ture for 12 hr. The flask was opened and the polymer was precipitated into 200 ml of rapidly stirred methanol.

(3) The presence of living polymer of 2-(4′-vinyl)phenyl-5-phenyltetrazole was confirmed as follows. Into a glass vessel equipped with a breakable seal (A) was added 0.4633 g (1.87 mmol) of 2-(4′-vinyl)phenyl-5-phenyltetrazole and 15 ml of tetrahydrofuran. To an identical vessel (B) was added 0.5747 g (2.32 mmol) of 2-(4′-vinyl)phenyl-5-phenyltetrazole and 15 ml of tetrahydrofuran. Both vessels A and B were sealed *in vacuo* and attached to a mixing flask (C). To this flask was also attached an empty glass vessel (D). The flask C was evacuated and 0.25 ml of 0.1 *M n*-butyllithium in *n*-heptane was added under a nitrogen atmosphere. The flask was further evacuated to remove the *n*-heptane. It was then sealed *in vacuo* and cooled to −78°. The 2-(4′-vinyl)phenyl-5-phenyltetrazole solution in vessel A was introduced into the flask *via* a breakseal and stirred for 15 min after the addition was complete. One-fifth of the solution was transferred into the empty vessel D and sealed, and the 2-(4′-vinyl)phenyl-5-phenyltetrazole solution in vessel B was then introduced into the reaction flask C *via* a breakseal and stirred for 1 hr after the addition was complete. The contents in the reaction flask C and in vessel D were emptied separately into excess methanol. The white polymer was collected, dried *in vacuo*, and weighed. From vessel D, 0.0604 g of white polymer ($[\eta] = 0.45$, $M_n = 11{,}000$) was obtained; from the reaction flask C, 0.6529 g of white polymer ($[\eta] = 0.78$, $M_n = 18{,}000$) was obtained.

(4) The copolymerization of **2** with isoprene was carried out as follows. Into a glass vessel equipped with a breakable seal was added 0.2543 g (1.03 mmol) of **2** and 30 ml of *n*-heptane. To an identical vessel was added 3.405 g (44.8 mol) of isoprene and 10 ml of *n*-heptane. Both vessels were sealed *in vacuo* and attached to a mixing flask. After 0.3 ml of 0.1 *M n*-butylithium in *n*-heptane had been introduced into the flask and the heptane had been removed, the flask was sealed *in vacuo* and cooled to −78°. The solution of isoprene was introduced and stirred for 15 min after the addition was complete. The solution of **2** was then added and after the addition was complete, the reaction mixture was slowly stirred at room temperature for 12 hr. The polymer was then precipitated into 400 ml of rapidly stirred methanol: $[\eta] = 0.43$.

Emulsion Polymerization. The emulsion polymerization of **2** was carried out as follows. To 40 ml of deionized water in a pressure bottle was added 1 g of dodecyl sodium sulfate and 0.05 g of potassium persulfate. In 5.5 g (52.9 mmol) of styrene was dissolved 0.8071 g (3.2 mmol) of **2** and 0.1 g of *n*-dodecyl mercaptan. This styrene solution was added to the pressure bottle. This bottle was cooled in an ice–water bath and approximately 18 g of butadiene was added. The excess butadiene was left in the bottle. The bottle was then capped and immersed in a mechanically tumbled constant-temperature bath and heated at 50 ± 1° for 21 hr. It was then cooled and 2 ml of distilled water containing 0.5 g of phenyl-β-naphthylamine was added. The coagulated polymer was filtered. It was purified by reprecipitation from benzene solution into methanol and dried *in vacuo* to afford 14.8 g (73%) of rubbery white polymer: $[\eta] = 0.91$.

Cross-Linking Reaction. Polymer samples were cross-linked by first determining their decomposition temperatures by tga. Samples were then either heated dry to the appropriate temperature for a few minutes or heated in a solvent with a suitable boiling point at the reflux temperature. Solubility of the polymer which had been cross-linked dry was then tested in a variety of good polymer solvents. In the case of cross-linking in a solvent, precipitation started within minutes.

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Preparation and Characterization of Four-Branched Star Polystyrene

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ABSTRACT: A method is described for the preparation of well-defined four-star polystyrenes involving coupling of polystyryllithium with 1,2-bis(methyldichlorosilyl)ethane. Nine samples were prepared over a 30-fold range of molecular weight. Osmotic and light-scattering techniques were used to measure number- and weight-average molecular weights where possible. Intrinsic viscosity and sedimentation coefficients were measured in cyclohexane at 35 and 50° and in toluene at 35°. The ratio g' ($[\eta]$(branched)/$[\eta]$(linear)) was found to be 0.76 under θ conditions and slightly lower in better solvents. The value falls between theoretical estimates. The corresponding ratio of sedimentation coefficients (h) was found to be 0.93–0.94 compared with a theoretical value of 0.89.

The synthesis of well-defined branched polymers became feasible with the discovery of anionic polymerization systems that are free of chain transfer and termination reactions. Attempts to synthesize star polymers by anionic methods have generally run along two lines. The research group at Mellon Institute treated living polystyryllithium with tri- and tetra(chloromethyl)benzene compounds in a mixture of benzene and tetrahydrofuran.[1,2] Although the desired tri- and tetrafunctional star polymers were obtained in good yield, the presence of higher molecular weight polymer made it particularly difficult to purify them. To avoid higher molecular weight coupling products, larger percentages of tetrahydrofuran and higher temperatures had to be used. Under these conditions polystyryllithium becomes unstable. The use of potassium as the counterion avoids difficulties at the coupling stage but tends to widen the molecular weight distribution of the polymer.[3] The same method was used recently with hexa[*p*-(chloromethyl)phenyl]benzene to produce six-branched star polystyrene.[4]

The second route to star polymers uses the reaction of living polymers with polyfunctional silicon chloride com-

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pounds in hydrocarbon solvents. The reaction of polystyryllithium with silicon tetrachloride yields a mixture of three- and four-branched polystyrene.[5,6] Gervasi reports that only four chlorine atoms are substituted when polystyryllithium is treated with 1,2-bis(trichlorosilyl)ethane.[7] However, the reaction of polybutadienyllithium with methyltrichlorosilane and tetrachlorosilane gave three- and four-branched polymer, respectively.[8]

Two other methods have been employed more recently to couple polystyryllithium into more complex structures. Branched star polymers with an average of 10–15 branches have been prepared by addition of *p*-divinylbenzene to living polystyrene.[9] Tri(allyloxy)-2,4,6-*s*-triazine is a new coupling agent with which trifunctional star polystyrene is obtained.[10]

Previous work on four- and six-star polystyrene has been limited, because of experimental difficulties, to one or two samples of each functionality. To better determine the effects of branching on physical properties, a wide range of well-characterized samples of different molecular weight and given functionality is obviously desirable. This paper describes a method of preparing such a set of samples without great difficulties. Four-branched star polystyrene was produced by treating polystyryllithium with 1,2-bis(methyldichlorosilyl)ethane, in which only two chlorine atoms are attached to each silicon atom. Molecular weight, intrinsic viscosity, and sedimentation coefficient measurements are reported.

Experimental Section

1,2-Bis(methyldichlorosilyl)ethane was prepared by the slow addition of methyldichlorosilane to methylvinyldichlorosilane in the presence of a trace of chloroplatinic acid, followed by heating at 140° for 4 hr. The yield is almost quantitative.[11] The product was distilled (bp 95° (13 mm)) and further purified in a sealed vacuum system by crystallization from *n*-hexane, followed by three crystallizations from the bulk (mp 32°). It was diluted in *n*-hexane and subdivided into fragile bulbs or ampoules with breakseals. The concentration of the silicon–chlorine bonds was determined by acid–base titration.

Polymerizations and coupling reactions were carried out in benzene in sealed vacuum systems. All glassware was washed with a *n*-butyllithium solution and rinsed by repeated distillation of solvent from a reservoir. The reaction vessel was equipped with an optical cell which allowed the polymerization reaction (decrease of styrene absorption at 291 mμ) and the coupling reaction (decrease of the polystyryllithium absorption at 333 mμ) to be followed spectrophotometrically.

Narrow molecular weight distribution polystyryllithium was obtained by using *sec*-butyllithium as the initiator and benzene as the solvent.[12] After polymerization during 12 half-lifetimes a sample of the precursor polymer was sealed off. The coupling agent was then added. The ratio of polystyryllithium to silicon–chlorine bonds was between 1.2 and 1.8 in order to ensure complete coupling. At the end of the reaction, residual polystyryllithium was terminated by *tert*-butyl alcohol.

Fractionations of the polymers were carried out by adding methanol to polymer solutions in methyl ethyl ketone or benzene at 30°. Fractionation was performed in two steps. A crude fractionation from a 1% polymer solution removed nearly all the precursor. The high molecular weight branched polymer fraction was carefully refractionated from a 0.25% solution. In most cases, the first fraction was pure four-branched polymer. High molecular weight star polymers were sometimes refractionated. Sedimentation velocity ultracentrifugation in cyclohexane was used as a fast qualitative method for estimating the extent of the coupling reaction and the efficiency of the polymer fractionation.

Number-average molecular weights were determined in toluene at 35° with a high-speed membrane osmometer (Mechrolab 503). Weight-average molecular weights were determined with a Sofica photogoniometer in cyclohexane at 35°. Unpolarized light of wavelength 4358 Å was used. Scattering intensities were measured over an angular range from 30 to 150° at five concentrations. The Rayleigh ratio for benzene at 35° was taken as 50.79×10^{-6}; the refractive index increment for polystyrene in cyclohexane was taken as 0.181 cm³/g. Intrinsic viscosities were measured in cyclohexane at 35°, in cyclohexane at 50°, and in toluene at 35° with Cannon-Ubbelohde viscometers.

Sedimentation coefficients were determined on a Spinco Model E analytical ultracentrifuge at 59,780 rpm (42,040 rpm for the highest molecular weight polymers in cyclohexane). Sedimentation coefficients were derived from the slopes of plots of the logarithm of the radial distance (r) of the boundary maximum against time. Measurements were limited to $\log r/r_0 < 0.015$ (r_0 = the radial distance of the meniscus). Correction for radial dilution was applied according to

$$c_{\mathrm{av}} = c_0(r_0/r_{\mathrm{av}})^2$$

Pressure correction to 1 atm according to

$$s^0 = s\{1 - m[(r_{\mathrm{av}}/r_0)^2 - 1]\}$$

where $m = {}^1/_2\omega^2\rho_0\mu r_0^2$ with μ equal to 1×10^{-9} in toluene and 1.8×10^{-9} in cyclohexane.[13] Extrapolation of s^0 to zero concentration gives s_0^0

$$\frac{1}{s^0c_{\mathrm{av}}} = \frac{1}{s_0^0}(1 + k_{\mathrm{s}}c_{\mathrm{av}})$$

Intrinsic frictional coefficients were calculated from

$$[f] = \frac{M_{\mathrm{w}}(1 - \bar{v}_2\rho_0)}{s_0^0N_{\mathrm{A}}\eta_0}$$

with the following constants: $\bar{v}_2 = 0.919$ cm³/g, $\rho_0 = 0.8530$ g/cm³, and $\eta_0 = 4.93 \times 10^{-3}$ P for toluene at 35° and $\bar{v}_2 = 0.928$ cm³/g, $\rho_0 = 0.7644$ g/cm³, and $\eta_0 = 7.67 \times 10^{-3}$ P for cyclohexane at 35°.

Results and Discussion

By following the decrease of the polystyryllithium concentration it was observed that two molecules of polystyryllithium react with each molecule of 1,2-bis(methyldichlorosilyl)ethane in the short time (5 min) required to mix the reagents. These fast steps are followed by a reaction over a period of 8–24 hr, depending on the concentration of the reagents, which resulted in the reaction of one more polystyryllithium per molecule of coupling agent. In order to incorporate the fourth polystyrene chain the reaction has to be taken to 48° for periods of 4 days to 2 weeks. Figure 1 shows the ultracentrifugation pattern of samples taken at various times during the coupling. It clearly confirms the stepwise nature of the formation of a four-branched star polystyrene. It should be pointed out that the boundaries are only qualitatively related to the amounts of the various species because of radial dilution and the Johnston–Ogston effect. Both effects make area measurements underestimate the faster moving polymer concentration. In the absence of values for the sedimentation coefficients and their concentration dependence for three- and four-

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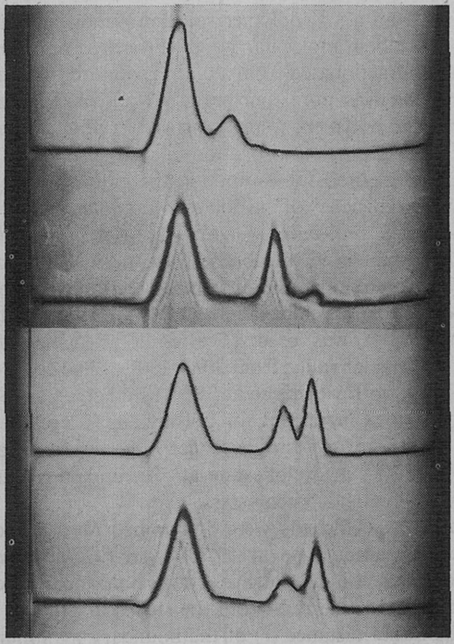

Figure 1. Sedimentation ultracentrifugation pattern of S14; samples taken during the coupling reaction, from top to bottom, after 1 hr, 24 hr, 6 days, and 2 weeks.

Table I
Molecular Weight Data for Polystyrene

	Branched star polystyrene			
Sample	$10^{-4}\cdot(M_n)_{prec}$	$10^{-4}\cdot(M_n)_{star}$	$10^{-4}\cdot(M_w)_{star}$	$(M_n)_{star}{}^a/(M_n)_{prec}$
S091A	4.67	18.73	19.30	4.01
S101AAA	11.09		45.4	(4.09)
S111A	3.63	14.73	15.4	4.06
S121A	2.26	8.85	9.35	3.92
S131A	1.16	4.55	5.07	3.92
S141AA	12.03	46.2	52.1	3.84
S161A[b]	8.45	32.7	35.1	3.86
S181A[b]	24.9		102.7	(4.12)
S191AA[b]	33.4		139.0	(4.14)

	Linear polystyrene	
Sample	$10^{-4}M_n$	$10^{-4}M_w$
MS1–3	2.93	3.42
PS-100	11.4	11.5
PS-150	20.5	21.6
PS-800		67.5
PS-1000		179

[a] Values in parentheses are $(M_w)_{star}/(M_n)_{prec}$. [b] Prepared by the isoprene method.

Table II
Intrinsic Viscosity and Sedimentation Coefficients for Four-Branched Star and Linear Polystyrene

	$[\eta]$			$10^{13}s_0{}^0$	
Sample	c-C_6H_{12}, 35°	c-C_6H_{12}, 50°	C_7H_8, 35°	c-C_6H_{12}, 35°	C_7H_8, 35°
S131A	0.141	0.151_5	0.197	3.38	3.60
S121A	0.191	0.209	0.301	4.72	4.59
S111A	0.256	0.275	0.435	6.17	5.81
S091A	0.278		0.509		
S161A	0.384	0.454	0.783	9.34	8.33
S101AAA	0.420		0.933		
S141AA	0.448	0.551	1.04_3	11.9_8	9.75
S181A	0.635	0.865	1.72_5	16.2_3	13.1_6
S191AA	0.740	1.020	2.14	18.6_6	14.4_9
MS1-3	0.151	0.159	0.201		
PS-100	0.279	0.308	0.478		
PS-150	0.383	0.462	0.757		
PS-800	0.684	0.900	1.71		
PS-1000	1.245	1.71	3.61		

branched star polystyrene, a reasonable estimate of the ratio of these two components can be made by sedimenting the sample at different total concentrations and extrapolation of the apparent ratio to zero concentration.

Low molecular weight four-branched star polystyrene could be prepared essentially free of three-branched material. In the preparation of higher molecular weight polymers, the speed of coupling of the fourth unit becomes progressively slower as the attempted molecular weight is increased. Side reactions of polystyryllithium occur in extended times and it becomes increasingly impractical to keep the amount of three-star polymer down to reasonable limits in the crude product. For instance, a star polymer of molecular weight 5 × 10^5 is obtained in 85% yields (15% trifunctional polymer). The percentage of four-branched polymer can be increased to >98% after two fractionations of the first rough top fraction. The increasing impracticality of separating higher molecular weight polymers necessitates the preparation of pure star polymers. This can be realized by treating the polystyryllithium with three molecules of isoprene, converting the active chain end to an isoprenyllithium group. The coupling reaction then follows the same stepwise addition but goes smoothly. The trifunctional star is formed in less than 3 hr at 30° and the tetrafunctional star is completed in 1–2 days. Four-branched star polystyrene uncontaminated by three-star material of molecular weight up to 1.4 × 10^6 could be prepared in this way. Using stoichiometric amounts of living polymer and coupling agent a pure star polymer was prepared, indicating that this method is free of any side reactions. However, the time required to complete such a reaction makes it less attractive than the use of excess lithium compound, particularly since precursor molecules are always easy to remove. The stepwise character of the coupling reaction is brought about by the decreased mobility of the Si–Cl bonds when they become embedded in the center of a macromolecule after the first two reaction steps. The different reactivity of polystyryllithium and polyisoprenyllithium indicates that local steric factors are also important.

Molecular weight characterization data on the star polymer and their linear precursors are collected in Table I. The best measure of the degree of branching achieved is given by $(M_n)_{star}/(M_n)_{prec}$.[5] Unfortunately, osmotic pressure measurements are determinable to the desired accuracy only at molecular weights <5 × 10^5. In view of the narrow molecular weight distribution of our samples, light-scattering weight-average molecular weights are used to calculate the degree of branching of the other polymers. Within the experimental error of the molecular weight determinations, the data indicate that the tetrafunctional star polystyrene samples are homogeneous and have molecular weight distributions comparable to anionically prepared linear polystyrene.

Intrinsic viscosities and sedimentation coefficients for the four-branched star polystyrene polymers are collected in Table II. The intrinsic viscosity–molecular weight relationships for regular star polystyrene in three solvents are shown in Figure 2. The properties of the star polymers prepared by the isoprene method cannot be distinguished from the ordinary star polystyrene. The constants in the Mark–Houwink–

Sakurada relations are given in Table III. Within the molecular weight range covered by this study, the exponent in the $[\eta]$-M relations for the branched polystyrene are equal to those for the linear polymer. The constants for the analogous sedimentation coefficient *vs.* molecular weight relation are given in Table III.

In order to compare quantitatively the properties of the star polymers and linear polystyrene, new samples of linear polystyrene were prepared anionically. Experimental results on these polymers are also included in Tables I, II, and III. The constants of the intrinsic viscosity-molecular weight relationships for the linear polystyrenes are in good agreement with the data of Flory[14] and Berry[15] for cyclohexane solutions at 35° and with those of Papazian[16] at 50°. The values for toluene solutions differ slightly from those in an earlier publication.[17] This can be attributed to differences in the calibration of the light-scattering instruments. Data for the corresponding sedimentation coefficient–molecular weight relationship were taken from reference[18] after checking several of the points.

The ratio g' of the intrinsic viscosity of four-branched star polystyrene to that of the linear polymer of the same molecular weight can be found in Table IV together with values available in the literature.[1,5,10,19] Two theoretical treatments of the viscosity ratio g' have appeared. Zimm and Kilb calculated the viscosity of some regular star polymers and came to the conclusion that $g' \approx g^{1/2}$, where $g = (\bar{s}^2)_{\Theta b}/(\bar{s}^2)_{\Theta l}$, the ratio of the mean-square radius of the branched polymer to that of the linear polymer of the same molecular weight.[20] According to Zimm and Stockmayer, g for star branched polymers is given by

$$g = (3f - 2)/f^2$$

where f is the number of branches in the molecule.[21] On the other hand, Stockmayer and Fixman calculated the ratio of the frictional constant of star branched polymer to that of the linear polymer of the same molecular weight

$$\frac{[f]_b}{[f]_l} = h = f^{1/2}[2 - f + 2^{1/2}(f - 1)]^{-1}$$

and extended this to the intrinsic viscosity by the approximation that $[\eta]_b/[\eta]_l = h^3$.[22] Both theories are limited to Θ solvent conditions.

Our experimental values of g' fall between $g^{1/2}$ and h^3 and confirm the better results from Table IV. The lower values of g' in the good solvents seem to be genuine, although the difference from the Θ solvent value is close to the experimental precision. Star polymers of higher branch functionality will be needed to decisively establish the validity of the $g^{1/2}$ and h^3 rules.

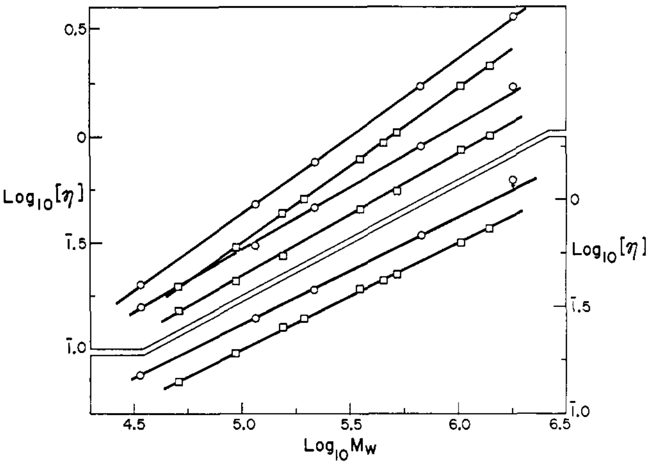

Figure 2. Log $[\eta]$ *vs.* log M_w for linear and four-branched star polystyrene. From top to bottom, toluene 35°, cyclohexane 50°, and cyclohexane 35°. ○, linear; □, star polystyrene.

TABLE III
INTRINSIC VISCOSITY AND SEDIMENTATION CONSTANTS FOR FOUR-BRANCHED STAR POLYSTYRENE

	$[\eta]$			s_0^0		
Solvent	α	$K_b \times 10^4$	$K_l \times 10^4$	α	$K_{sb} \times 10^{15}$	$K_{sl} \times 10^{15}$
Cyclohexane, 35°	0.50	6.31	8.3	0.50	1.57	1.48
Cyclohexane, 50°	0.58	2.65	3.7			
Toluene, 35°	0.73	0.74	1.02	0.425	3.64	3.38

TABLE IV
EXPERIMENTAL VALUES OF g' FOR STAR POLYSTYRENE

No. of samples	$c\text{-}C_6H_{12}$, 35°	C_6H_6, 25°	C_7H_8, 25°	Ref
Trichain, $g^{1/2} = 0.882$, $h^3 = 0.850$[a]				
1	0.85	0.87_4	0.88	1
1	0.94		0.90	5
5	0.83_5	0.81		10
Tetrachain, $g^{1/2} = 0.79$, $h^3 = 0.71$[a]				
1	0.75			19
1	0.82		0.84	5
9	0.76[b]		0.72_4[c]	This work

[a] $g' = g^{1/2}$ according to the theory of B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19 (1959). $g' = h^3$ according to the theory of W. H. Stockmayer and M. Fixman, *Ann. N. Y. Acad. Sci.*, **57**, 334 (1953). [b] 0.73 at 50°. [c] At 35°.

Measurement of the sedimentation coefficient of star polymers gives a direct determination of Stockmayer's h without the assumptions involved in the transposition to intrinsic viscosity. For the four-branched star polymers, $h = 0.89$ according to the above equation. Unfortunately, the precision of sedimentation coefficient measurements is not as high as that of intrinsic viscosity. The experimental values of h (0.94 under Θ conditions and 0.93 in toluene) are somewhat higher than the theoretical one. In any case, this would confirm the trend observed in the intrinsic viscosity measurements.

Intrinsic viscosity measurements could form a first basis for the investigation of the effect of branching on the thermodynamics of polymer solutions. In order to do this, short- and long-range interaction parameters have to be separated. Every theory of polymer solution performs this in a different way, and there is no general agreement on which is correct. The simplest method is that proposed by Stockmayer and Fixman[23]

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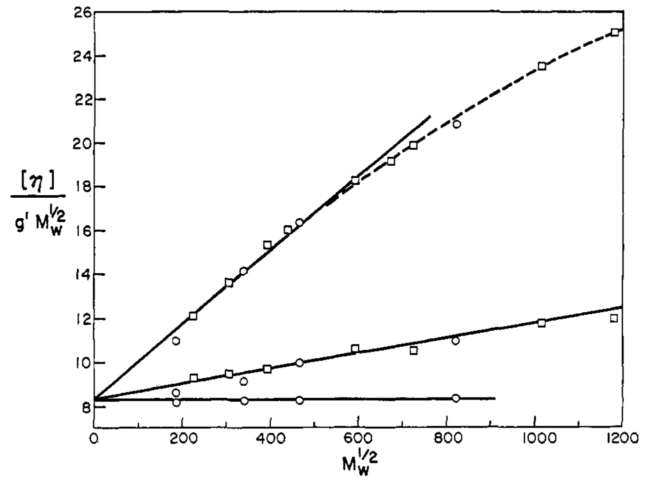

Figure 3. Stockmayer–Fixman plot of intrinsic viscosity data of four-branched star polystyrene. From top to bottom, toluene 35°, cyclohexane 50°, and cyclohexane 35°.

$$\frac{[\eta]}{M^{1/2}} = \Phi_0'\left[\left(\frac{(\bar{s}^2)_\Theta}{M}\right)^{3/2} + 0.51BM^{1/2}\right]$$

It is based on the approximation that

$$\alpha_\eta{}^3 \sim 1 + 1.55z$$

over a wide range of excluded volume. It is certainly inaccurate,[24] as the plots of $[\eta]/M^{1/2}$ *vs.* $M^{1/2}$ show curvature and there are doubts that the method gives a correct value of B $(=\beta M_0{}^2)$. Some efforts have been made to correct the coefficient 0.51 to bring the experimentally determined B value in closer agreement with those determined by thermodynamic methods. A comparison of the properties of branched and linear polymers can, as a first approximation, be made bearing these difficulties in mind. If we assume that the star polymer can be described as normal polystyrene with only a different segment distribution and hence different values of Φ_0', and that the coefficient 1.55 is unchanged, we would expect the Stockmayer–Fixman equation to be modified to

$$\frac{[\eta]}{M^{1/2}} = g'\Phi_0'\left[\left(\frac{(\bar{s}^2)_{\Theta \mathrm{l}}}{M}\right)^{3/2} + 0.51BM^{1/2}\right]$$

where $(\bar{s}^2)_{\Theta \mathrm{l}}$ and B are the values appropriate to normal linear polystyrene. The experimental results are plotted in Figure 3 with $g' = 0.724$. The points for branched and linear polymers fall within experimental error on the same (curved) lines, which suggests that whatever the inadequacies of the equation, the results can be fitted by a common B and hence β value. Similarly, the intercepts are the same, as expected.

Evidence as to the equivalence of B values of linear and branched polystyrenes is contradictory at the present time. Near the Θ temperature, Orofino found a significantly decreased value for a single sample of three-star polystyrene.[1] Berry, however, found B unchanged from its value for a linear polymer with a four-star sample.[19] These determinations were made from the temperature dependence of A_2 near Θ conditions. It is hoped in a later publication to examine this point in more detail for a series of four- and six-star polymers.

Formally, the intrinsic viscosity of a branched polymer can be represented by a Flory–Fox-type equation[1]

$$[\eta]_{\Theta \mathrm{b}} = \Phi_\mathrm{b}'\left(\frac{(\bar{s}^2)_{\Theta \mathrm{b}}}{M}\right)^{3/2} M^{1/2}$$

Since $[\eta]_\mathrm{b}/[\eta]_\mathrm{l}$ is not proportional to $g^{3/2}$, it follows that Φ_b' is not equal to Flory's universal constant for linear polymers Φ_l'. Indeed, the chain segment density distribution on which Φ depends will be different for a branched polymer and a linear polymer. To calculate Φ_b' from our viscosity results, a value for $((\bar{s}^2)_{\Theta \mathrm{b}}/M)$ has to be known. This can be derived from the corresponding value of the linear polymer by the theoretical relation $(\bar{s}^2)_{\Theta \mathrm{b}}/(\bar{s}^2)_{\Theta \mathrm{l}} = 0.625$ using $\Phi_\mathrm{l}' = 3.94 \times 10^{22}$,[25] or directly from the angular dependence of light-scattering measurements extrapolated to zero concentration. The former method leads to a value for $((\bar{s}^2)_{\Theta \mathrm{b}}/M)$ of 4.95×10^{-18}, the latter applied on sample S181A yields 5.1×10^{-18}. Taking into account the low accuracy of the experimental determination of the radius of gyration, the agreement between the two values justifies the use of the theoretical dimension of the star polymer to calculate Φ_b'. Thus, one obtains 5.81×10^{22} for Φ_b', *i.e.*, 1.48 Φ_l'. Similarly, P_b in

$$[f]_{\Theta \mathrm{b}} = P_\mathrm{b}\left[\frac{(\bar{s}^2)_{\Theta \mathrm{b}}}{M}\right]^{1/2} M^{1/2}$$

is equal to $1.17P_\mathrm{l}$ for four-branched star polystyrene.

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