Star-Branched Polymers. 5. The θ Temperature Depression for 8- and 12-Arm Polyisoprenes in Dioxane

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Abstract: The θ temperature depression for a series of low molecular weight 8- and 12-arm polyisoprene stars has been measured in dioxane. Previously, Hadjichristidis and Roovers demonstrated that the low molecular weight 4- and 6-arm star-shaped polyisoprenes did not show, in dioxane, depressed θ temperatures. This was ascribed to the $\frac{1}{3} - \chi_2$ term having a near-zero value in this solvent. However, our results show that the $\frac{1}{3} - \chi_2$ term values are greater than zero for the 8- and 12-arm star cases and that these values increase as the degree of branching increases. Values for the term $\frac{1}{3} - \chi_2$ have been calculated for two separate cases of g values, to wit, g theoretical and g (limiting) as $\overline{M}_w \rightarrow \infty$. The calculation of the $\frac{1}{3} - \chi_2$ values was accomplished using a modification of the three-parameter theory of Candau, Rempp, and Benoit. The modification was necessary since the Candau, Rempp, and Benoit treatment was found to poorly approximate the experimentally observed decrease in θ temperature of the 8- and 12-arm polyisoprenes.

The solution properties of a series of uniformly branched star-shaped polystyrenes and polyisoprenes have been evaluated[2-4] for 4- and 6-armed materials under θ conditions, i.e., where the Flory temperature[5,6] was taken as that where $A_2 = 0$. These studies have shown that the θ temperature behavior of these model branched polymers cannot be satisfactorily described by the usual two-parameter theories. Generally, the deviations of the star-branched polymer θ temperature (θ_{A_2}) from the value observed for linear polymers (θ) are such that $\theta - \theta_{A_2}$ increases as the degree of branching increases and the arm molecular weight decreases. The differences between θ and θ_{A_2} seem to correlate with the increased segment density found in star-branched polymers.

Candau, Rempp, and Benoit[7] (C-R-B) were the first to theoretically describe the experimentally observed θ temperature lowering for comb- and star-shaped polymers. Their treatment is based on Flory's[8] lattice treatment. The initial description by Flory expresses the chemical potential in terms of the interaction parameter, χ. Subsequent refinement by Orofino and Flory[9] defined the chemical potential in the semiempirical form:

$$\mu_1 - \mu_1{}^0 = RT\left[\ln(1 - v_2) + (1 - x^{-1})v_2 + \sum_{i=1} \chi_i v_2{}^{i+1}\right] \tag{1}$$

where v_2 denotes the volume fraction of polymer, x is the ratio of molar volumes of polymer and solvent, and the first term of the summation is the original approximation. Orofino and Flory[9] included the second term in their calculations.

The C-R-B treatment uses different but equivalent parameters in expressing the first two terms of the summation. Flory's approach was utilized to generate an expression for the second virial coefficient in terms of the first two χ terms:

$$A_2 = \left(\frac{2^4}{3^{3/2}}\right) N_A \pi \left(\frac{g^{3/2}\alpha^3}{M^{1/2}}\right)\left(\frac{\langle S^2\rangle_\theta}{M}\right)^{3/2} I \tag{2}$$

where N_A is Avogadro's number, α is the chain expansion factor, and M is the molecular weight. g is the theoretical[10] ratio of the mean square radius of gyration of the branched polymer to that of the linear analogue of the same molecular weight and $\langle S^2\rangle_\theta/M$ is a constant of the system. I is the integral:

$$I = \int_0^\infty [1 - \exp(-Ke^{-y^2} - K'e^{-4/3y^2})]y^2\,dy \tag{3}$$

where y is related to the separation of the center of gravity, l, of the molecules and the radius of gyration:

$$y = \left(\frac{l}{2^{1/2}}\right)\left(\frac{3}{2\langle S^2\rangle_\theta}\right)^{1/2} \tag{3a}$$

The variables K and K' are defined as

$$K = 4C_M\psi\left(1 - \frac{\theta}{T}\right)\frac{M^{1/2}}{\alpha^3 g^{3/2}} \tag{4}$$

$$K' = 2C'_M/\alpha^6 g^3 \tag{5}$$

where

$$C_M = \frac{1}{16}\left(\frac{3}{\pi}\right)^{3/2}\left(\frac{\bar{v}^2}{N_A v_1}\right)\left(\frac{\langle S^2\rangle_\theta}{M}\right)^{-3/2} \tag{4a}$$

$$C'_M = \frac{3^{5/2}}{2^4}\left(\frac{1/3 - \chi_2}{\pi^3}\right)\left(\frac{\bar{v}^3}{N_A{}^2 v_1}\right)\left(\frac{\langle S^2\rangle_\theta}{M}\right)^{-3} \tag{5a}$$

C_M and C'_M are constants of the polymer–solvent system, ψ is the entropy parameter, $\bar{v}$ is the polymer partial specific volume, and v_1 is the solvent molar volume. The chain expansion factor is expressed in terms of K and K' as

$$\alpha^2 - 1 = K/2 + K'/3 \tag{6}$$

All of the terms in eq 2 are nonzero except for I. In order to calculate $\theta - \theta_{A_2}$ the values of K and K' must be found that cause the integral in eq 3 to be zero. This integral cannot be solved analytically. This difficulty has been avoided by the expedient of assuming that K is small, by expanding exp $(-Ke^{-y^2})$ and by keeping only the first two terms. The integral is then reduced to

$$I_{\text{C-R-B}} = \int_0^\infty [1 - \exp(-K'e^{-4/3y^2}) \times (1 - Ke^{-y^2})]y^2\,dy \tag{7}$$

The solution of this integral, however, remains a difficult task even though the variables K and K' are separated.

The C-R-B expression for the second virial coefficient is

$$A_2 = \pi^{3/2}N_A\left(\frac{\langle S^2\rangle_\theta}{M}\right)^{3/2}\left[\frac{C'_M}{M^{1/2}\alpha^3 g^{3/2}}J(K') + \frac{2^4}{3^{3/2}}C_M\psi\left(1 - \frac{\theta}{T}\right)G(K')\right] \tag{8}$$

Both $J(K')$ and $G(K')$ are infinite summations and have been tabulated elsewhere.[7]

The chain expansion factor at θ_{A_2} should be close to 1. If this

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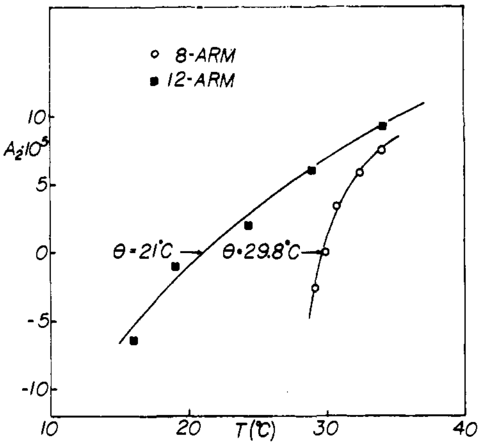

Figure 1. Temperature dependence of the light scattering second virial coefficients (A_2) for 8-VIIIA and 12-IXA.

is true, then eq 6 predicts that K and K' are the same order of magnitude. An approximation of the type used by C–R–B can be applied to the K and K' terms, to wit:

$$I' = \int_0^\infty (K'e^{-4/3y^2} + Ke^{-y^2})y^2\,\mathrm{d}y$$

$$= \frac{\pi^{1/2}}{4}K + \frac{\pi^{1/2}3^{3/2}}{32}K' \quad (9)$$

This integral can be solved analytically with a result that is a simple function of K and K'. If K is small, K' should be small and the approximation $I \simeq I_{\mathrm{C-R-B}} \simeq I'$ would hold. For the case where K is large, eq 6 predicts that K' will be large and of the opposite sign. This leads to a situation where I' will be closer to I than $I_{\mathrm{C-R-B}}$. Since K and K' are of opposite signs, the sum of the K and K' exponential terms will be, on the average, closer to zero than either term alone. Hence, the double approximation of I' should cause less error than that of C–R–B.

The calculation of θ_{A_2} by the use of the I' approximation is equivalent to the results obtained by Orofino and Flory.[9] In their results $A_2 = 0$ when

$$\ln\left[1 + \frac{\pi^{1/2}}{4}K + \left(\frac{\pi^{1/2}3^{3/2}}{32}\right)K'\right] = 0 \quad (10)$$

Both calculations give $A_2 = 0$ when $K = -(3^{3/2}/8)K'$.

Experimental Section

The star-branched polyisoprenes were synthesized with the use of polyfunctional chlorosilanes following procedures described elsewhere.[2-4,11] The characterization of these polymers was carried out with the use of the Fica 50 or the Sofica PGD light scattering photometers. The molecular parameters for the 4- and 6-arm polyisoprenes have been reported.[4] The $\overline{M}_w$ values for the 8- and 12-arm stars are based on results obtained in dioxane and cyclohexane while the $\overline{M}_n$ values of the star-branched and linear polyisoprenes were determined from Hewlett-Packard osmometers. Toluene solutions, at 37 °C, were used. Dioxane was purified following the procedure of Hadjichristidis and Roovers.[4] Analysis of the dioxane by GC and the 300-MHz ^{1}H NMR revealed no impurities.

The concentration dependence of light scattered was used to derive A_2 for each star. The temperature dependence of A_2 was used to determine θ_{A_2}. An example is shown in Figure 1. The accuracy of the quoted θ_{A_2} values is estimated at ±0.5 °C. Physical constants used in eq 4a and 5a were $\bar{v} = 1.10$ cm^3/g, $v_1 = 85.53$ cm^3/g·mol, and $(\langle S^2\rangle_\theta/M) = 11.2 \times 10^{-18}$ cm^2·mol/g, and in eq 4 $\psi = 0.35$. The latter was derived from the slope A_2 vs. $(1 - \theta/T)$ at $T = \theta$, Figure 2. It was found that ψ for the stars was the same as for linear polyisoprene.

Characterization of the linear "parent" polyisoprenes by gel permeation chromatography showed that these polymers possessed near-monodisperse molecular weight distributions ($\overline{M}_z/\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ ratios of 1.1 or less were determined). The characteristics of the seven-column Styragel column set used for this analysis have been described elsewhere.[12-14] As before,[12-14] the osmometric and GPC number-average molecular weights were found to agree with each other within the limits of ±6%. No corrections for column broadening effects were made for the GPC molecular weights.

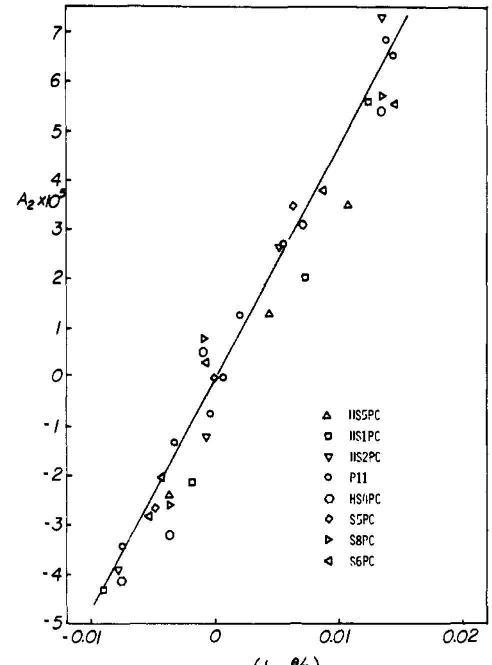

Figure 2. Light scattering second virial coefficient (A_2) vs. $(1 - \theta/T)$ in dioxane. The polyisoprenes used are those of ref 4.

The microstructures of the polyisoprenes prepared in this work were measured in CCl$_4$ with the 300-MHz ^{1}H NMR Varian spectrometer. The cis, trans, and 3,4 contents of these materials were essentially identical with those of the branched polyisoprenes examined by Hadjichristidis and Roovers.[4]

The star-shaped polyisoprenes were fractionated in order to remove the linear precursor chains. GPC measurements showed that the 8- and 12-arm polyisoprenes used in this work were free of linear material. Sporadic characterization via osmometry, light scattering, and GPC over an 18-month period showed no evidence of polymer degradation, branching, or cross-linking.

The values for the parameter $\frac{1}{3} - \chi_2$ were calculated by the following procedure. A value of $\alpha = 1$ was assumed. The experimental data was used to calculate K by the use of eq 4 and 4a. K' was then calculated from eq 6. The integral was evaluated numerically by the use of eq 3, 7, or 9 which represent respectively the exact solution or the two approximate solutions. α was varied by the use of Newton's method until a value was obtained that caused the particular form to have a magnitude of less than 10^{-5}. This produced a value of K' that was then used with eq 5 and 5a to give a value of $\frac{1}{3} - \chi_2$. These calculations were done on an IBM 370/158 computer.

Results and Discussion

Table I shows the characterization data for the 8- and 12-arm polyisoprene stars examined in this work. The influence of both arm molecular weight and the extent of branching on θ_{A_2} can be seen in Figure 3. These results can be compared to those found[4] for linear, 4-, and 6-arm polyisoprenes in dioxane. There it was reported that the linear polyisoprenes exhibited a θ temperature of 34.1 °C[17] while the values for the 4- and 6-arm stars were 33.4 and 33.5 °C, respectively. These values for θ_{A_2} are in good agreement with the corresponding 8- and 12-arm materials that exhibit constant θ_{A_2} values.

From Figure 3 the influence of the degree of branching and branch molecular weight on θ_{A_2} can be seen. For the 8- and 12-arm polyisoprenes the initial θ temperature depression is seen at an arm molecular weight of about 2.5×10^4 g mol^{-1}.

Table I. Molecular Characteristics of 8- and 12-Arm Polyisoprene Stars

sample[a]	$\overline{M}_n$(arm)[a] × 10^{-3}	$\overline{M}_w$(arm)[b] × 10^{-3}	$\overline{M}_n$(star)[a] × 10^{-4}	$\overline{M}_w$(star)[b] × 10^{-4}	f[c]	$\theta_{A_2=0}$, °C
8-VIIIA	5.1		3.9	4.1	8.0	$29._8$
8-VIIAA	14.0		10.4	11.0	7.9	$31._0$
8-IAA	37.4	39.0[d]	27.0	27.6	7.4	$32._8$
8-IIAAAA	88.0	88.0[d]		61	6.9	$32._9$
8-IIIAAAA	98.0	100		79.5	8.1	$32._7$
8-VIAAA	217	227		172 (170)[e]	8.1	$32._7$
8-IVAAA	225	241		176	7.8	$33._2$
8-VAAAA	528[d]	550		440	8.3	$32._6$
8-IXAAAAA	750[d]	760		590 (610)[e]	7.9	$33._5$
12-IXA	3.5		4.0	4.1	11.7	$21._0$
12-IVA[f]	8.3		10.0	9.6	11.6	$25._8$
12-VIIAAA	21.0	21.8[d]	24.7	25.0	11.9	$28._7$
12-IA	35.6	36.0[d]	41.5	41.2	11.6	$32._6$
12-IIAAA	68.9	69.0[d]		81.0	11.8	$32._0$
12-IIIAA	112	120		144	12.0	$32._9$
12-VIAAA	270	280		248	9.2	$32._6$
12-VIIIAAAA	315	320		379 (400)[e]	12.0	$33._0$
12-VAAAA	430	445		526 (530)[e]	12.2	$33._0$

[a] Membrane osmometry, except where noted. [b] Light scattering, except where noted. [c] Degree of branching ($\overline{M}_w$(star)/$\overline{M}_n$(arm)). The best measure of the degree of branching is given by ($\overline{M}_n$(star)/M_n(arm)).[15] The near-monodisperse nature of the stars allows the use of $\overline{M}_w$(star) rather than $\overline{M}_n$(star) without introducing significant error into the value of f. [d] Via GPC. [e] Via the Fica 50 photometer; average values from dioxane and cyclohexane. [f] This sample was synthesized by capping the chain end with several units of butadiene prior to the linking reaction. It has previously been reported[16] that the incorporation of trace amounts of foreign monomer units does not alter the θ temperature. The remaining samples in the above table which showed a θ temperature lowering contained no butadiene.

Table II. Values of α_{A_2} and $1/3 - \chi_2$ for 8- and 12-Arm Polyisoprene Stars ($g = g_{\text{theor}}$)[a]

			I_{exact}		$I_{\text{C-R-B}}$		I'	
sample	$\overline{M}_w \times 10^4$	g	α_{A_2}	$1/3 - \chi_2$	α_{A_2}	$1/3 - \chi_2$	α_{A_2}	$1/3 - \chi_2$
12-IXA	4.1	0.236	1.069	0.054			1.024	0.045
12-IVA	9.6	0.236	1.062	0.049			1.023	0.042
12-VIIAAA	25.0	0.236	1.068	0.054			1.024	0.045
8-VIIIA	4.1	0.344	1.007	0.024	0.987	0.021	1.005	0.024
8-VIIAA	11.0	0.344	1.009	0.029	0.982	0.024	1.006	0.028

[a] $g = (3f - 2)/f^2$ (ref 10).

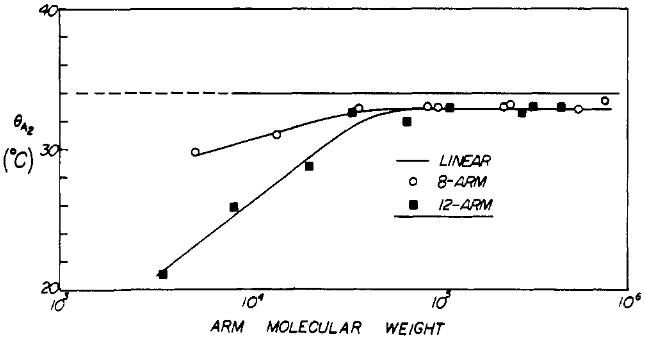

Figure 3. Dependence of θ_{A_2} on star arm molecular weight ($\overline{M}_n$) and degree of branching.

This behavior is in contrast to that observed by Hadjichristidis and Roovers[4] for the 4- and 6-arm polyisoprene stars in dioxane where the θ depression is zero even for stars with arm molecular weights as low as 7.1 × 10^3. The independence of θ_{A_2} for the 4- and 6-arm polyisoprenes in dioxane was ascribed to a near-zero value for the ($1/3 - \chi_2$) term in the relation[7]

$$\frac{\theta}{\theta_{A_2}} - 1 = \frac{3^{3/2} C_M'(1/3 - \chi_2) H(K')}{2^4 C_M \psi M^{1/2} g^{3/2} \alpha^3} \qquad (11)$$

where $H(K')$ is the ratio between $J(K')$ and $G(K')$.

Table II shows the various results for the 8- and 12-arm polyisoprene stars that exhibited θ temperature lowering in dioxane. Solution of the exact integral, eq 3, produces values for ($1/3 - \chi_2$) of ~0.05 for the 12-arm stars and ~0.025 for the 8-arm stars. The I approximation of C-R-B, eq 7, produces lower values of $1/3 - \chi_2$ and in three cases no solutions were possible. The values of K and K' were 0.7 or larger. It is these large values which cause the C-R-B approximation to fail. The double approximation of eq 9 yields results closer to the exact solution and has the advantage of having an analytical solution.

The variation of ($1/3 - \chi_2$) with the number of branches suggests that ($1/3 - \chi_2$) for 4- and 6-arm stars would be even smaller than observed for the 8- and 12-arm stars. This would make θ_{A_2} experimentally indistinguishable from θ for polyisoprene stars with few branches.[4] Similarly, a possible dependence of ($1/3 - \chi_2$) on the number of branches (or g) on polystyrene stars explains qualitatively why no θ temperature depressions are found for low molecular weight linear polystyrene.[3] This variation of ($1/3 - \chi_2$) with branching apparently indicates the need to include additional χ terms. Alternatively ($1/3 - \chi_2$) could be made temperature, g, or segment density dependent. Data are presently too few to introduce another parameter into the model, however.

θ temperature lowering for branched polymers can be of two kinds: θ_{A_2} for $A_2 = 0$ and θ_α when $\alpha = 1$. C-R-B derived[7] the relationship

$$\frac{\theta - \theta_{A_2}}{\theta - \theta_\alpha} = \frac{3^{5/2}}{2^4} \frac{H(K')}{\alpha_{A_2}^3} \qquad (12)$$

Equation 12 predicts $\theta_\alpha < \theta_{A_2} < \theta$ with the requirement that K' is close to zero. For larger values of K', the opposite is possible, i.e., $\theta_{A_2} < \theta_\alpha < \theta$. Table II shows that this is indeed the case for our experimental data since at θ_{A_2}, $\alpha_{A_2} < 1$ in the C-R-B approximation. The exact solution and the double approximation on the other hand give $\alpha_{A_2} > 1$ and the order

Table III. Experimental and Theoretical Values of g and α^2 for Star-Shaped Polymers

	g_{th}	g_{exp}[a]	α_θ^2	α^2 [b]
4-arm polystyrene[2]		0.633	1.01	1.08
polyisoprene[4]	0.625	0.65	1.04	
6-arm polystyrene[3]		0.458	1.03	1.11
polyisoprene[4]	0.444	0.46	1.04	
8-arm polyisoprene	0.344	0.415[c]	1.20	1.19
12-arm polyisoprene	0.236	0.33[d]	1.40	

[a] Limit at high molecular weight. [b] Reference 18. [c] Based on samples 8-VIAAA, $\langle S^2\rangle_\theta = 8.0 \times 10^4$ Å^2, and 8-IXAAAAA, $\langle S^2\rangle_\theta = 2.75 \times 10^5$ Å^2. [d] Based on samples 12-VIIIAAA, $\langle S^2\rangle_\theta = 1.55 \times 10^5$ Å^2, and 12-VAAAA, $\langle S^2\rangle_\theta = 1.97 \times 10^5$ Å^2.

Table IV. Values of α_{A_2} and $1/3 - \chi_2$ for 8- and 12-Arm Polyisoprene Stars

sample	$\overline{M}_w \times 10^{-4}$	g[a]	I_{exact}		$I_{\text{C-R-B}}$		I'	
			α_{A_2}	$1/3 - \chi_2$	α_{A_2}	$1/3 - \chi_2$	α_{A_2}	$1/3 - \chi_2$
12-IXA	4.1	0.33	1.035	0.080			1.015	0.073
12-IVA	9.6	0.33	1.032	0.073			1.014	0.067
12-VIIAAA	25.0	0.33	1.035	0.079			1.015	0.072
8-VIIIA	4.1	0.415	1.005	0.032	0.993	0.028	1.004	0.031
8-VIIAA	11.0	0.415	1.006	0.038	0.990	0.033	1.004	0.037

[a] Limiting value as $M \to \infty$.

$\theta_\alpha < \theta_{A_2} < \theta$.

The calculations in Table II are based on theoretical predictions[10] for g. Measurements of $\langle S^2\rangle_\theta$ for 4- and 6-arm star polystyrenes and polyisoprenes[2-4] indicate that the experimental g values are only marginally larger than the theoretical g. In Figure 4 an example of the experimental infinite dilution scattering function of a high molecular weight 12-arm polyisoprene at θ_{A_2} is shown. As can be seen, the theoretical scattering function is followed very closely at low scattering vectors and $\langle S^2\rangle_{\theta(A_2)}$ can be derived with a fair degree of accuracy. It is found in this way that the experimental g values for 8- and 12-arm stars progressively further deviate from g theoretical as shown in Table III. It is of interest to note that, although the Mazur-McCrackin treatment[18] overestimates the α^2 values for the 4- and 6-arm polymers, their assessment is seemingly accurate for the octaarm star system.

Following Mazur and McCrackin,[18] these expanded radii are doubtless due to excluded volume effects present in the central region of these stars even at θ_{A_2}. For the lower molecular weight stars, $\langle S^2\rangle_{\theta(A_2)}$ seem to be even more expanded than in the high molecular weight limit.[19] The expansion of the radii of gyration for these stars cannot be accounted for in the simple lattice theory of polymer solutions. A detailed discussion of the dilute solution characteristics for these 8- and 12-arm polyisoprenes will be presented[19] at a later time.

Table IV contains a recalculation of the $1/3 - \chi_2$ term using the limiting values of g listed in Table III. Near-constant results were obtained which are larger than those found when the theoretical values of g were used. These combined results, Tables II and IV, show that $(1/3 - \chi_2)$ is a constant within each star-polymer series with the variation of this term becoming more pronounced for the case where values of g_{exp} (limit at high molecular weight) are used. The value of g_{exp} (limit at high molecular weight) can be expressed as $\equiv g_{\text{th}}(\sigma_b/\sigma_l)^2$, where σ_b/σ_l is the ratio of the flexibility factors of branched and linear chains, and represents a new segment length characteristic of the polymer but dependent upon the extent of branching. In agreement with this, the $\alpha_{\theta(A_2)}$ values (Table IV) calculated using $g_{\text{exp(limit)}}$ are lower than $\alpha_{\theta(A_2)}$ with g_{th} (Table II). In any case, it is clear that the value of the $1/3 - \chi_2$ term can depend upon the extent of branching present in the polymer under consideration.

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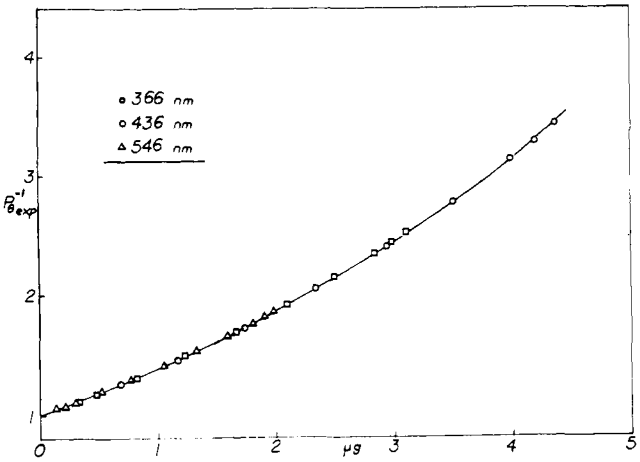

Figure 4. Experimental infinite dilution scattering function at θ_{A_2} for 12-VAAAA. $\mu = h^2\langle S^2\rangle_z$. Theoretical line calculated with $\langle S^2\rangle = 1.97 \times 10^5$ Å^2.

References and Notes

(1) (a) The Institute of Polymer Science; (b) The Department of Chemistry, Industrial Chemistry Division, The University of Athens, Athens, Greece; (c) Division of Chemistry, National Research Council of Canada.
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(17) We wish to mention that the reported[4] value of 34.1 °C for the linear polyisoprene θ temperature *may* be slightly high. The measurements of θ for a linear polyisoprene with an M_w of 1.3×10^6 indicate a value of 33.4 °C. The dioxane used for this measurement was from the same source as that used for 8- and 12-arm stars. This value of 33.4 °C is, though, within the limits reported elsewhere.[4] It should also be noted that the value[4] of 0.511 for the Mark-Houwink exponent indicates that θ for linear polyisoprenes may be slightly less than 34.1 °C. These small differences are due, we believe, to the dioxane quality.
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(19) N. Hadjichristidis, B. J. Bauer, and L. J. Fetters, to be published.