Randomly Branched Styrene/Divinylbenzene Copolymers. II. Solution Properties and Structure

M. R. AMBLER and D. McINTYRE, *Institute of Polymer Science, The University of Akron, Akron, Ohio 44325*

Synopsis

The $[\eta]$ of randomly branched PSty/DVB continually decreases from linear polystyrene with increasing conversion. On the other hand, the relation of the $\langle S^2 \rangle$ to M of both low and high conversion series is equivalent, although the actual size is smaller than that of linear polystyrene of the same M. This fact, in conjunction with the previously published reactivity ratios, allows the following interpretation of the mechanism of copolymerization: namely, that branched molecules are formed in which the center core is higher in DVB content than is the periphery. Only about $\frac{1}{7}$ of the available DVB units act as effective tetrafunctional branch points. An analysis of GPC data correlated with light scattering and viscosity dimensions allows the g value to be determined in the lightly and highly branched fractions. The viscosity ratio is related to g^x, where x is 0.65 for low conversion fractions (A series) and becomes 1.41 for high conversion fractions (B series). This change in exponent is postulated to arise from an increase in branching density as conversion increases. The ratio of the hydrodynamic radius to the radius of gyration is higher for branched than for linear polymers. The theta temperature (θ) in cyclohexane for randomly branched polystyrene compared to linear polystyrene is always higher and can be as much as 2° higher.

INTRODUCTION

The solution properties of branched polymers have been the subject of many research efforts, and extensive reviews have been presented by Graessley[1] and Grechanovskii.[2] The polymerization and solution properties of polystyrene/divinylbenzene (PSty/DVB) copolymers have been studied by Thurmond and Zimm,[3] Kurata, Abe, Iwama, and Matsushima,[4] Abe, Iwama, and Homma,[5] and Meyerhoff and Cantow.[6]

All fundamental studies of branching require a knowledge of g and α defined in eqs. (1) and (2):

$$g = \frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} \tag{1}$$

where $\langle S^2 \rangle_b$ and $\langle S^2 \rangle_l$ are the respective radii of gyration of branched and linear polymers of the same molecular weight in a theta solvent, and

$$\alpha = \frac{\langle S^2 \rangle^{1/2}}{\langle S^2 \rangle^{1/2}_\theta} \tag{2}$$

where $\langle S^2 \rangle^{1/2}$ and $\langle S^2 \rangle^{1/2}_\theta$ are the radii of gyration of the same linear or same branched polymer in a good solvent and in a theta solvent. These parameters

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(g, α) can be obtained for any polymer. However, they require characterization in a theta solvent.

The theta temperature of star-branched and comb-branched (*graft*) polystyrenes has recently been reported by Candau, Rempp, and Benoit[7] to be as low as 29°C in cyclohexane; however, Kurata, Abe, Iwama, and Matsushima[4] found a more normal θ temperature of 34.7°C for randomly branched polystyrene, and Berry and Casassa[8] report an increase in θ of about two degrees for a graft polystyrene. It appears that at the moment, the effect of branching upon the theta temperature is a confused field experimentally. It is important in the characterization of randomly branched polymers to know whether the θ temperature for linear and branched polymers is the same, particularly for sedimentation analyses.

Another parameter that indicates some of the same information is the exponent γ in the relation

$$\langle S^2 \rangle \propto M^\gamma \tag{3}$$

For linear polymers, γ is 0.5 in a θ solvent and >0.5 for good solvents. Few studies have been made to measure the exponent γ from randomly branched samples over a large molecular weight range. Usually, the unknown polydispersity corrections have precluded a convincing analysis.[3]

Finally, it is most important from a characterization point-of-view to understand the relationship between intrinsic viscosity $[\eta]$ and g because viscosity measurements are most frequently used and often alone. Usually, it is generally assumed that $[\eta]$ is related to a power of $\langle S^2 \rangle$ for any polymer. Cantow, Meyerhoff, and Schulz[9] found that the decrease of intrinsic viscosity obeys the following relationship for lightly branched polystyrene:

$$\frac{[\eta]_b}{[\eta]_l} = g^{0.65 \pm 0.15} \tag{4}$$

in agreement with that expected by Zimm and Kilb[10] under theta conditions:

$$\frac{[\eta]_{b,\theta}}{[\eta]_{l,\theta}} = g^{0.5} \tag{5}$$

where g is the theoretical branching parameter of Zimm and Stockmayer[11] which is defined experimentally in eq. (1). As pointed out by Berry and Cassasa,[8] eq. (1) must be modified to account for changes in branching, particularly where high branching is encountered. In this general case,

$$\frac{[\eta]_{b,\theta}}{[\eta]_{l,\theta}} = \left[\frac{\langle S^2 \rangle_{b,\theta}}{\langle S^2 \rangle_{l,\theta}} \right]^\epsilon = g^\epsilon \tag{6}$$

where ϵ is a parameter which could range from $\frac{1}{2}$ for light branching and star polymers to a limit of $\frac{3}{2}$ at high branching in theta solvents. The viscosity in good solvents is less clear. Corrections for excluded volume must be included. Berry and Cassasa suggest an equation of the form

$$\frac{[\eta]_b}{[\eta]_l} = g^\epsilon \left(\frac{\alpha_b}{\alpha_1} \right)^3 \tag{7}$$

Equation (7) has never been verified experimentally for randomly branched samples.

The copolymerization of styrene and DVB has been studied extensively by Malinsky and co-workers.[12] Their reactivity ratios for the free-radical copolymerization at 70°C of styrene and DVB indicate a tendency for alternating copolymerization to occur. This suggests that at low DVB contents, there is a rapid decrease in the DVB level in the monomer feed as conversion increases. The possibility exists that the branching may change with conversion because of this fact, since obviously the DVB bound into the chain will also change with conversion. Further, the heterogeneous nature of the copolymerization mechanism could result, at high conversion, in branched molecules having a complex structure. The influence of the heterogeneous copolymerization on the solution properties of the resultant branched polymers represents one of the investigations to be made here.

The basis for the effectiveness of the solution parameter analyses in this paper is the use of the GPC analysis of molecular weights discussed in the preceding paper.[13] By this technique, radii and viscosities have been weighted correctly to determine their functional dependence on a given molecular weight average. Consequently, although no radii are measured in theta solvents, it is possible to evaluate the exponents of g in eq. (6), γ in eq. (3), and a in the equation below:

$$[\eta] = KM^a$$

The theta temperature was also determined, and work is in progress to determine g and a values of the same polymers.

EXPERIMENTAL

Materials and experimental techniques are described in reference 13: A series is a low-conversion styrene/DVB sample; B series is a high-conversion styrene/DVB sample. Fractions 9A5, 9A3, 9A1 and 9B3, 9B2-2, 9B2-1 were used in this study.

Table I lists the radii of gyration and virial coefficients determined by light scattering measurements as well as the intrinsic viscosities. The M_w values are from the light scattering measurements. Table II lists the data for the virial coefficients of two branched polystyrene samples (9A3, 9B3) and a linear polystyrene sample (WA 41984).

Figure 1 shows the smoothed data that were obtained from GPC elution volumes for branched and linear samples using the light-scattering radii $\langle S^2 \rangle_z$

TABLE I
Solution Parameters of Randomly Branched Polystyrenes in THF at 30°C

Sample	M_w, g/mole	$\langle S^2 \rangle_z^{1/2}$, A	$A_2 \times 10^4$, mole cm^3/g^2	$[\eta]$
9A5	88,400	165	7.0	0.456
9A3	402,000	291	5.7	0.977
9A1	585,000	367	3.3	1.305
9B3	233,000	307	5.4	0.714
9B2-2	2,230,000	1249	2.9	1.201
9B2-1	5,240,000	1622	0.7	2.109

TABLE II
Second Virial Coefficients from Light Scattering: Cyclohexane

Sample	Temp., °C	$A_2 \times 10^4$, mole cm^3/g^2
41984	35.5	0.6
	36.7	1.4
9A3	36.9	0.5
9B3	36.4	−0.2
	40.3	1.3

analyzed in the same manner as $[\eta]$ and M_w were analyzed in reference 13. That is, the $\langle S^2 \rangle_z$ radii of the fractions given by the light scattering measurements were made to equal the appropriate summation over the chromatogram for the polydisperse fractions by assuming that there did exist an $\langle S^2 \rangle$ curve for monodisperse branched samples. The curve in Figure 1 was used to determine the radii of "monodisperse" fractions.
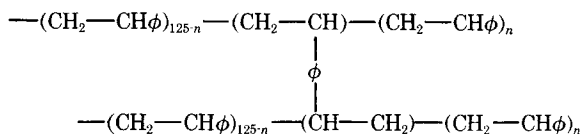
DISCUSSION

$[\eta]$–M Relationship

In Figure 2, $[\eta]$ and $\overline{M}_w$ data points for linear polystyrene were taken from reference 13. The equation of the line for linear polymers taken from reference 13 is found to be

$$[\eta] = 1.05 \times 10^{-4}\, \overline{M}_w{}^{0.731}$$

The dotted line for the series A fractions and the dashed line for the series B fractions were generated by a point-by-point combination of the curve-fitted GPC data as a function of elution volume. The GPC calibration curves of ln $[\eta]$ and ln M versus elution volume also are from reference 13. Superimposed are the $[\eta]$ and $\overline{M}_w$ values of the fractions of the two branched series taken from Table I. It is evident that the fractions which were found to be very broad in distribution fell below the corresponding curve-fitted line, owing presumably to the fact that $\overline{M}_w > \overline{M}_v$. The highly branched series B shows a larger $[\eta]$ deviation from the linear plot than the low-branched series A at constant molecular weight, indicating that there is a higher degree of branching in series B.

Both series A (low branching) and series B (high branching) began to deviate from the linear $[\eta]$–M line at $M \cong 175,000$. This suggests that at molecular weights lower than 175,000, the molecules act hydrodynamically like a linear polymer. This is not to say that they are linear, but rather that the extent of branching is sufficiently low to be unimportant in hydrodynamic effects. Both series A and B were polymerized at 0.4% DVB monomer charge. If the copolymerization were perfect, this would mean that the "repeat unit" contains one DVB unit for every 250 styrene units, or
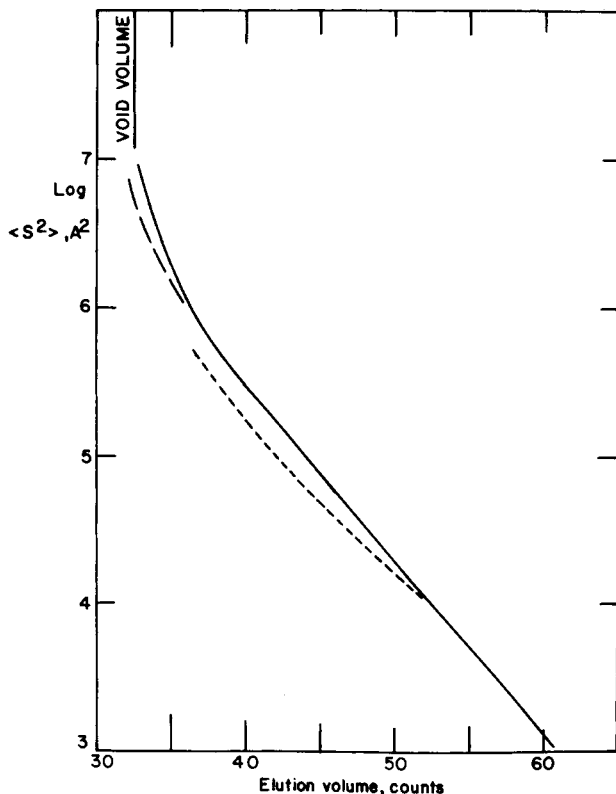
$$\mathrm{-(CH_2\!-\!CH\phi)_{125\text{-}n}\!-\!(CH_2\!-\!CH)\!-\!(CH_2\!-\!CH\phi)_n}$$
$$|$$
$$\phi$$
$$|$$
$$\mathrm{-(CH_2\!-\!CH\phi)_{125\text{-}n}\!-\!(CH\!-\!CH_2)\!-\!(CH_2\!-\!CH\phi)_n}$$

Fig. 1. Final curve-fitted mean-square radius of gyration ($\langle S^2 \rangle$) calibration curves for branched polystyrene in Ana-Prep GPC: (———) linear; (— —) 9B series.

A tetrafunctional branching structure with about 250 styrene units connected to a branch point is conceivable. In such a case, the possible molecular weight interval between branch points would be about 25,000. The break in Figure 2 begins far above this molecular weight, namely, 175,000. Since the interval
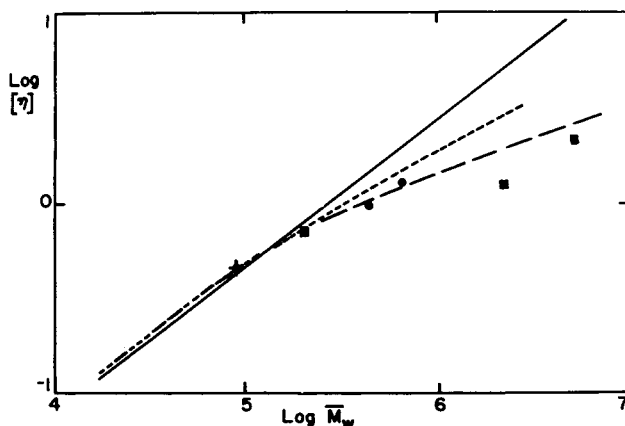

Fig. 2. Mark–Houwink plots of log [η] vs log M for branched and linear polystyrenes in THF at 30°C. Curves are curve-fitted lines (see text). Points are experimental data for fractions: (———) linear; (— ■ —) 9B series; (- - - ● - - - -) 9A series.

TABLE III
Data for Determining the Branching Parameter ϵ

Series	M	$[\eta]_b$	$[\eta]_l$	$\langle S^2 \rangle_b$	$\langle S^2 \rangle_l$	$\langle S^2 \rangle_{l\theta}$
9A	3,000,000	3.5	6.3	4.40×10^5	1.14×10^6	2.95×10^5
	560,000	1.37	1.75	1.13×10^5	1.65×10^5	5.50×10^4
	200,000	0.76	0.80	4.40×10^5	5.00×10^4	1.93×10^4
9B	5,200,000	2.55	9.80	6.80×10^3	2.08×10^6	5.25×10^5
	2,200,000	1.88	5.10	3.50×10^5	8.20×10^5	2.20×10^5
	200,000	0.77	0.80	4.40×10^4	5.50×10^4	1.93×10^4

between branches is of the order of 175,000 and not 25,000 as it would have been if all double bonds had reacted ideally to form the repeat unit shown above, all of the available DVB does not participate in forming effective or ideal tetrafunctional branch points. The explanation of this discrepancy requires a discussion of the copolymerization reaction. This discussion is made after a consideration of the $\langle S^2 \rangle$–M relationship.

$\langle S^2 \rangle$–M Relationship

$\langle S^2 \rangle_z$ and $\overline{M}_w$ for linear polystyrene were taken from reference 14 and plotted in Figure 3 to form the $\langle S^2 \rangle$–M line. Although these sizes were obtained in benzene, it was assumed they were equivalent to the dimensions in THF, since it had been found that $[\eta]_{THF} = [\eta]_{BZ}$ for these samples.[14] The data of reference 14 had to be extrapolated below 412,000 molecular weight. The dotted lines for series A and B were taken from the final curve-fitted data of the GPC. Values of $\overline{M}_z$ and $\langle S^2 \rangle_z$ were taken from Table VI of reference 13 and the present Table I, respectively, for the six fractions. These are also shown. It is observed that, although for a given elution volume series A and B had different M and $\langle S^2 \rangle$ values, the data reduce to a common $\langle S^2 \rangle$–M line when plotted in Figure 3. This means that the higher-branched series B does not have a larger depression in $\langle S^2 \rangle$, in contrast to the viscosity results discussed earlier.

A difference in the effect of branching on the static equilibrium dimensions and on the hydrodynamic dimensions might be expected due to the higher power

TABLE IV
Results of Calculations for the Branching Parameter ϵ

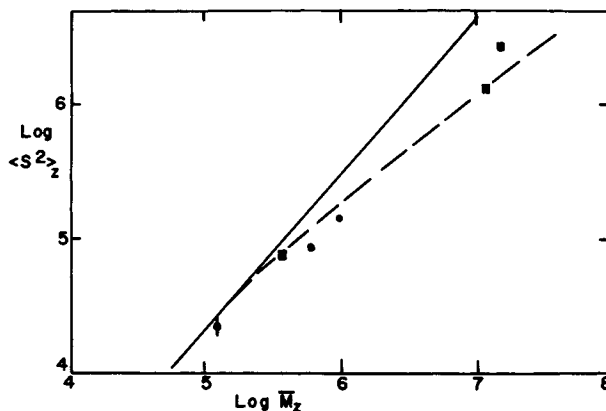| Series	M	Case 1 ($\alpha_{sb} = \alpha_{\eta b} = 1$) Minimum chain expansion		Case 2 ($\alpha_{sb} = \alpha_{sl}$; $\alpha_{\eta b} = \alpha_{\eta l}$) Maximum chain expansion	
		$\dfrac{[\eta]_b}{[\eta]_l} \times \alpha_{sl}^{2.43}$	$\dfrac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} \times \alpha_{sl}^2$	$\dfrac{[\eta]_b}{[\eta]_l}$	$\dfrac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l}$
9A-1	3,000,000	2.86	1.49	0.56	0.39
	560,000	2.95	2.05	0.78	0.69
	200,000	3.03	2.28	0.95	0.88
9B	5,200,000	1.39	1.31	0.26	0.33
	2,200,000	1.84	1.60	0.37	0.43
	200,000	3.05	2.28	0.96	0.88

Fig. 3. Logarithmic relation between the z-average radius of gyration $\langle S^2 \rangle_3$ and the z-average molecular weight $\overline{M}_z$. Curves are curve-fitted lines (see text). Points are experimental data for fractions: (———) linear; (— —■— —) 9A series; (- - - ● - - -) 9B series.

dependence of the intrinsic viscosity on size compared to the measured radius of gyration. Nevertheless, it seems clear that the effect on equilibrium size is smaller than expected. It seems reasonable to ascribe this difference to the different branched structures formed at low and high conversion and to correlate this difference with the mechanism of the copolymerization (branching) reaction.

Mechanism of Copolymerization

The DVB monomer used in this work was a mixture of m-DVB and p-DVB. Malinsky and co-workers[12] reported the reactivity ratios for the free-radical copolymerization at 70°C of styrene (1) and the initial vinyl group in DVB (2) to be $r_1 = 0.54$, $r_2 = 0.58$ for m-DVB; and $r_1 = 0.15$, $r_2 = 1.22$ for p-DVB, indicating that the vinyl group is more reactive in p-DVB than the vinyl group in m-DVB. The pendent vinyl groups of both m-DVB and p-DVB have the same reactivity, evidently close to that of the vinyl group in styrene. The reactivity ratios indicate a tendency for alternating copolymerization. This means that at a low mole fraction of the DVB monomer charge, more DVB will be in the copolymer formed than in the monomer feed at any time before complete polymerization. For example, when the mole fraction of either m-DVB or p-DVB is 0.0032 (corresponding to the 0.4% DVB in these experiments at the start of the polymerization), the mole fraction of DVB in the early polymer is 0.0059. That is, the polymer formed early in the polymerization will have almost twice the DVB content as the overall DVB content governed by the initial concentration of DVB.

The polymerization therefore can be considered to yield a heterogeneous polymer, as illustrated in Figure 4. The first polymer molecules formed will be higher in DVB concentration than the DVB concentration in the monomer feed. That is, although the average number of possible branch points in the polymer at the end of the polymerization must be 1 in 120, the number of possible branch points at the beginning of the polymerization would be 1 in 60. A linear polymer molecule upon dissolution immediately assumes a Gaussian segment density
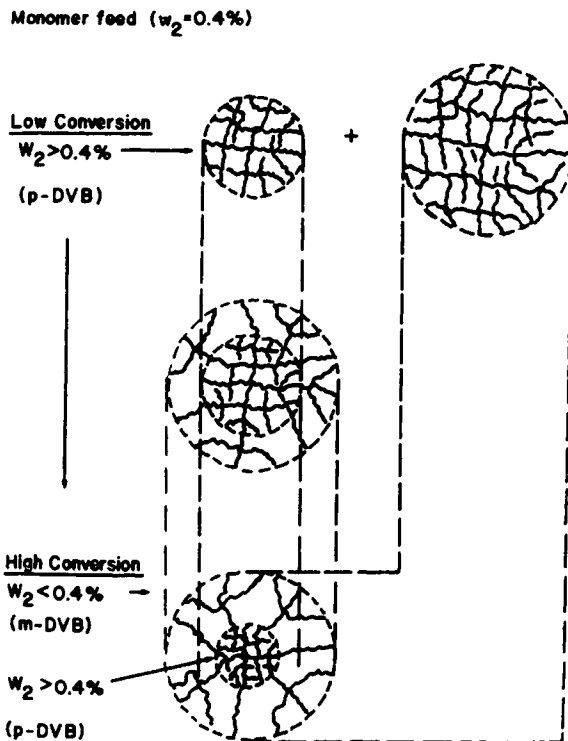
Fig. 4. Schematic representation of growth of DVB/styrene copolymers. On left is the proposed branched growth for the actual case involving different monomer reactivities. On right is the branching that would occur with monomers of equal reactivity. Notice difference in branching density of center.

with a higher segment density at the center. This can also be expected to occur to the copolymer chains formed in the bulk polymerization. The DVB branch points on the polymer chains must be initiated to form branched polymers. However, if the concentration of the initiator (benzoyl peroxide) is less in the center of the coil than in the surrounding monomer, then initiation of the pendent vinyl groups in the center will be retarded compared to the initiation of the pendent vinyl group on the periphery. There is a decrease of initiator concentration in the center core (after a finite conversion), and it cannot be replenished owing to the slower diffusion of molecules as a result of the higher viscosity in the center of the coil. This is analogous to the well-known Tromsdorff effect that slows the polymerization rate at high conversions because of the hindered diffusion of the growing chains.

Also as polymerization proceeds, growing chains add fewer DVB molecules than during the first phase of polymerization because of the decrease in the feed ratio resulting from the different reactivities of DVB and styrene. Since any branching that occurs between the growing chains and the pendent vinyl groups in the already formed chains will occur preferentially in the outer regions of the coil where the segment density is less due to the increase of initiator as discussed above, chains grow radially out from their centers, with the DVB content decreasing along a radial distance from the center. A competing reaction involves

intramolecular branching with the pendent vinyl groups. This reaction occurs when monomer has been depleted and polymer segment densities become more uniform throughout the system. When intramolecular branching does occur, it would be more frequent in the center core because of the higher population of unreacted pendent vinyls in the center. Malinsky observed a decrease of pendent vinyl groups in polymers formed at high conversions. Microgel might be considered to be an extension of this model to a preliminary gel state in which the core is extensively polymerized. Macrogel is the final gel state in which both the core and periphery have polymerized and interconnections between adjacent peripheries occur.

The model can be used to interpret the solution properties. At a low conversion, the branched polymer will have reduced $[\eta]$ and $\langle S^2 \rangle$, but not all DVB units will be functioning as active branch points. As discussed above, intramolecular branching in the center core will be the dominating polymerization reaction at high conversions. This reaction increases the local branch point density and decreases the volume of the center core. However, it will have little effect on $\langle S^2 \rangle$, since $\langle S^2 \rangle$ depends more on changes in the longest lengths (not the shortest lengths) and the growth of branch points in the outer periphery is slower. At low conversions, both $[\eta]$ and $\langle S^2 \rangle$ would, therefore, be lower than linear polymer; but at higher conversions, only $[\eta]$ would show a significant decrease beyond the low-conversion decrease. Of course, a randomly branched polymer made in a dilute solution might have a quite different distribution of branch points since viscosity effects are minimized.

This mechanism also suggests that the DVB concentration of the low-conversion series would be higher than the high-conversion series due to the ever-decreasing monomer feed ratio. This implies that series A has the possibility of being higher in branching than series B. However, the $[\eta]$–M and $\langle S^2 \rangle$–M lines for both series A and B intersect the linear $[\eta]$–M and $\langle S^2 \rangle$–M line at approximately the same molecular weight, indicating similar effective branching densities. This suggests that the higher concentration of DVB in the low-conversion series still is in the form of pendent vinyl groups and not in the polymerized form of tetrafunctional branch points. This explains the fact discussed earlier that only $1/7$ (25,000/175,000) of all the original DVB molecules function as effective branch points.

However, the values of $\overline{M}_w$ are probably not precise enough to register small differences in branching at extremely low molecular weights. For example, in Figure 2, the ($[\eta]$, $\overline{M}_w$) point for 9A5 actually fell slightly above the linear line and the curve-fitted line was above the $[\eta]$–M line. These two trends are physically impossible, and consequently they allow a $\pm 5\%$ estimate of the reliability of M_w to be made. This error is far less than the observed differences in the three $[\eta]$–M lines at high molecular weights. For $\langle S^2 \rangle$, an error of $\pm 30\%$ at an $\langle S^2 \rangle^{1/2}$ value of 150 Å must be assigned in order to account for the deviation of 9A5 in Figure 3. The physical phenomena surrounding the changing structure differences strongly suggest different hydrodynamic properties. This will be investigated further.

Branching Factor g

Figures 2 and 3 allowed the study of the change in branching with conversion, i.e., series A versus series B. However, eq. (6) is only applicable to theta solvents
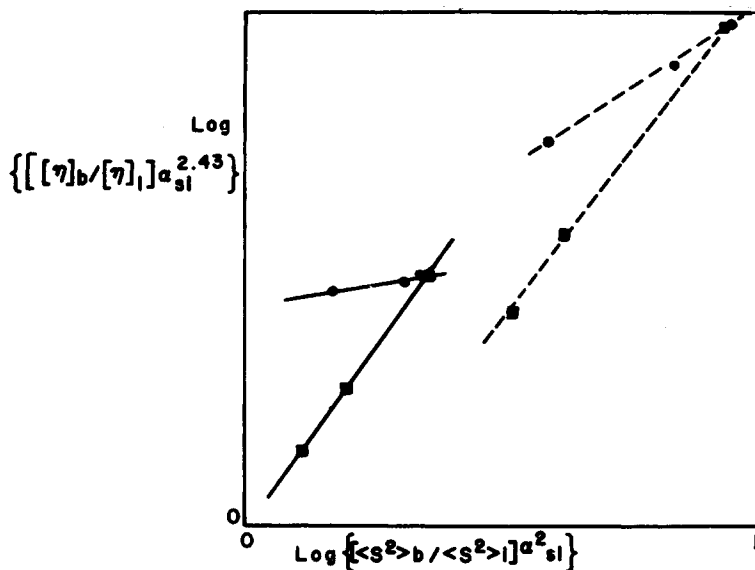
Fig. 5. Evaluation of branching function g^ϵ from eq. (10) in which ϵ gives the hydrodynamic correction to the usual g value for the ratio of radii for branched and linear samples. Case 2, eq. (11), for equal expansion of linear and branched polymers is shown by the dotted line. In case 1, eq. (10), unequal expansion is the full line: (-●-) 9A series; (-■-) 9B series.

for theoretically calculated g values. The expansion of the molecules in good solvents like THF must be accounted for. Expanding on the reasoning of Berry and Cassassa,[8] the defining relations

$$\alpha_s{}^2 = \frac{\langle S^2 \rangle}{\langle S^2 \rangle_\theta} \qquad \text{and} \qquad \alpha_\eta{}^3 = \frac{[\eta]}{[\eta]_\theta}$$

when substituted into eq. (6), becomes eq. (8):

$$\frac{[\eta]_b}{[\eta]_l} = \left[\frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l}\right]^t \times \left[\frac{\alpha_{s,l}}{\alpha_{s,b}}\right]^{2t} \times \left[\frac{\alpha_{\eta,b}}{\alpha_{\eta,l}}\right]^3 \tag{8}$$

which is fundamentally related to eq. (7).

Since for linear polymers in good solvents[15]

$$\alpha_{\eta,l}{}^3 = \alpha_{s,l}{}^{2.43}$$

eq. (8) reduces to

$$\frac{[\eta]_b}{[\eta]_l} \times \left(\frac{\alpha_{s,l}}{\alpha_{\eta,b}{}^3}\right)^{2.43} = \left[\frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} \times \left(\frac{\alpha_{s,l}}{\alpha_{s,b}}\right)^2\right]^\epsilon \tag{9}$$

A double-logarithmic plot of eq. (9) allows ϵ to be calculated from the slope. This was done for both series A and B. Values of $[\eta]$ and $\langle S^2 \rangle$ were interpolated from Figures 2 and 3 for specific arbitrarily chosen values of M covering as wide a range as possible. $\alpha_{s,l}$ was interpolated from the data of reference 14. The data used in the calculations are listed in Tables III and IV and the results are shown in Figure 5. The M values for the B series were chosen to be approximately near the M_w values of the fractions used to establish the curve; however, the M values
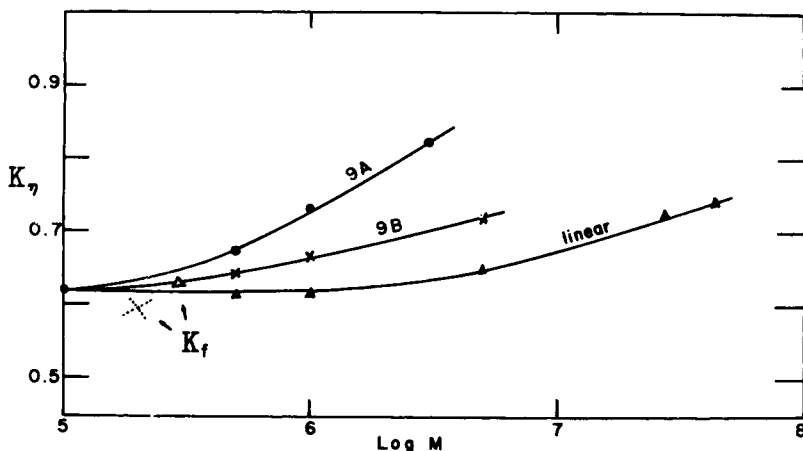
Fig. 6. K_η, the proportionality between R_η and S, as a function of molecular weight for branched and linear polystyrene. Points marked K_f represent points for the free-draining model.

for the A series were primarily chosen to encompass the same range of M as used for the B series.

The first calculation, case 1, was made assuming in each series that $\alpha_{s,b} = \alpha_{\eta,b} = 1$, that is, there was zero chain expansion. In this case, eq. (9) reduces to

$$\frac{[\eta]_b}{[\eta]_l} \times \alpha_{s,l}{}^{2.43} = \left[\frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} \times \alpha^2{}_{s,l} \right]^\epsilon \qquad (10)$$

These parameters were plotted for both series in Figure 5 and are shown as the solid lines. A second calculation, case 2, was made for both series, assuming the chain expansion was the same as for linear polymer, i.e., $\alpha_{s,b} = \alpha_{s,l}$; $\alpha_{\eta,b} = \alpha_{\eta,l}$. Equation (9) reduces in this case to

$$\frac{[\eta]_b}{[\eta]_l} = \left[\frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} \right]^\epsilon \qquad (11)$$

The dotted lines in Figure 5 represent case 2, where the parameters of eq. (11) are multiplied by 10 to be able to plot them on the same graph. These two cases represent extremes, that is, maximum (case 2) and minimum (case 1) possible chain expansion. Although $\alpha_{s,b}$ is sometimes greater than $\alpha_{s,l}$ for combs and stars[8] of polystyrene, $\alpha_{s,b}$ is less than $\alpha_{s,l}$ for randomly branched polystyrene.[3] Therefore $\alpha_{s,b} = \alpha_{s,l}$ seems a reasonable upper limit.

The results provided some insight into the branching structure, considering that boundary conditions exist at $\epsilon = \frac{1}{2}$ (light branching) and $\alpha = \frac{3}{2}$ (high branching). At low conversion, the calculated values of ϵ ranged from 0.17 assuming zero chain expansion to 0.65 assuming maximum chain expansion. Chain expansion has to be somewhere between these two cases. Considering the boundary condition of 0.5, which means that ϵ cannot be less than 0.5, the value of 0.17 is an absurdity. Obviously, chain expansion does occur. The value of 0.65 suggests light branching at low conversion. At high conversion, ϵ ranged from 1.41 assuming zero chain expansion to 1.30 assuming chain expansion. The extent of chain expansion cannot be deduced, but whether or not corrections for chain expansion are made does not appreciably affect the result. The higher
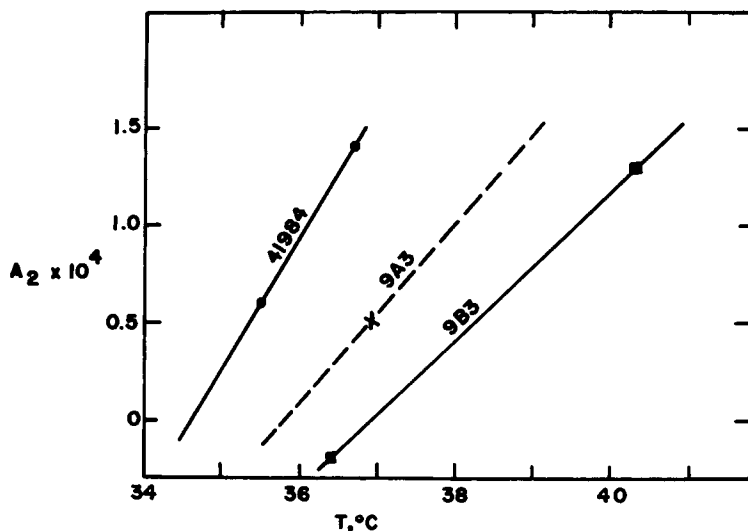
Fig. 7. Virial coefficients A_2 as a function of temperature to determine θ at $A_2 = 0$ for a linear sample 41984 and two branched polymers 9A3 and 9B3.

value of ϵ for the high-conversion series and the proximity to the boundary value of 1.5 suggest high branching. It would be suspected that chain expansion would be less than in series A due to the increased branching.

As pointed out earlier, it is generally accepted in the literature that ϵ should range from 0.5 at low branching to a maximum of 1.5 at high branching. The observed changes in ϵ indicated that series B was higher in branching than the low-conversion series A. This is what might be expected from the polymerization process. Series B was polymerized to just short of gelation, and branching would be expected to be close to the maximum, as suggested by $1.30 < \epsilon < 1.41$. In series A, branching would be light since polymerization had barely begun, as suggested by $0.5 < \epsilon < 0.65$.

For flexible polymers, the Kirkwood–Riseman theory relates $[\eta]$ to the hydrodynamic radius of an equivalent sphere, namely,

$$[\eta] = \frac{10}{3} \pi \frac{N_A}{M} R_\eta{}^3 \tag{12}$$

where R_η is related to $\langle S^2 \rangle^{1/2}$ by the relation

$$R_\eta = K_\eta \langle S^2 \rangle^{1/2} \tag{13}$$

and K_η is a proportionality factor between R_η and $\langle S^2 \rangle^{1/2}$. This expresses the fact that a part of the dissolved flexible coil is related in some way to the amount of the coil that is impenetrable to solvent flow.

Values of K_η were calculated for various arbitrarily chosen molecular weight levels. Figure 6 shows a graph of the results. Linear polystyrene remained relatively constant at 0.62, except above 10^6 molecular weight. At 5,000,000 molecular weight, it had increased to 0.65, and at 44,000,000, K_η was 0.74. Series A started out at low molecular weights with $K_\eta = 0.62$, but K_η quickly increased to as high as 0.9 or greater at a molecular weight above 10^7. Series B had an intermediate character. K_η ranged from 0.62 at low molecular weight to 0.72 at 5,000,000 molecular weight.

The explanation for these trends is found in the chemical structure changes in the branching at low and high conversion. For linear polystyrene, the constancy of K_η was expected, but the increase in K_η at high molecular weight may reflect a loss of flexibility or an increase in segment density deep within the coil. At low conversion, where the looping of the inner core through pendent vinyl group polymerization had not yet become extensive, the branched molecule would be expected to have higher segment densities (relative to linear polymer) throughout the chain. This would create a more highly impermeable core, increasing K_η and reducing the "free draining" character of the chain. At higher conversion, the pendent vinyl group polymerization has occurred, preferentially tightening the inner core but not decreasing $\langle S^2 \rangle^{1/2}$. This has the effect of shrinking the amount of the impermeable core; creating a more "free draining" molecule even though branching continues to increase.

The light-scattering data of Table II were analyzed for the determination of the theta temperature of linear standard 41984 and branched fractions 9B3 and 9A3. A_2 was plotted versus temperature in Figure 7. All three samples were similar in $\overline{M}_w$. The linear standard 41984 was found to have a θ temperature of 34.7°C, slightly lower than most reported values[14] but quite typical of linear polystyrene. Fraction 9B3 had a θ temperature of 36.9°C, an increase of over 2° from linear polymer. Fraction 9A1 had a θ temperature of 35.8°C. Two experimental points were available for both linear sample 41984 and highly branched sample 9B3, thus defining a line of slope dA_2/dt. For the lightly branched sample 9A3, only one experimental point was available; but because of its intermediate branching character, it was felt probable that its slope dA_2/dt lay between the two for 41984 and 9B3. An intermediate slope value was assigned to it through the one experimental point for 9A3. Regarding the changes in A_2, Figure 7 reveals two trends. First, A_2 increases with temperature at a faster rate for linear polystyrene than for highly branched polystyrene. Second, θ increases with increasing branching. This last observation is contrary to what was expected from the data on star shaped polystyrenes reported by Benoit and coworkers.[7] They reported a large decrease of θ for star polystyrenes. These data indicate a decreased thermodynamic interaction with the solvent as branching increases and indicate that an infinite molecular weight branched polystyrene would be less soluble than the linear species.

The effect that polydispersity has on A_2 from light scattering was investigated. According to Berry and Casassa,[8] a sample that has a broad molecular weight distribution will have a larger A_2 than a narrow-distribution sample of the same molecular weight $\overline{M}_w$. However, the effect is not large, A_2 being only about 1.1 times greater than an $\overline{M}_w/\overline{M}_n$ of 2. Both 9A3 and 9B3 have $\overline{M}_w/\overline{M}_n < 2$; consequently, a reduction of A_2 by a factor of 1.1 would add only about 0.1°C to θ. The effect seems less than experimental error, but certainly the θ determined here for the branched species can be regarded as a minimum value, at least with respect to distribution corrections.

CONCLUSIONS

The following conclusions can be drawn about the branched polystyrene fractions of series A and B:

a. The fractionation produces broader fractions as both molecular weight and branching increased.

b. The *dn/dc* for highly branched and linear polystyrene is the same.

c. No corrections for peak dispersion of the GPC are required to develop a precise calibration curve over the entire elution volume interval.

d. The $[\eta]$ data indicate that an increase in conversion increases the branching.

e. Not all the pendent vinyl groups of DVB react during polymerization to produce effective branch points. The copolymerization is found to be extremely complex.

f. Both the high- and low-conversion series obey the same $\langle S^2 \rangle - M$ line even though they differ in branching and in GPC elution characteristics.

g. The branching factor g^ϵ has differing values of ϵ, ranging from 0.65 for low-conversion polymers to 1.41 for high-conversion polymers. According to simple viscometric theory, these represent the two extremes in branching density.

h. The ratio of hydrodynamic radius to radius of gyration for branched polymer is higher than for linear polymer and increases with molecular weight.

i. The theta temperature of randomly branched polystyrene is as much as 2°C higher than linear polystyrene and increases with branching.

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