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Preparation of Six-Branched Polystyrene. Thermodynamic and Hydrodynamic Properties of Four- and Six-Branched Star Polystyrenes

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ABSTRACT: A number of six-branched star polystyrenes have been prepared by an anionic technique. Their dilute solution viscosities were determined in cyclohexane and toluene in order to compare the effect of branching on $[\eta]$ with theoretical predictions. Unperturbed dimensions of these polymers and of the four-branched star polystyrenes prepared earlier were determined and found to be in good agreement with values calculated from Gaussian-chain statistics. Second virial coefficients were measured in a temperature range around Θ (34.5°). They became zero at temperatures increasingly below Θ as the total molecular weight decreased and as the branch number increased. Values of B_0 (or ψ_1) were found to be independent of branching for these samples. The results are discussed in terms of modifications to the smoothed-density Gaussian-coil model of polymer structure.

In a previous publication the synthesis of narrow molecular weight distribution star polystyrenes with four equal branches was described.[1] It was shown that anionic polymerization techniques together with coupling reactions using a tetrafunctional silicon chloride compound led to the desired polymers. The hydrodynamic properties of dilute solutions of a series of four-branched polymers were compared to those of linear polymers. In particular, it was found that $g' = [\eta]_{br}/[\eta]_{lin}$ changed from 0.76 in a Θ solvent (cyclohexane 35°) to 0.724 in a good solvent (toluene 35°). These values were compared with two theoretical predictions: $g' = 0.79$ proposed by Zimm and Kilb[2] and $g' = 0.71$ proposed by Stockmayer and Fixman[3] both strictly speaking applying under Θ conditions. To distinguish between these two proposals, which differ by not more than 11%, puts severe demands on the quality of the polymers and the accuracy of the physical measurements. It was thought of interest to investigate the behavior of six-branched polymers. Indeed, for six-branched polymers $g' = 0.666$ according to Zimm–Kilb[2] and 0.51 according to Stockmayer–Fixman[3] a difference of nearly 30%.

This paper describes the synthesis and characterization of a series of six-branched polystyrenes and the measurements of their intrinsic viscosity in the same solvents as were used for the four-branched polymers. There are three references to six-branched polystyrene. The synthesis of one sample by coupling of living polymer with the cyclic trimer of phosphonitrilic chloride has been described.[4] Fractionation and molecular weight determinations have also been reported.[5] For one sample, obtained by coupling with hexachloromethylated benzene, no intrinsic viscosity measurements are available.[6] Two six-branched star polymers, obtained by coupling with hexa[*p*-(chloromethyl)-phenyl]benzene unfortunately contain an important amount of 11-branched material.[7]

We also report on some equilibrium thermodynamic properties of the four- and six-branched polystyrenes and compare them with the properties of linear polymers. Theoretical studies are available that predict the behavior of A_2,[3,8] $\langle S^2\rangle_0$,[3,9,10] and $\alpha^2 = \langle S^2\rangle/\langle S^2\rangle_0$[3,11] for such polymers. Data are available on one four-branched star polymer.[6] Some A_2 values in different solvents for one six-branched polystyrene are also given.[6]

Experimental Section

Polymer Preparation. The preparation of the four-branched star polystyrenes was fully described previously.[1] The six-branched polystyrenes were prepared along the lines described for the synthesis of the four-branched star polymers. 1,2-Bis(trichlorosilyl)ethane was used as the coupling agent. This compound was purchased from Chemicals Procurement Laboratories Inc. and was distilled before use. A middle fraction boiling between 83 and 85° under 16-mm pressure[12] was immediately transferred to a vacuum line system and degassed. All further manipulations were performed under high vacuum. To 25 g of the compound, 15 ml of *n*-hexane was added and three partial crystallizations were performed. At this point the product crystallized at 10°. Six recrystallizations gave a constant melting point at 24° (Literature 25.2[13]). This material (0.67 g) was diluted in *n*-hexane and subdivided into fragile bulbs. The silicon–chlorine bond concentration was determined by acid–base titration.

Polymerization and coupling reactions were carried out in benzene at 30°. All glassware was washed with *n*-butyllithium and rinsed by distilling benzene from a reservoir. Benzene was finally

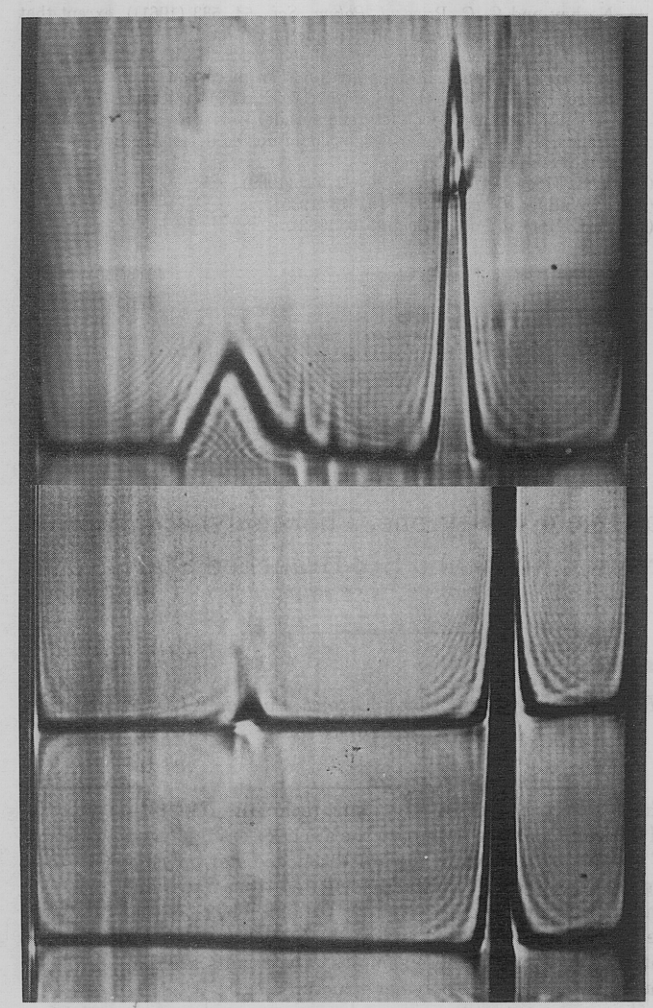

Figure 1. Sedimentation ultracentrifugation patterns in cyclohexane at 35° of HS111A before (top), after the first fractionation (center), and after the second fractionation (bottom).

distilled into the reaction vessel and the reservoir with residual *n*-butyllithium was sealed off. *sec*-Butyllithium was used to initiate the polymerization of styrene.[14] The styrene concentration could be monitored at 292 mμ by means of a uv quartz optical cell. After a minimum of 12 half-life times a 1-g polymer sample was removed to characterize the star precursor (single branch). The polystyryllithium was then converted to isoprenyllithium ends by the addition of 2 equiv of isoprene/chain. The coupling reaction was performed with a 20% excess of C–Li over Si–Cl. The reaction was followed by measuring the decreasing isoprenyllithium absorption at 290 mμ. After the reaction had gone to completion, excess C–Li bonds were destroyed by *tert*-butyl alcohol. The 1% polymer solution was fractionally precipitated from a benzene–methanol mixture. The first fraction (about 50% of the total) was refractionated from a 0.25–0.3% solution. The first fraction of this was retained for measurements.

Polymer Characterization. Reagent grade Eastman Kodak cyclohexane was freed from 2,2′,4-trimethylpentane by fractional distillation from calcium hydride. It was 99.98% pure gas chromatographically. It contained no aromatics as determined by the absence of uv absorption in the 250–270-mμ region. Reagent grade BDH toluene was fractionated from calcium hydride. A 50% middle cut was retained. Master polymer solutions and all dilutions were made by weight.

Number-average molecular weights were determined in toluene at 35° with a high-speed membrane Mechrolab 500 osmometer. Weight-average molecular weights were routinely measured with a Sofica photogoniometer in cyclohexane at 35°. Solvents and solutions were filtered through 0.2-μ Flotronics membranes. Unpolarized light of wavelength 4358 Å was used. The Rayleigh ratio for benzene was taken as 50.79×10^{-6} and the refractive index increment for polystyrene in cyclohexane as 0.181 cm^3/g. Molecular weights were reproducible to 1%. Each star-branched polymer was checked for the absence of precursor and lower branched material by sedimenting cyclohexane solutions at 35° in a Spinco Model E analytical ultracentrifuge at 59,780 rpm. The large Johnson–Ogston effect, acting under those conditions, allows the presence of 1–2% of five-branched polymers to be easily detected.[1] Figure 1 illustrates the effectiveness of the two-stage fractionation on isolation of six-branched polymers.

Measurement of Thermodynamic and Hydrodynamic Properties. Two light-scattering instruments were available for the measurements of $\langle S^2 \rangle$ and A_2. A Sofica photogoniometer was used either with unpolarized or vertically polarized incident beams of wavelength 4358 Å. Measurements could be made between angles of 30 and 150°. The alignment of the instrument was better than 1% in this range, as determined from the scattered intensities from benzene. The sample compartment was thermostated with an external circulating Haake water thermostat. The major limitation of the instrument lies in the instability of the water-cooled mercury lamp. Therefore, regular checks of the incident light intensity by means of a glass standard were required. In order to do this the sample cell had to be removed from the bath reducing the temperature control of the solution.

Temperature variation work was mostly performed with a double-beam Fica 50 light-scattering instrument. Alignment of the instrument was better than 0.5% between 37.5 and 150° and about 1% at 30° as measured by the fluorescence of Rhodamine B in methanol, excited with light of wavelength 366 mμ and using a Corning 2-62 filter in front of the photomultiplier. Alignment was also checked with a benzene standard using a vertically polarized incident beam of wavelength 4358 Å. The thermostating provided with the instrument was backed up by an external circulating water Haake thermostat, which provided some cooling in order to produce a more regular on–off cycle. The temperature, stable to about 0.1°, was monitored with a copper–constantan thermocouple. The overall light stability of the instrument was about 0.1% over a period of 10–20 min necessary for temperature equilibration of the polymer solution and scanning of 11 angles between 30 and 150°. The major difficulty with the Fica instrument is the slightly different position of the lamp arc on every start up of the instrument. Since refinement of the alignment to better than 1% at 30° was time consuming, correction factors were derived daily from the angular scattering intensities of the benzene standard and applied to the polymer solutions.

Second virial coefficients were determined from at least five polymer solutions covering a seven- to eight-fold concentration range. For measurements in cyclohexane up to 50°, the second virial coefficient was, within experimental error, identical whether calculated from either c/I or $(c/I)^{1/2}$ *vs.* c plots. In the case of the lower molecular weight polymers $(c/I)_{90°}$ was used instead of the theoretical $(c/I)_{0°}$. When a measurable angular dissymmetry was observed in cyclohexane solutions $(c/I)_0$ was not more than 10% larger than $(c/I)_{90°}$, the extrapolation to zero angle introducing a somewhat larger uncertainty in the A_2 values.

Experimental errors leave about 10% uncertainty when the second virial coefficients are about 1×10^{-5} cm^3/g mol. The limit of uncertainty decreases to 2–3% at A_2 values of the order 1×10^{-4} and increases when second virial coefficients are smaller and negative. Θ temperature determinations (*cf.* Results) derived from A_2 temperature curves were reproducible to within about 1°.

The mean-square radius of gyration was obtained from the dependence of $(c/I)_{c=0}$ on $\sin^2 \theta/2$. Such plots showed a definite upward curvature for the highest molecular weight samples. Whenever $\mu = 16\pi^2 \langle S^2 \rangle (n/\lambda)^2 \sin^2 \theta/2 \geq 1$, higher terms in the expansion of $P(\theta)$ become important and cannot be neglected. Furthermore, the $P(\theta)^{-1}$ function varies with the architecture of the polymer.[15] To obtain the initial slope of $(c/I)_{c=0}$ against $\sin^2 \theta/2$ plots, the method of Zimm was used.[16] A value of $\langle S^2 \rangle$ was estimated and used to calculate μ for every angle. The correction factor by which each $(c/I)_{c=0,\mu}$ has to be multiplied is equal to $P(\theta)_\mu[1 + (\mu/3)]$, $P(\theta)$ depending on the type of branching in the polymer. The corrected $(c/I)_{c=0,\mu}$ values allow the determination of a better $\langle S^2 \rangle$, which can be used to recycle the experimental results, until no further difference in $\langle S^2 \rangle$ is found. If the starting $\langle S^2 \rangle$ is judiciously chosen, one correction cycle is sufficient. The method is based on two assumptions. First, the polymers are considered monodisperse in molecular weight, and secondly, the Gaussian coil form is assumed in poor and good solvents. The first assumption is justified in view of the method of synthesis of the polymers, especially for the star polymers in which the polydispersity of the precursor is further reduced by coupling into one molecule. Furthermore, the correction factors do not change much with small deviations from

Table I
Molecular Weight Data for Six-Branched Star Polystyrene

Sample	$10^{-4}(M_n)_{prec}$	$10^{-4}(M_n)_{star}$	$10^{-4}(M_w)_{star}$	Deg of Branching[a]
HS071A	1.09	6.44	6.53	5.90
HS061A	1.77	10.73	11.0	5.83
HS011A	3.74	23.2	23.7	6.19
HS011B[b]			22.5	(6.01)
HS101A	5.44	31.2	31.7	5.73
HS041A	8.43		50.9	(6.04)
HS111A	10.0		59.1	(5.91)
HS051A	18.5		109.0	(5.90)
HS091A	27.9		167.4	(6.00)
HS121A	29.9		182.0	(6.09)

[a] $(M_n)_{star}/(M_n)_{prec}$, values in parentheses $(M_w)_{star}/(M_n)_{prec}$. [b] Second fraction of refractionation.

Table II
Intrinsic Viscosity Data on Six-Branched Star Polystyrenes

Sample	c-C_6H_{12}, 35°	c-C_6H_{12}, 50°	Toluene, 35°
HS071A	0.136	0.144	0.185
HS061A	0.177	0.193	0.275
HS011A	0.269	0.294	0.468
HS101A	0.302	0.363	0.619
HS041A	0.374	0.461	0.801
HS111A	0.405	0.489	0.895
HS051A	0.557	0.699	1.41
HS091A	0.680	0.918	1.90
HS121A	0.723	0.973	2.09

monodispersity.[16] The second assumption has now been found experimentally to hold true to fairly high values of μ, *e.g.*, for polymers of molecular weights of 2 to 3 × 10^6 in good solvents.[17-19] The accuracy with which the radius of gyration can be determined is overridingly influenced by the clarification of the solutions. The results obtained were reproducible to about 10%.

Intrinsic viscosities of the six-branched star polymers were measured with Cannon–Ubbelohde viscometers in cyclohexane at 35 and 50° and in toluene at 35°. A Hewlett-Packard 5901B automatic timer triggered by photosignals was used. Since flow times could be determined to 10^{-2} sec, somewhat lower concentrations could be used than with manual timing thereby facilitating extrapolation to zero concentration.

Results and Discussion

Synthesis and Characterization of Six-Branched Star Polymers. As was observed also in the preparation of four-branched polystyrene,[1] the addition of the first two polymer chains to the coupling agent proceeds very rapidly. Four branches are added in about 24 hr, while the reaction to incorporate the last two branches takes from 3 days for a 6 × 10^4 to 3 weeks for the 1.4 × 10^6 molecular weight six-branched star polystyrene. An experiment in which the isoprene was omitted confirmed the observation of Gervasi *et al.*[4] that only four polystyrene branches could be added directly to 1,2-bis(trichlorosilyl)ethane. No satisfactory product was obtained when the isoprene was added to the residual polystyryllithium after four pure polystyrene branches had been attached to the coupling agent. The isoprenyl end groups seem to have steric properties which make them superior in such chain-crowded coupling reactions. Sample HS091A contains about 5% five-branched material as determined by ultracentrifugal analysis. As will be shown later, its properties do not significantly differ from those of the other essentially pure six-branched polymers.

The molecular weight characterization data on the six-branched star polystyrenes and their linear precursors are given in Table I. Whenever experimentally accessible, the number-average molecular weight ratio of star and precursor polymer was used to calculate the degree of branching of the star-branched polymers. The values for samples HS071A and HS051A are changed slightly from those quoted in a preliminary communication[20] after a reinvestigation of the number-average molecular weights of their respective precursors. The choice of weight-average molecular weight data to evaluate the average number of branches in the star polymers is less desirable but necessary in the case of the high molecular weight star polymers. Comparison between M_w and M_n data where they are available indicate that, by using M_w to evaluate the degree of branching, apparently slightly higher degrees of branching are to be expected. The degrees of branching quoted in the last column of Table I are within the limits 5.8 and 6.2, *i.e.*, within 3.3% of the theoretical value. Such difference should be ascribed to the experimental error in the determination of the molecular weights rather than to the presence of 20% polymer with five or seven branches. This conclusion is supported by the inspection of the sedimentation patterns in which 1 or 2% of lower branched material could be easily detected.

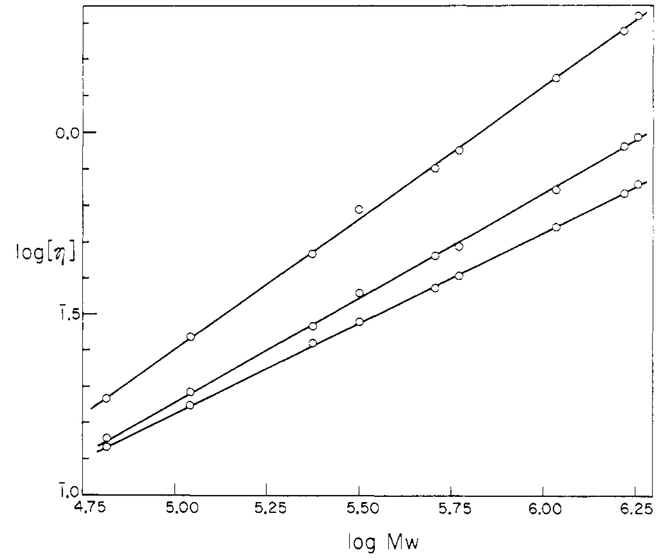

Figure 2. Log $[\eta]$ *vs.* log M_w for six-branched regular star polystyrene. From top to bottom, toluene 35°, cyclohexane 50°, and cyclohexane 35°.

Hydrodynamic Properties of Six-Branched Star Polystyrene. Intrinsic viscosity data on the six-branched polystyrene samples in cyclohexane at 35 and 50° and in toluene at 35° are given in Table II. The values in cyclohexane at 35° were communicated previously.[20] The intrinsic viscosity–molecular weight relation is shown in Figure 2. For the six-branched polystyrene, the constants in the Mark–Houwink–Sakurada relation $[\eta] = KM^{\alpha}$ are $\alpha = 0.50$,

Table III
Literature Values of $g' = [\eta]_{br}/[\eta]_{lin}$ for Star-Shaped Polystyrenes

No. of Samples	c-C_6H_{12}, 35°	C_7H_8, 35°	Ref
	Four-star, $g^{1/2} = 0.79$, $h^3 = 0.71$[a]		
1	0.75		6
1	0.82	0.84[b]	24
9	0.76	0.72	1
4	0.76[c]	0.68	7
	Six-Star, $g^{1/2} = 0.67$, $h^3 = 0.51$[a]		
2	0.57	0.46	7
9	0.63[d]	0.57	This work

[a] $g^{1/2}$ according to ref 2, h^3 from ref 3. [b] At 25°. [c] 0.73 at 50°. [d] 0.60_5 at 50°.

Table IV
θ_{A_2} for Star Polystyrenes in Cyclohexane

Sample	$10^{-4}M_w$	Θ_{A_2} (°C)
	Four-Branched Polymers	
S131A	5.02	29.2
S121A	9.33	31.8
S111A	15.2	32.1
	Six-Branched Polymers	
HS071A	6.6	25.3
HS061A	10.9	27.8
HS011B	22.5	30.2
HS101A	31.7	32.0
HS111A	59.1	33.4

0.58, and 0.72_6 and $K = 5.24 \times 10^{-4}$, 2.24×10^{-4}, and 5.8×10^{-5} for cyclohexane at 35°, cyclohexane at 50°, and toluene at 35°, respectively. The values of the exponents are identical with those for linear and four-branched star polystyrenes.[1] As a result, a constant ratio is found between the intrinsic viscosity of the six-branched star polymers and linear polystyrene in the molecular weight range investigated.

$$[\eta]_{br}/[\eta]_{lin} = K_{br}/K_{lin} = g'$$

Using K_{lin} values derived previously,[1] $g' = 0.631$, 0.605, and 0.56_8 for cyclohexane at 35°, at 50°, and toluene at 35°, respectively. Zimm and Kilb[2] calculated $g' \approx g^{1/2} = (\langle S^2\rangle_{0,br}/\langle S^2\rangle_{0,lin})^{1/2}$ which equals 0.666 for the six-branched star polymers. Stockmayer and Fixman[3] calculated the ratio of the friction constant $[f]$ of the branched and linear polymer and extended this to the intrinsic viscosity by the approximation $[\eta]_{br}/[\eta]_{lin} \approx h^3 = ([f]_{br}/[f]_{lin})^3$ which equals 0.51 for six-branched star polymers. The experimental values fall between the predictions of the two theories and are definitely lower than the values from the most exact calculations which give g' somewhat greater than $g^{1/2}$.[2] In a recent publication, Osaki and Schrag[21] have expanded the Zimm–Kilb theory to include variation of the number of segments and the drainage factor. The slightly smaller values of g' than $g^{1/2}$ for the four- and six-branched polymers could indicate a small deviation from the non-free draining limit. Such effect, however, is opposite to that expected for polymers with a higher segment density. The decrease of g' with increasing solvent power was also found for the four-branched polymers.[1]

Table III summarizes published results for four and six star-branched polystyrene. Results for three star-branched polystyrene are given by Herz *et al.*[22] The average experimental value of g' is close to 0.76 for four-branched polymer, definitely lower than the exact Zimm–Kilb calculation which predicts 0.814. The deviation appears to increase with increased branching for although an exact calculated value is not available for six-star polymers, it is clear from the approximate formulas presented[2] that it would be close to 0.69. This is confirmed by recent results of Zilliox[23] who has published intrinsic viscosity data on a series of highly branched star-shaped polystyrenes. The average number of branches ranged from 6 to 15.5. In all cases $g' < g^{1/2}$, the inequality increasing with increasing number of branches. In a similar way, g' in benzene was slightly less than in a Θ solvent.

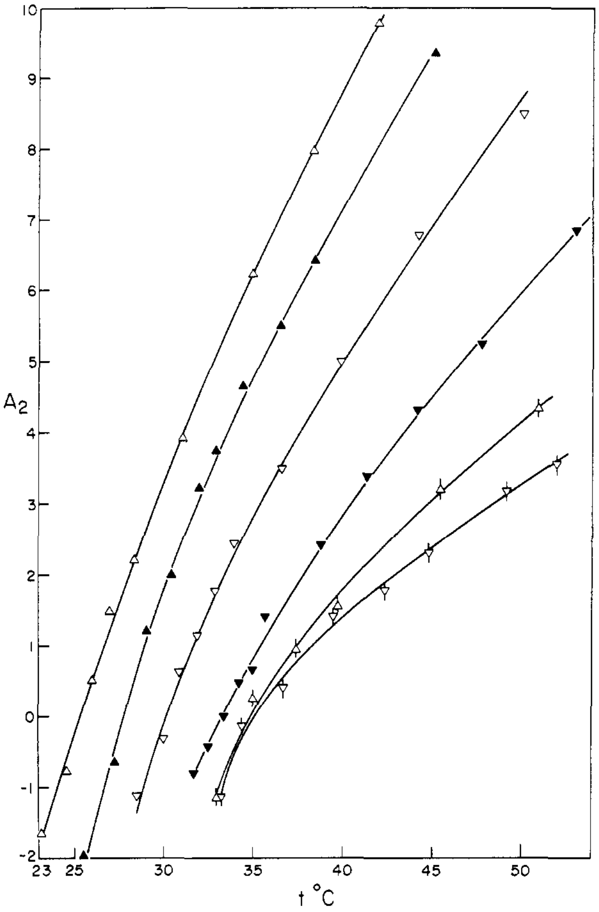

Figure 3. A_2 *vs.* temperature data for six-branched star polystyrenes in cyclohexane: (△) HS071A; (▲) HS061A; (▽) HS011A; (▼) HS111A; (⍋) HS051A; (⍒) HS121A.

As will be shown in the following section of this study, the Θ temperatures of the lowest molecular weight four- and six-branched polymers in cyclohexane are lower than 34.5°, the value for linear polymers. This would imply that the data for cyclohexane at constant temperatures (34.5°) are not obtained under the same thermodynamic conditions. Measurement of $[\eta]$ at the Θ temperature (as determined by $A_2 = 0$), however, showed that for the low molecular weight polymers $[\eta]_{\Theta_{A_2}}$ differed from $[\eta]_{35°}$ by not more than the experimental error.

Thermodynamic Properties of Four- and Six-Branched Polystyrenes. a. Θ Temperature of Star-Branched Polymers. Light-scattering studies of the dependence of the second virial coefficient of cyclohexane solutions of the branched polymers on temperature revealed that the Θ temperature defined as the temperature for which $A_2 = 0$ (Θ_{A_2}) is not constant as in the case of linear polystyrenes but decreases with decreasing molecular weight of the branched polymers. An example of experimental results is shown in Figure 3.

The experimental values of Θ_{A_2} are given in Table IV. Higher molecular weight star polymers have their Θ tem-

Table V
Unperturbed Dimensions of Linear and Star-Shaped Polystyrenes in Cyclohexane at 34.5°[a]

Sample	$\langle S^2\rangle_0 \times 10^{12}$ cm²	$\langle S^2\rangle_0/M_w \times 10^{18}$	g_{expt} (Av)	g_{th}
Linear				
PS800f2	5.2 (5.3)	7.6 (7.9)		
PS1000f2	14.0 (14.55)	7.75 (8.2)		
Four branched				
S101AAA	(2.3)	(5.0)		
S141AA	(2.7)	(5.2)		
S221AA	4.25	4.75	0.633	0.625
S181A	(5.34)	(5.1)		
S191AA	6.55 (6.95)	4.9 (5.0)		
Six branched				
HS051A	3.7 (3.65)	3.4 (3.35)		
HS091A	(6.1)	(3.65)	0.458	0.444
HS121A	6.6 (7.1)	3.65 (3.9)		

[a] The values are from measurements with the FICA 50, values in parentheses are from measurements with the Sofica instrument.

perature within experimental error equal to that of the linear polymers (34.5°). Similar decreases of the Θ temperature were found recently for heavily branched comb polystyrenes[25-27] and also for star-shaped polystyrenes with 7 to 15.5 branches.[23] An empirical relation $\Delta\Theta = f(p/M_{br})$ has been proposed, to account for the dependence of the Θ-point lowering on the molecular weight of the branches and number of branches (p) for comb-type polymers. For the present polymers, if p is put equal to $f - 2$, where f is the number of branches in the star, the Θ temperatures of the four- and six-branched polymers do in fact fall on a single curve. The agreement is however probably fortuitous and in addition not all comb-type polymers obey this relationship.

b. Unperturbed Dimension of Star-Shaped Polymers. In section (a) it was shown that for star-shaped polymers that have high enough molecular weights to measure their dimension in solution by light scattering, the Θ_{A_2} temperature is unchanged from the Flory Θ temperature for the linear polymers. The values of the unperturbed dimension at the Flory Θ temperature can therefore be compared with the random-flight statistics calculations for star polymers. The experimental results for $\langle S^2\rangle_0$ are summarized in Table V.

The mean value for the $\langle S^2\rangle_0/M_w$ ratio for linear polystyrene was found to be 7.9×10^{-18} (cm² mol)/g in satisfactory agreement with values of 7.6×10^{-18},[28] 7.5×10^{-18},[29] and 8.4×10^{-18},[19] in cyclohexane at 34.5° and 7.6×10^{-18},[30] in hexyl-*m*-xylol at 16°. The $\langle S^2\rangle_0/M_w$ for the four-branched star polystyrenes are in excellent agreement with the average $(5.03 \pm 0.2) \times 10^{-18}$ obtained by Berry.[6] In conclusion, the unperturbed dimensions of four- and six-branched polystyrenes for which measurements are available follow the theoretical predictions based on random-flight statistics. The unperturbed dimensions of star polystyrenes with more branches seem also to conform closely to the theoretical calculation.[23]

c. A_2 and $\langle S^2\rangle$ Dependence on Temperature near the Θ Temperature. In order to compare experimental results with current polymer solution theories near the Θ temperature, the method of Berry[28] was followed

$$A_2 = 4\pi^{3/2}N_A BF'(z) \tag{1}$$

where

$$B = (1/4\pi)^{3/2}(n/M)^2\beta \tag{2}$$

in which N_A is Avogadro's number, $F'(z)$ is a monotonically decreasing function describing the noninterpenetration function of two polymer chains as a function of z with $F'(z) = 1$ for $z = 0$, and β is the mutually excluded volume per pair of segments.

$$z = (3/2\pi\langle b^2\rangle)^{3/2}n^{1/2}\beta = BA^{-3}M^{1/2} \tag{3}$$

Equation 3 defines (z) with n the number of segments in the chain, b the effective length per segment, and $A^2 = \langle S^2\rangle_0/M$. The middle term in eq 3 defines z on the molecular level; the right-hand side contains experimentally accessible parameters. Berry assumes that the temperature variation of B is of the form

$$B = B_0(1 - (\Theta/T)) \tag{4}$$

B_0 is derived from A_2 measurements near the Θ temperature as the initial slope in a plot of A_2 against $1 - (\Theta/T)$ assuming that $F'(z) \rightarrow 1$. When B_0 is obtained, z can be calculated through eq 4 and 3. $F'(z)$ can then be estimated from an appropriate theoretical function for $F'(z)$

$$F'(z) = 1 - Cz + 0(z^2) \tag{5}$$

$A_2/F'(z)$ is then replotted against $1 - (\Theta/T)$ allowing an improved B_0 to be derived.

Equation 1 can be rearranged to

$$A_2M^{1/2}/4\pi^{3/2}A^3N_A = zF'(z) \tag{6}$$

A plot of the left-hand side of eq 6 against z yields an experimental $F'(z)$ function, which should be independent of the molecular weight and temperature and which can be compared with theoretical closed expressions.

The method has been criticized[31] on the basis that Berry assumes a constant excess entropy of mixing with temperature (B_0 in eq 4). Also the z values obtained in this way led to some abnormal conclusions on the hydrodynamic properties of polymers.[32] Nevertheless, for the purpose of comparing the polystyrenes of different architecture in the small range from Θ to Θ + 15° the method can be considered useful, its main advantage being that data on lower molecular weight polymers can be used.

The A_2 data were processed as a function of T (examples are shown in Figure 3) along the lines outlined by Berry. $F'(z)$ corrections were carried through for values of $z < 0.05$ with C values in eq 5 equal to the theoretical values 2.865, 3.875, and 5.390 for linear, four-, and six-branched poly-

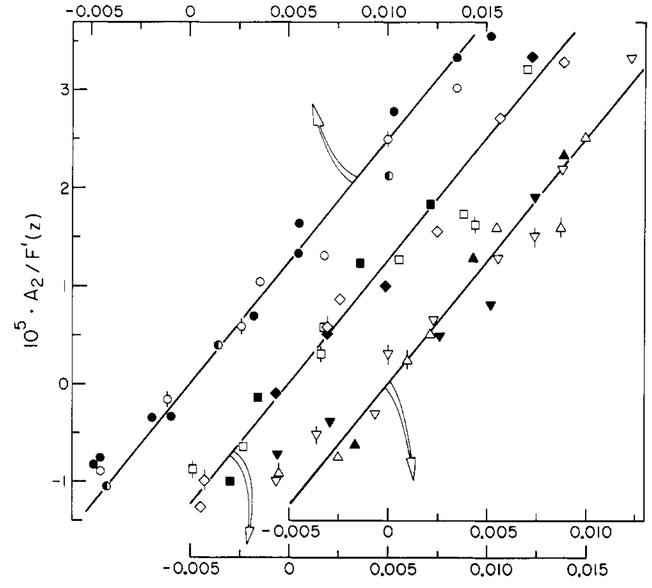

Figure 4. $A_2/F'(z)$ *vs.* $1 - (\Theta/T)$. ψ_1 or B_0 is derived from the slope. Left: linear polystyrene: (○) PS100f2; (●) PS150f2; (◐) PS800f2; (ϕ) PS1000f2. Center: four-branched polystyrene: (□) S131A; (■) S121A; (◇) S111A; (◆) S161A; (ф) S221A; (ϕ) S191A. Right: six-branched polystyrene, symbols as in Figure 3.

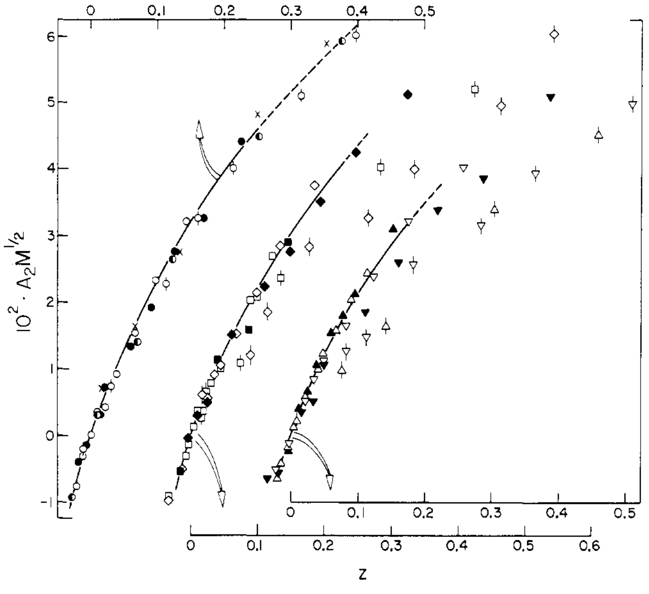

Figure 5. $A_2M^{1/2}$ *vs.* z for linear (left), four-branched (center), and six-branched (right) polystyrenes. Symbols as in Figures 3 and 4; (×) ref 19.

mers.[8] Values of Θ_{A_2} were used in calculating the function $1 - (\Theta/T)$. This raises no problem for the polymers of higher molecular weight where $\Theta_{A_2} = 34.5°$ but since z values less than 0.05 are difficult to obtain for these polymers, the data are heavily biased toward polymers of lower molecular weight where $\Theta_{A_2} \neq \Theta$. The implications of this choice will be considered in a later section. Figure 4 shows that the initial slopes in $A_2/F'(z)$ *vs.* $1 - (\Theta/T)$ plots are, within experimental error, identical for linear, four-, and six-branched polymers. The value of $B_0 = 0.186 \times 10^{-27}$ can be derived, which is 9% lower than Berry's value for polystyrene in decalin.[28] Berry reported B_0 for one four-branched polystyrene equal to the value for linear polystyrene and B_0 for one six-branched polymer 0.9 $B_{0,\mathrm{lin}}$.[6] The latter difference is probably within the experimental error. Closer inspection of Figure 4 reveals that data for the higher molecular weight polymers fall generally below the average line, despite the fact that the $F'(z)$ correction will tend to make $A_2/F'(z)$ values too high (since only the first term in the series is applied). The phenomenon is more pronounced the more branches the polymer has. The same effect is shown more clearly in Figure 5, where $A_2M^{1/2}$ is plotted *vs.* z over a wider range of z values. The latter is calculated from eq 3 with the experimental value of B_0 and $\langle S^2\rangle_0/M_w = 7.9 \times 10^{-18}$ (cm^2 mol)/g. The superposition of molecular weight and temperature data, a consequence required for Berry's assumption, seems of limited applicability. In the extreme, A_2 values would have to be about 30% higher for superposition to pertain. Such deviations are clearly outside experimental error. In Figure 5 some published experimental data on linear polystyrene are included.[19]

d. Three-Parameter Theories. Use of the Θ_{A_2} temperature in the normal two parameter theory in the previous section to evaluate B_0 (or ψ_1) raises some questions, for this theory cannot predict a decrease below the normal value of 34.5°. The smoothed density model of polymer molecules has been modified by Orofino and Flory[33] and by Candau, Rempp, and Benoit[34] to include higher interaction terms. The introduction of a χ_2 term converts the standard theory into a three-parameter theory. Such a modification could be expected to be important in the case of solutions of branched polymers because of their appreciably higher segment density.[34] Both treatments involve the same basic assumptions and differ only in the approximations made in the calculation of the second virial coefficient.

In summary chain expansion and Θ-point depression are given by

$$\alpha^2 - 1 = 2C_m\psi_1\left[1 - \frac{\Theta}{T}\right]\frac{M^{1/2}}{\alpha^3 g^{3/2}} + \frac{2}{3}\frac{C_m'}{\alpha^6 g^3} = \frac{K}{2} + \frac{K'}{3} \qquad (7)$$

$$(\alpha^5 - \alpha^3)_{\Theta_{A_2}} = \frac{2}{3}\frac{C_m'}{\alpha^3 g^3}\left[1 - \frac{3^{5/2}}{2^4}H(K')\right] \qquad (8)$$

$$1 - \frac{\Theta}{\Theta_{A_2}} = -\frac{3^{3/2}}{2^4}\frac{C_m}{C_m\psi_1}\frac{H(K')}{M^{1/2}\alpha^3 g^{3/2}} \qquad (9)$$

where C_m is the normal Flory constant for a linear polymer and C_m' is defined as

$$\frac{3^{5/2}}{2^3}\frac{(1/3) - \chi_2}{2\pi^3}\left[\frac{\bar{v}^3}{N_a^{\,2}V_1}\right]A^{-3}$$

The function $H(K')$ is unity according to Orofino and Flory but increases above unity as K' increases, reaching a value of ~1.5 at moderate values of K' according to Candau *et al.* Use of eq 8 and 9, together with various assumed values of (⅓) − χ_2, enables one to fit the experimental values of Θ_{A_2} of both four- and six-star polymer to a single parameter. This is 0.045 (C–R–B) or 0.055 (O–F) as shown in Figure 6 for the former case. A similar plot constructed from the Orofino–Flory approach gives an equally good fit. It is clear that qualitatively at least, such modifications of standard polymer solution theory can account for the results observed. More careful examination, however, shows that the Θ_{A_2} depression falls more rapidly to zero than predicted as the polymer molecular weight is increased. For the same reason, use of the values of χ_2 appropriate to branched polymers predicts that a linear polystyrene of mol wt 30,000 should have a small Θ_{A_2} depression of 2° which is not observed experimentally.

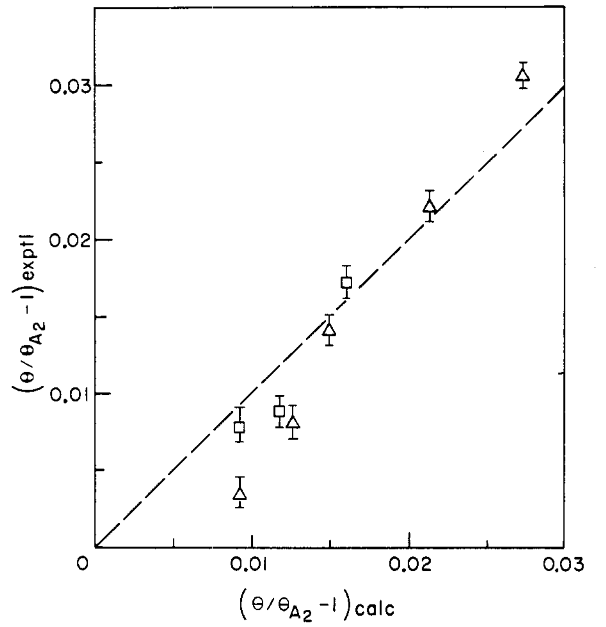

Figure 6. Experimental *vs.* calculated depression of Θ_{A_2}. Dotted line, calculated from eq 9 using $(1/3) - \chi_2 = 0.045$.

The three parameter theories modify the dependence of A_2 on temperature. For example close to Θ_{A_2} the second virial coefficient is given by

$$A_2 = (2^4/3^{3/2})\pi^{3/2}N_aA^3C_m\psi_1[1 - (\Theta_{A_2}/T)]G(K') \quad (10)$$

An additional term occurs which involves C_m' but this is quite negligible at Θ_{A_2}. $G(K')$ is the function plotted by Benoit *et al.*[34] and has a value ~0.7 at Θ_{A_2} for our six-star polymers. The temperature coefficient of A_2 around Θ_{A_2} should be 30% lower than for linear polymers assuming ψ_1 is unchanged, contrary to the observed results. It is clear, however, that G should really be a function of both K, and K', if the series expansion of K had not been truncated at the linear term. At Θ_{A_2}, for the six-star polymers, the solution of eq 8-9 gives $K \sim -1$, $K' \sim 1.5$ which suggests that this approximation is not valid for these polymers. This is confirmed by an examination of the Orofino–Flory approach. Here an approximate analytic expression is provided for A_2

$$A_2 = \frac{16\pi N_a}{3^{3/2}}A^3\frac{g^{3/2}\alpha^3}{M^{1/2}}\ln\left[1 + \left(\frac{\pi^{1/2}}{4}\right)K + \left(\frac{\pi^{1/2}3^{3/2}}{32}\right)K'\right] \quad (11)$$

Expansion of the logarithm in series shows that A_2 close to Θ_{A_2} is still given by eq 10 with $G(K,K')$ given by

$$1 - \frac{\pi^{1/2}}{8}K + \frac{\pi}{3 \times 2^4}K^2 - \frac{\pi^{3/2}}{2^8}K^3\ldots - \frac{\pi^{1/2}3^{3/2}}{2^5}K' + \frac{\pi 3^3}{2^{10}}K'^2 - \frac{\pi^{3/2}3^{9/2}}{2^{15}}K'^3\ldots$$

The K' terms reproduce the K' function of Benoit *et al.* very closely and the K terms the Flory $F(X)$ function with reasonable accuracy. Inclusion of the K terms (which reduce the deviation of G from unity at Θ_{A_2}) leads to the result that at this point G is very close to unity. The net result is that the variation of A_2 with $1 - (\Theta_{A_2}/T)$ around Θ_{A_2} is predicted to be the same for linear and branched polymers given a constant ψ_1.

It appears therefore that the solution behavior of branched polymers can be at least approximated by a three-parameter theory using ψ_1,Θ,χ_2 values which are independent of molecular architecture. Of course it is well known that the smoothed density model predicts the variation of α and A_2 only poorly. This can be circumvented to some extent around Θ by an arbitrary shift of the constants[36,37] and it is hoped that the three-parameter form could be similarly adjusted. The main result of the inaccuracy of this type is to produce errors in the value of $(1/3) - \chi_2$ evaluated from the data.

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(35) K, K' become X_1, X_2 in Ororfino–Flory notation. These authors make the approximation that $3^{5/2}/2^4$ equals unity (actual value 0.974). This leads to the conclusion that $\alpha = 1$ at Θ_{A2}. The more accurate expression allows a small deviation from $\alpha = 1$ at Θ_{A2}. The Candau–Benoit treatment allows a further deviation *via* the term $H(K')$. As in ref 34 in order to give manageable solutions the unjustified assumption is made that χ_2 is temperature independent.
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