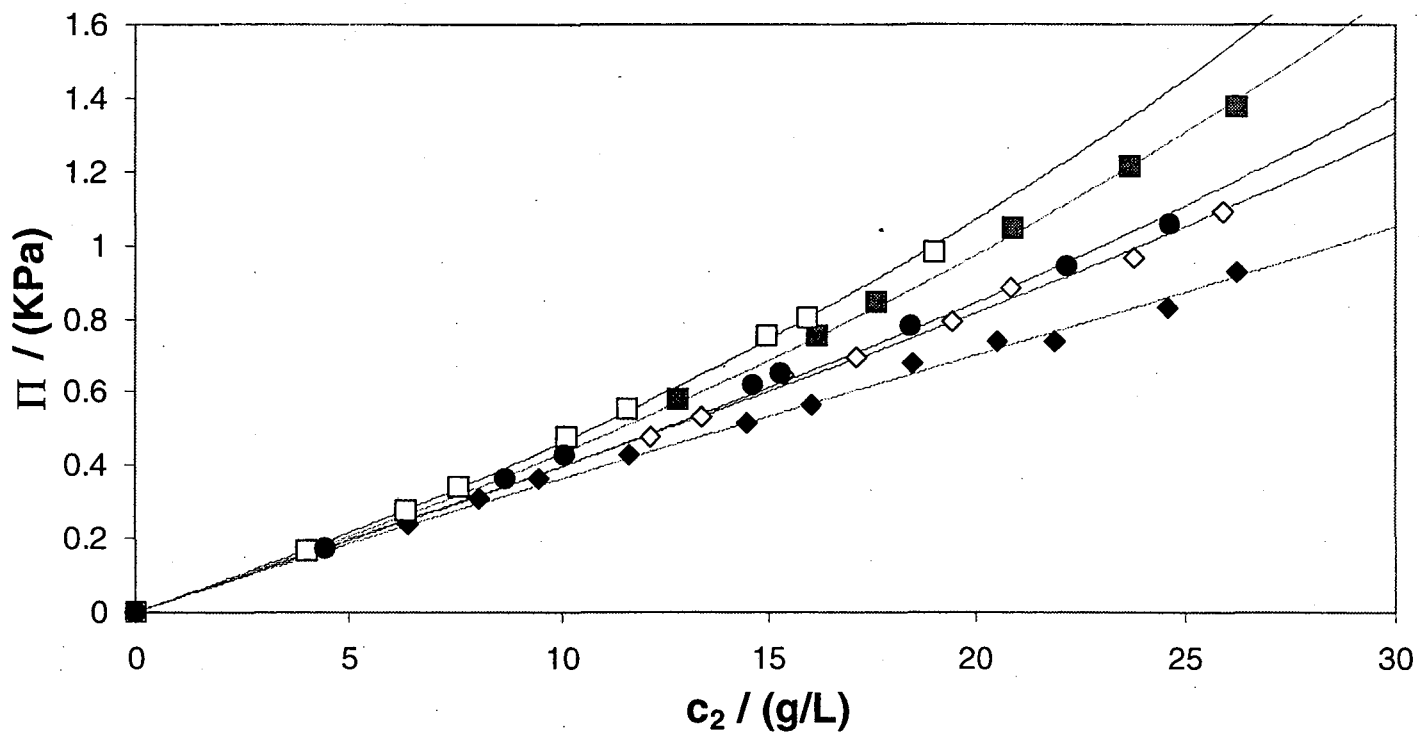


Fig. 7 Osmotic pressures for generation-zero arborescent polystyrene in different solvents. Symbols are experimental data; lines are calculated from equation 11. Squares are for data in toluene (filled at 38.6°C, empty at 47.7°C); circles are for data in cyclohexane at 32.2°C, and diamonds are for data in methylcyclohexane (filled at 32.6°C, empty at 41.6°C).

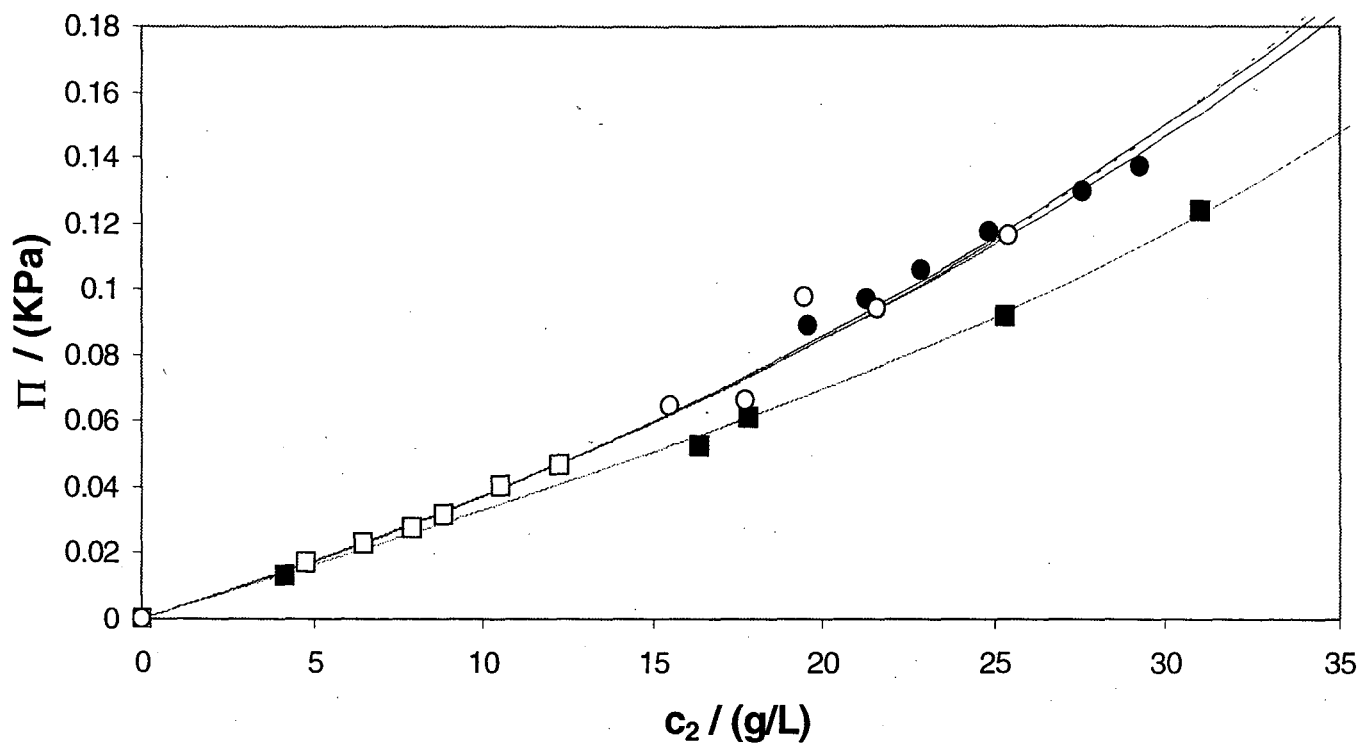


Fig. 8 Osmotic pressures for generation-one arborescent polystyrene in different solvents. Symbols are experimental data; lines are calculated from equation 11. Squares are for data in toluene (filled at 38.5°C, empty at 47.8°C); circles are for data in cyclohexane (filled at 32.2°C, empty at 43.0°C).

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