Osmotic Second Virial Coefficient, Intrinsic Viscosity and Molecular Simulation for Star and Linear Polystyrenes

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ABSTRACT: Experimental osmotic second virial coefficients are reported for polystyrene in toluene (good solvent), cyclohexane (Θ solvent) and methylcyclohexane (poor solvent) in the temperature range 10−60 °C. The Θ temperature for eight-arm star polystyrene in methylcyclohexane is 29 ± 3 °C. Intrinsic viscosity for polystyrene in cyclohexane and methylcyclohexane has been measured over a wide temperature range. A coil-globule transition has been observed for eight-arm star polystyrene in methylcyclohexane at temperatures close to the Θ temperature. The Θ point for star polymers with three, four, five, and six arms have been determined by standard Monte Carlo simulation calculations. For six-arm star polymers at the Θ point, defined as the well depth at which the radius of gyration squared scales linearly with the number of segments, the osmotic second virial coefficient is zero. As shown by others, for a branched polymer, the osmotic second virial coefficient at good solvent conditions and the Θ temperature are lower than those for a corresponding linear homologue in the same solvent.

Introduction

Regular star polymers are branched structures where equi-sized linear arms emanate from a central core. Star polymers with up to 450 arms with desired chemical and molecular weight asymmetries can be synthesized.[1−3] Possible industrial applications of star polymers have been discussed.[4,5]

For concentrated solutions, the effect of polymer structure upon solvent sorption is small.[6,7]

Numerous experimental and computer simulation studies have been reported for dilute solutions of linear and star polymers in good and Θ solvents. Universal ratios express differences in thermodynamic properties, such as radius of gyration, osmotic second virial coefficient, and intrinsic viscosity between star and linear polymers in good or Θ solvents.[2,8] Osmotic second virial coefficients, B_{22}, and mean-square radii of gyration in dilute solutions have been measured.[9−13] In good solvents, B_{22} is smaller for branched polymers than that for the homologue linear polymers. Several studies[3,8] show that branching lowers the Θ temperature of a solvent−polymer system. Deviations of Θ from that for a linear polymer with the same molecular weight increase as the number of arms increases.[14−16] However, Dondos and co-workers[17] recently proposed a theoretical model that predicted Θ for linear and star polymers. For lightly branched (up to six arms) star polymers, the predicted Θ values were lower than those for the linear counterparts. But for highly branched star polymers, the predicted Θ values were higher than those for the linear counterparts. Dondos et al.[17] showed experimentally that Θ for a 17-arm star polystyrene in cyclohexane is about 41.5 °C.

This work provides further evidence to support conclusions based on previously published research. B_{22} for eight-arm star polystyrenes are reported not only in toluene and cyclohexane, good and Θ solvents, respectively, but also in methylcyclohexane, a poor solvent for linear polystyrene. The coil-to-globule transition for star polystyrene in methylcyclohexane is observed through intrinsic-viscosity measurements. Finally, osmotic second virial coefficients for six-arm star polymers in a variety of solvent conditions are computed by standard molecular simulation. All new results reported here are consistent with a Θ temperature depression due to branching.

Experimental Section

Osmotic pressures were measured with a membrane osmometer, model 231, from Jupiter Instrument Co., Jupiter, FL. The temperature was kept constant at ±0.2 °C over a 12 h period with an electric-resistance heater. Polymers were kept under vacuum 2 or 3 days before an osmotic-pressure measurement to ensure removal of low-molecular-weight impurities. Table 1 shows polymer characteristics. Solvents, used as received, were toluene (99.8% purity), cyclohexane (99.7% purity), and methylcyclohexane (99% purity). Toluene and cyclohexane were supplied by Fisher Scientific, methylcyclohexane by Aldrich. Cellulose acetate membranes were supplied by Jupiter Instrument Co.; the molecular-weight-cutoff was 20 000.

Table 2 shows B_{22} and M_n obtained from fitting the experimental data to the customary virial expansion truncated after the second term. When polydispersity is taken into account, M_n is comparable to that obtained from the supplier, except for high-molecular-weight linear polystyrene (LPSHM) in cyclohexane, where M_n is too high to be determined accurately by osmometry. These results show that different molecules of low-molecular-weight star polystyrenes (SPSLM) do not aggregate at the temperatures tested.

In agreement with others,[3,8,10] B_{22} for star polymers are smaller than those for linear polymers of the same molecular weight. The ratio between B_{22} for low-molecular-weight star and linear polystyrenes, about 0.82, agrees with results reported for star polystyrenes with different number of arms.[8] The ratio increases to about 0.90 for high-molecular-weight samples.

B_{22} for LPSLM in cyclohexane shows a strong dependence on temperature and Θ close to the literature value (34.5 °C).

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Table 1. Polymer Properties

polymer	acronym	branch molecular weight	total molecular weight	polydispersity	supplier
linear polystyrene	LPSLM		73000[a]	1.04	Polymer Source, Inc.
linear polystyrene	LPSHM		343700[a]	1.05	Polymer Source, Inc.
eight-arm star polystyrene	SPSLM	9800	74000		Polymer Source, Inc.
eight-arm star polystyrene	SPSHM	46700	391000		Polymer Source, Inc.

[a] From size-exclusion chromatography.

Table 2. Experimental Osmotic Second Virial Coefficients for Polystyrene (PS), Linear (L), and Eight-Arm Star (S), of Low (LM) or Relatively High Molecular Weight (HM)

polymer	solvent	temp (°C)	$M_n \times 10^3$	B_{22} (10^{-7} L mol/g^2)
LPSLM	toluene	48.5	77 ± 2	3.95 ± 0.20
LPSHM	toluene	47.1	435 ± 80	3.95 ± 0.15
SPSLM	toluene	10.8	73 ± 1	3.6 ± 0.1
SPSLM	toluene	31.0	78 ± 1	3.90 ± 0.06
SPSLM	toluene	47.6	76.0 ± 0.5	3.22 ± 0.03
SPSLM	toluene	61.2	81 ± 3	3.3 ± 0.2
SPSHM	toluene	31.2	370 ± 50	3.5 ± 0.5
SPSHM	toluene	47.7	*a*	3.57 ± 0.08
LPSLM	cyclohexane	23.3	55.0 ± 0.2	−2.87 ± 0.02
LPSLM	cyclohexane	27.8	73.0 ± 3.5	−1.10 ± 0.25
LPSLM	cyclohexane	33.8	77 ± 3	−0.12 ± 0.01
SPSLM	cyclohexane	23.3	59 ± 1	2.20 ± 0.25
SPSLM	cyclohexane	34.2	80 ± 5	1.5 ± 0.4
SPSLM	cyclohexane	43.1	80 ± 3	2.35 ± 0.60
SPSHM	cyclohexane	34.0	342 ± 9	0.79 ± 0.04
LPSLM	methylcyclohexane	45.7	*b*	−2.8 ±0.1
SPSLM	methylcyclohexane	32.5	75 ± 3	0.18 ± 0.03
SPSLM	methylcyclohexane	42.0	77.5 ± 1.5	1.03 ± 0.02
SPSLM	methylcyclohexane	50.0	74 ± 1	1.3 ± 0.4

[a] Molecular weight is too high to be determined by membrane osmometry. [b] Molecular weight cannot be measured in this poor solvent.

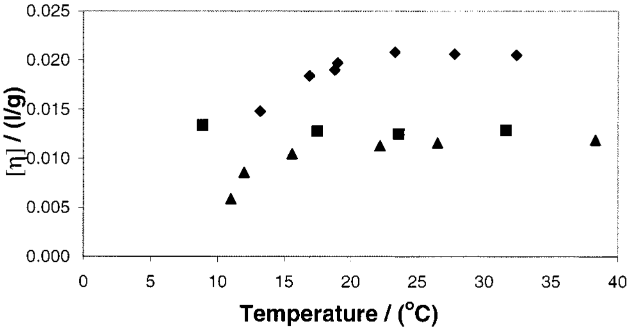

Figure 1. Intrinsic viscosity for different polystyrenes as a function of temperature. Diamonds represent LPSLM in cyclohexane, squares SPSLM in cyclohexane, and triangles SPSLM in methylcyclohexane.

B_{22} for SPSLM in the same solvent is positive and nearly independent of temperature, indicating that Θ in cyclohexane is lower than that for the linear molecule. The lowering of Θ caused by branching may follow from the high segment density close to the core[16] or from "end-chain" effects.[9] These results agree with other experimental evidence obtained for different polymers.[3,8]

Extrapolating B_{22} for SPSLM in methylcyclohexane to the temperature where B_{22} equals zero, our results show that Θ is 29 ± 3 °C. By contrast, for linear polystyrene in methylcyclohexane, Θ lies between 60 and 70 °C.[18]

Intrinsic viscosity, [η], was measured by a conventional capillary viscometer of the Ubbelohde type. A water bath was used to maintain the temperature to ±0.2 °C. [η] for eight-arm star polystyrene is here reported not only in cyclohexane but also in methylcyclohexane. Figure 1 shows [η] as a function of temperature. The ratio between [η] for star and linear polystyrene in cyclohexane at 35 °C is about 0.55, in agreement with results reported for 18-arm star polystyrene.[19] While for LPSLM in cyclohexane a coil-to-globule transition is evident in the temperature range investigated,[20−24] no transition is observed for SPSLM in the same solvent, suggesting that Θ is lower than that for the linear counterpart. However, a coil-to-globule transition is observed for SPSLM in methylcyclohexane. Figure 2 shows expansion factor α as a function of reduced temperature τ multiplied by the square root of the molecular weight for LPSLM in cyclohexane and for SPSLM in methylcyclohexane.[20−22] τ was computed assuming Θ = 34.5 °C for LPSLM in cyclohexane and 30.5 °C for SPSLM in methylcyclohexane. Because the plot appears to follow a universal law for the description of the collapse near Θ, this experimental observation provides independent evidence for Θ = 29 ± 3 °C for SPSLM in methylcyclohexane.

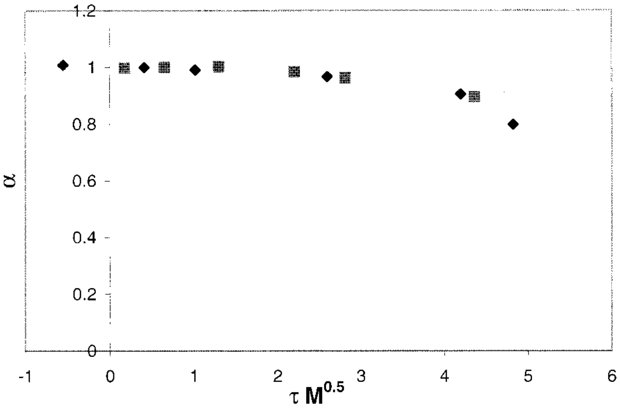

Figure 2. Expansion factor, $\alpha = ([\eta]/[\eta]_0)^{1/3}$, as a function of reduced temperature $\tau = 1 - T/\Theta$ multiplied by the square root of the polymer molecular weight for LPSLM in cyclohexane (squares) and SPSLM in methylcyclohexane (diamonds). The plot has been obtained assuming a Θ temperature of 34.5 °C for LPSLM in cyclohexane and of 30.5 °C for SPSLM in methylcyclohexane.

Molecular Simulation

B_{22} values for star polymers have been calculated by simulation at good solvent conditions.[25−27] The Θ depression due to branching has been shown through the comparison of conformational properties for linear and 12-arm star polymers.[28,29] Bruns and Carl[30] showed a Θ depression due to branching in a lattice system. In this work, some properties of star polymers with three, four, five, and six arms are calculated using an off-lattice model. The Pivot algorithm is used to generate independent configurations of polymer molecules. The system is equilibrated with 1.5 million trial moves. In the production phase, 1000 independent conformations are stored and used to compute geometric characteristics. Data for linear polymers obtained with the same method are available.[31] Because the polymers are studied at different solvent conditions, the effect of branching on thermodynamic properties could be established at different temperatures, to facilitate comparison with experiments. The solvent is considered a continuum. The segment−segment interactions are represented by hard-

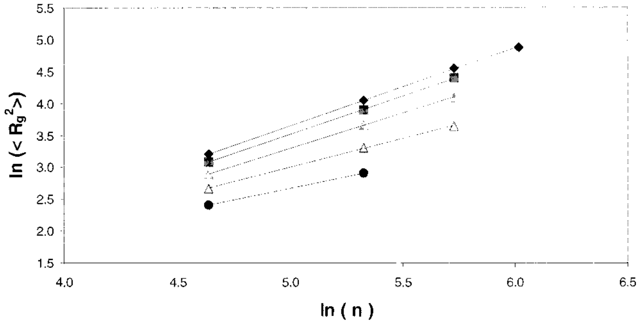

Figure 3. Radii of gyration squared, $\langle R_g^2\rangle$, as a function of the number of polymer segments, *n*, for six-arm star polymer at different solvent conditions. Diamonds represent athermal conditions and squares well-depth equal to −0.15, full triangles −0.30, empty triangles −0.40, and circles −0.50 k_BT.

sphere repulsion and by square-well attraction between nonbonded segments. Well width was set to half the segment diameter σ. Well depth ϵ ranges from 0 to −0.50 k_BT.

Table 3 gives the ensemble-average radius of gyration squared, $\langle R_g^2\rangle$; asphericity, $\langle A\rangle$; arm radius of gyration squared $\langle R_{arm}^2\rangle$; center-to-end distance squared, $\langle D_{CTE}^2\rangle$; and osmotic second virial coefficient, $B_{22}' = B_{22}M_n^2/N_A$, computed at different solvent conditions. Table 3 is available as Supporting Information.

Figure 3 shows $\langle R_g^2\rangle$ for six-arm star polymers as a function of the total number of segments, *n*, at different well depths. A scaling law between $\langle R_g^2\rangle$ and *n*, can be observed at each ϵ. Interpolating the scaling factors, the conditions at which the scaling exponent equals unity for three-, four-, five-, and six-arm star polymers correspond to −0.34 ± 0.02, −0.35 ± 0.02, −0.355 ± 0.015, and −0.355 ± 0.015 k_BT, respectively. These results show that Θ decreases with rising number of arms. Given the accuracy of these calculations, no appreciable difference is observed between five- and six-arm star polymers.

The potential of mean force, *W*(*r*), is computed following the algorithm proposed by Hall and co-workers,[31] slightly modified by Lue and Prausnitz.[32] One million polymer pairs were used at each separation *r* between the centers of mass of the polymers. Results reported are the average of at least three different runs. Figure 4 shows *W*(*r*) as a function of *r* for athermal star polymers with different number of arms and comparable molecular weight. At good solvent conditions, B'_{22} decreases with rising number of arms[25,26] due to declining $\langle R_g^2\rangle$. For six-arm star polymer, *W*(*r*) diverges at *r* less than half the radius of gyration. Following the description provided by Daoud and Cotton,[33] Likos and co-workers[34,35] proposed a colloidal-like potential of mean force to interpret experimental results obtained with many-arm star polymers. According to this picture, a star polymer is made by a rigid core surrounded by a flexible corona. Our results show that six-arm star polymers with up to 205 segments follow this behavior at all solvent condition tested. However, our results for asphericity[36] show that star polymers are not spherical in dilute solutions, even though they are more spherical than linear polymers.[37,38] Our results show that for fixed molecular weight, asphericity decreases with rising number of arms; for fixed number of arms, asphericity increases with rising arm length.

From *W*(*r*), B'_{22} was computed for six-arm star polymers of two different molecular weights under different solvent conditions. Theta conditions are those where B'_{22} is zero. Interpolating, the Θ states for six-arm star polymer of 103 and 205 total segments correspond to −0.35 ± 0.01 and −0.35 ± 0.015 k_BT, respectively. The difference in molecular weight between the two polymers is not enough to change Θ, given the uncertainties of our calculations.

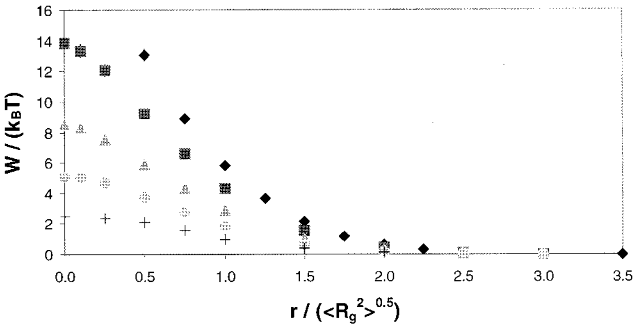

Figure 4. Potential of mean force as a function of the distance between the centers of mass of the polymers, *r*, for athermal star polymers of comparable molecular weight but different number of arms; *r* is normalized by the radius of gyration of the polymer. Circles represent results for three-arm star, 33 segments per arm; triangles for four-arm, 25 segments per arm; squares for five-arms, 20 segments per arm; diamonds for six-arm, 17 segments per arm. Crosses are for linear chains of 100 total segments.[30] Symbols are larger than the uncertainty.

Our results for SPSLM in methylcyclohexane show that Θ is 29 ± 3 °C. For the linear homolog, our simulation results predict a Θ of about 60 ± 15 °C, in rough agreement with the literature value.[18]

Arm radii of gyration squared show a stretching of the arm at low arm-molecular weight caused by the high segment density around the core;[39] stretching increases with rising number of arms and decreasing solvent quality.

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Supporting Information Available: Table 3, giving the ensemble-average radius of gyration squared, asphericity, arm radius of gyration squared, center-to-end distance squared, and osmotic second virial coefficient, computed at different solvent conditions, and Table 4, giving the estimated asphericity for random-walk star polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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