Randomly Branched Styrene/Divinylbenzene Copolymers. I. Preparation, Molecular Weight Characterization, and GPC Analysis

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Synopsis

A series of randomly branched copolymers of styrene and divinylbenzene were prepared using a benzoyl peroxide-initiated free-radical bulk polymerization at 78°C. DVB contents were varied from 0.01% to 2%. Two samples were polymerized with 0.4% DVB to different conversions: series 9A at 6% conversion and series 9B at 15% conversion (just short of the gelation point). Both samples were fractionated and the fractions characterized by ultracentrifugation, light scattering, osmometry, viscometry, and gel permeation chromatography. The data indicated that the fractions were not of narrow MWD and that the breadth of the MWD of the fractions from series 9B were greater than those of 9A. GPC calibration curves of M, $[\eta]$, and $M[\eta]$ were generated for both 9A and 9B fractions by employing curve-fitting techniques to the GPC data. For all of the fractions 9B, the molecular weight calibration provided accurate values of $\overline{M}_z$, $\overline{M}_w$, and $\overline{M}_n$, suggesting that no serious peak spreading had occurred in the GPC experiments. The universal calibration parameter $M[\eta]$ for the 9A fractions agreed with that of linear polystyrene, while that of the high-conversion series 9B did not. It will be shown in a later paper that series 9B is highly branched, while 9A is lightly branched. Consequently, it is recommended that any GPC analysis of branching units make an allowance for the deviation of highly branched polymers from the linear $M[\eta]$ calibration curve.

INTRODUCTION

There are several ways of preparing branched polymers. Branched structure is always possible during polymerization if chain transfer to polymer occurs. Diene monomers also are subject to branching during their polymerization because of the residual double bonds in the chain. But branching which occurs in this fashion is largely uncontrollable. Branched polymers can be synthesized. Star and graft polymers are two branched structures which can be synthesized by anionic and cationic polymerization techniques. Polymerization of monomers with high functionality (and also copolymerization with multifunctional monomers) is also possible, either through polycondensation reactions or by free-radical polymerizations. The latter approach has been used successfully by several authors to prepare highly branched polymers. Thurmond and Zimm[1] copolymerized difunctional styrene (Sty) and tetrafunctional divinylbenzene (DVB) using free-radical polymerization to prepare a highly branched structure. The nature of the branching is such that a spherically shaped molecule should be formed since there is a large amount of DVB and consequently a high branch density.

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The possibility of analyzing the amount of branching in a polymer sample from gel permeation chromatography (GPC) has been known for some time.[2–11] However, the central point in any such analysis is the calibration curve to be used for such an analysis. In this paper, an experimental GPC calibration curve was obtained for randomly branched polymers. In particular, polystyrene/divinylbenzene copolymers were synthesized at different conversions. Fractions were then obtained over a large molecular weight range. The fractions were then characterized by molecular weight and intrinsic viscosity measurements.

The GPC calibration curves were then determined for M, $[\eta]$, and $[\eta]M$ as a function of elution volume for the branched fractions. It is demonstrated that none of the above functions lies on the same calibration curve as that obtained for linear polystyrene so that more attention must be given to the general behavior of branched versus linear polymers in their elution characteristics. It is further shown that only with extensive branching is there an appreciable error in using the common calibration curve based on linear polymers.

EXPERIMENTAL

Solvents

All solvents used in this study were dried and purified by distillation over finely ground calcium hydride. Nitrogen gas, dried by passage through 1-ft column of Drierite, was bubbled into the enclosed system through a fine capillary tube. The first 100 ml of distilled solvent was discarded. The center cut was collected in a 4-l. flask and stored.

The styrene and divinylbenzene monomers used in the polymerization studies were ACS reagent grade and practical grade, respectively.

Monomers

Just prior to its use, styrene was purified by bubbling nitrogen gas through it for 1 hr to remove dissolved oxygen. No attempt was made to remove inhibitor. Divinylbenzene was used as received from MCB, with no attempt to remove either dissolved oxygen or inhibitor. Impurity levels of DVB were checked by gas chromatography. It was found that the monomer as received is, as reported by the manufacturer and by Thurmond and Zimm,[1] of the order of 35% m-divinylbenzene, 16% p-divinylbenzene, 30% m-ethylvinylbenzene, and 13% p-ethylvinylbenzene.

Poly(divinylbenzene) is reported by MCB to be insoluble in its monomer; therefore, clarity of the monomer was used to check for polymer. Mixing the styrene with an excess of methanol will precipitate any dissolved polystyrene, and this test was used to check for polystyrene. Both monomers were found free of dissolved polymer.

Polymer Standards

The linear polystyrene samples used in this study were all of narrow molecular weight distribution. They were obtained from several sources, including samples prepared and characterized in these laboratories,[12] samples from Waters Asso-

TABLE I
Standard Polystyrene Samples

Sample no.	Ref.	M_w, g/mole	M_n, g/mole	$[\eta]^c$
D-I-1-1	12	9,600,000	—	14.4[d]
LJF-9	12	4,500,000	—	8.267
11b	PCC	4,000	—	—
7b	PCC	37,000	—	—
61970	WA	2,610,000	1,990,000	4.733
25167	WA	867,000	773,000	2.234
41984	WA	200,000	193,000	0.726
25170	WA	33,000	36,000	0.232
25171	WA	10,000	9,600	—
25168	WA	20,800	20,000	—
NBS 705	NBS	179,000[a]	171,000	—
		190,000[b]		
NBS 706	NBS	257,800[a]	—	—
		288,100[b]		

[a] Light scattering.
[b] Analytical ultracentrifuge.
[c] dl/g; THF at 30°C.
[d] Reference 12.

ciates (WA), Framingham, Mass., the National Bureau of Standards (NBS), Washington, D.C., and Pressure Chemical Company, Pittsburgh, Pennsylvania (PCC). The identification and molecular weights are given in Table I.

Ultracentrifugation

All sedimentation-equilibrium experiments were performed with a Beckman Model "E" analytical ultracentrifuge using either an AN-J four-place equilibrium rotor or an AN-F four-place rotor. The RTIC unit was calibrated with a mercury thermometer. The Rayleigh interferometric system was used for all sedimentation-equilibrium runs.

Initial concentrations were based on the volumetrically determined concentrations. Multicell runs were made with interference and/or Schlieren cells having +0.6°, 0.0°, and −0.6° wedge centerpieces. FC 43 oil was used to lift the solutions off the bottom of the cells so that the fringes could be properly read.

The sedimentation-equilibrium molecular weights were determined in cyclohexane. Values of 0.928 for $\bar{v}$, 0.764 for ρ, and 0.1705 for dn/dc were used based upon linear polystyrene.[12]

The following equations were used to determine the weight- and z-average apparent molecular weights, $M_{w,\text{app}}$ and $M_{z,\text{app}}$, respectively:

$$M_{w,\text{app}} = \frac{2RT}{(1-\bar{v})\omega^2} \cdot \frac{1}{(r_b{}^2 - r_m{}^2)} \cdot \frac{(C_b - C_m)}{C_0} \tag{1}$$

$$M_{z,\text{app}} = \frac{M_{w_b}C_b - M_{w_m}C_m}{C_b - C_m} \tag{2}$$

where R is the gas constant, $\bar{v}$ is the partial specific volume of solute, ρ is the solvent density, ω is the velocity in radian/sec, r is the distance from axis of

rotation in cm (b = cell bottom and m = cell meniscus), T is the absolute temperature, and ($C_b - C_m$) is the change in concentration in fringe numbers. M_{w_b} is equal to the weight-average molecular weight at the cell bottom and M_{w_m} is equal to the weight-average molecular weight at the cell meniscus.

Since most of the experimental runs were made at several degrees above the ideal temperature, all true $\overline{M}_w$ and $\overline{M}_z$ values were obtained by extrapolating the apparent values to zero concentration according to the method and following the equation given by Fujita[13]:

$$\frac{1}{M_{w,\text{app}}} = \frac{1}{M_w} + 2A_2\bar{c} \tag{3}$$

$$\bar{c} = \frac{C_b + C_m}{2} \tag{4}$$

where A_2 is the second virial coefficient and $\bar{c}$ is close to the original concentration. Correspondingly, $1/M_{z,\text{app}}$ is plotted versus $\bar{c}$ (g/cc) to obtain $\overline{M}_z$ at $c = 0$.

A second correction was occasionally needed. Ideally, in order to apply extrapolations like eq. (3), all apparent molecular weights must be determined such that the variable $[(1 - v)\omega^2 (r_b{}^2 - r_m{}^2)]/2RT$ is constant.

Light Scattering and Clarification of Solutions

A Phoenix low-angle light-scattering photometer had been modified extensively to include very low angles of observation.[12] This light-scattering photometer has the capability of measuring from 140° to 15° of observation angle. Secondary concentrations were prepared by volumetric dilution of a master solution. Samples were filtered through 0.2-μ membrane filters into the specially designed scattering cells equipped with dust traps. Optical cleaning was accomplished by centrifugation. The samples were centrifuged for 2 hr at 4000 rpm in a Sorvall SS-4 centrifuge equipped with a type HB-4 high-speed swinging bucket rotor. Solvents were centrifuged at 4000 rpm for a minimum of 8 hr. A specially constructed oven around the centrifuge allowed the handling of solutions above room temperature.

The standard Sofica light scattering photometer was employed for the lower molecular weight samples and was used over an angular range of 30°–150°. Clarification by repeated slow filtration of solutions through 0.2-μ filter membranes was followed by a visual check for dust in the instrument using the natural light of the mercury lamp viewed at low angles.

Differential Refractometry

A Brice–Phoenix differential refractometer was used with a constant temperature circulator maintaining control to ±0.2°C. The calibration constants in two solvents of differing refractive index, toluene and cyclohexane, were determined with polystyrene standard NBS 705 at 30°C. The values of dn/dc for cyclohexane at various temperatures were taken from the work of (O'Mara and McIntyre.[14] For THF, the value of dn/dc for all of the branched samples was determined to be 0.1963. There was no variation in dn/dc with either branching or molecular weight. The measured value is close to that reported by Jordan[15] for linear polystyrene, 0.1926.

Absolute Scattering Values

The scattering standard used in all cases was benzene. Its Rayleigh ratio for unpolarized light of 5461 Å wavelength and 23°C was taken to be[16] 1.58×10^{-5}. The Rayleigh ratio R_0 increases with temperature, and the equation of Carr and Zimm[17] was used for calculating the Rayleigh ratio at different temperatures:

$$R_{90,2} = R_{90,1} \frac{(T_2 n_2{}^2)}{(T_1 n_1{}^2)} \tag{5}$$

where the subscript 1 refers to the temperature given with the reported R_{90} value (23°C) and subscript 2 refers to the calculated value at another temperature, T_2.

The method of Zimm[18] was used to determine $\overline{M}_w$, $\langle S^2 \rangle_z$, and A_2; $\overline{M}_w$ is the weight-average molecular weight, $\langle S^2 \rangle_z$ is the z-average mean-square radius of gyration, and A_2 is the second virial coefficient. (c/I_c) was plotted versus $\sin^2 (\theta/C) + KC$, where K is an arbitrary constant, to give two limiting curves for zero concentration and zero angle.

Osmometry

The Mechrolab Model 502 membrane osmometer was used with toluene solutions for all except one sample that was used with tetrahydrofuran (THF) solutions. Temperatures were controlled at 35°C for the toluene experiments and at 24°C for the THF experiment. Gel cellophane 600-D-type membranes were used for the most part because of their tight porosity (10,000 molecular weight diffusion limit). Solutions were prepared as previously discussed. The osmotic height was measured for the solvent on both sides of the membrane first, then for each concentration, and again for solvent on both sides to ensure that the same readings were obtained and no diffusion or other problems had occurred. All data were linearly extrapolated to zero concentration.

Variable-Shear Capillary Viscometer

A Cannon–Ubbelohde variable-shear dilution viscometer was used to determine the intrinsic viscosity at low shear rates. Typical shear rates for organic solvents range from 300 to 3000 sec^{-1}. In no case was there a shear-rate dependence.

Gel Permeation Chromatography

A Waters Associates Ana-Prep gel permeation chromatograph (GPC) was used with THF at 40°C. The following set of 4-ft Styragel columns was used: one 7 $\times 10^5$ to 5×10^6 Å; one 1.5×10^5 to 7×10^5 Å; one 1.5×10^4 to 5×10^4 A; two 5×10^3 to 1.5×10^4 Å; and one 2000 to 5000 Å. The size designations are those given by Waters Associates. This particular column sequence had a plate count of 700 ppf using a 5-sec injection of o-dichlorobenzene. The solvent was THF at 40°C at a flow rate of 1 ml/min.

The standard differential refractometer detector was coupled with the Waters differential UV detector set at 254 mμ wavelength, providing dual detector capability. This arrangement was necessary in order to use the GPC at the low

TABLE II
Initial Sty/DVB Polymerization Batches

Bottle no.	% BP[a]	% DVB[b]	Temp., °C	Gelation time, hr
1	0.125	0.0125	76	16
2	0.120	0.0100	76	19
3	0.125	0.0617	76	14
4	0.126	0.2690	76	12
5	0.120	1.22	78	5
6	0.100	2.12	78	5

[a] BP = Benzoyl peroxide.
[b] DVB monomer as received.

concentrations required to eliminate corrections for concentration effects (0.05% for the linear polystyrene samples and 0.10% for the branched polystyrene samples). Samples were prepared on a weight/volume basis and filtered using 1-μ Millipore filter membranes. Full-loop injections were used both in generating the calibration curves and also in analyzing chromatograms as a function of elution volume. The above column set was found to be adequate in resolving all but the very high molecular weight ($> 10^6$) polystyrene samples.

Polymerization and Fractionation

A polymerization scheme similar to that of Thurmond and Zimm[1] was used, where PSty/DVB copolymer was synthesized by a free-radical bulk polymerization. In this work the inhibitors were not removed from the monomers prior to the polymerization.

The first series of polymerizations were designed to determine the relationship between DVB content and the time to visible gelation at 78°C. Table II lists the pertinent data for the batches run. The increase of gelation time from 5 hr to 19 hr as the DVB content decreased from 2% to 0.01% is in the expected direction. However, the 16-hr gelation time (obtained from the final calibration line) at 78°C and 0.06% DVB was faster than that observed by Thurmond and Zimm, who found 16 hr of gelation time at 67°C and 0.08% DVB content. This was undoubtedly due to the higher polymerization temperature.

Next, the polymerization rate was studied as a function of DVB content. Four batches were polymerized to predetermined total reaction times and stopped. The results are listed in Table III. Series 9, 1% DVB monomer charge, was found

TABLE III
Conversion Versus Polymerization Time

Bottle no.	Time, hr	% BP	% DVB[a]	Temp, °C	% Conversion
7	9	0.125	0.010	81	55.1
8	6	0.127	0.105	78	33.3
9A	2	0.125	0.988	78	5.7
9B	4	0.125	0.988	78	15.2

[a] Monomer as received.

to have a 15% conversion at the gel point. This value is consistent with the result of Malinsky,[19] who found 13%–14% conversion at gelation at 70°C.

For the low conversion, high DVB series 9A and 9B, percent conversion was plotted versus polymerization time and extrapolated to a time intercept of 48 min. This is the induction period for this polymerization. Undoubtedly, this high induction period is due to the inhibitors in the monomers. Straight lines were drawn through each of the remaining data points and the time intercept point. The slopes of these three lines, representing the polymerization rates, were plotted versus DVB content; and it was found that as DVB content increased from 0.01% to 1%, the polymerization rate decreased from 6.7%/hr to 4.7%/hr. These numbers may not be absolutely correct since they are based on the assumption that the 48-min induction period is constant for all DVB levels. But even if the induction period decreases as the DVB content decreases, the polymerization rate will still decrease as the DVB content increases. These results are not expected since Flory[20] and Malinsky[19] report that DVB is appreciably more reactive than styrene. However, the reduction in polymerization rate found here is probably due to the fact that DVB had 1200 ppm t-butylcatechol inhibitor while styrene had only 100 ppm t-butylcatechol. Thus, an increase in DVB causes an increased inhibition of the polymerization by reducing initiator concentration and reducing the rate of polymerization.

These three batches (7, 8, and 9) also served as a study of branching as a function of conversion. From each bottle, half (called A) was removed when polymerization had proceeded halfway toward its gel point time. The other half (called B) was allowed to polymerize to just short of the gel point. Of these six samples, the two of highest DVB content, batch 9, were selected for fractionation. The solution properties of the fractions were subsequently measured and considered to be typical randomly branched polymers. Series 9 was selected because of the relatively high branching. It contained 0.4% active DVB as compared to less than 0.1% DVB in the Thurmond and Zimm work[1] and 0.02% DVB in the GPC study of Tung.[21] Therefore, these polymers should be more highly branched than polymers in the previous studies and therefore more representative of highly branched commercial polymers.

All samples were checked for macrogel content by filtering 0.1% THF solutions through 1-μ filters (Millipore) and measuring the loss in concentration. None had any measurable macrogel. Checks for microgel were made in the course of making light-scattering measurements. Only the highest molecular weight fraction of the high-conversion polystyrene showed a sharp downward trend at 15°C, indicating the presence of a small amount of microgel.

The purified samples 9A and 9B were fractionated using a solution-precipitation technique. Approximately 1.5 g sample was dissolved in 150 ml benzene in a beaker and titrated dropwise with methanol to the point of heavy turbidity, heated to the point of clarity, and allowed to slowly recool to room temperature. The dispersion was added to 50-ml stainless steel tubes designed to fit the Sorvall Model SS-4 centrifuge and centrifuged at 5000 rpm for 1 min. The supernatant was poured back into the beaker for further fractionation. The swollen polymer phase in the centrifuge tubes was dissolved in benzene, collected, and dried. In this fashion, several crude fractions were prepared. One crude fraction, 9B2, was refractionated in the same manner into two subfractions, 9B2-1 and 9B2-2.

RESULTS AND DISCUSSION

Molecular Weight Characterization

Six fractions were selected for characterization studies to allow the widest possible spread in both branching and molecular weight. These are listed in Table IV. Three fractions are from the low conversion series (A): 9A1, 9A3, and 9A5. Three fractions are from the high conversion series (B): 9B2-1, 9B2-2, and 9B3.

All of the molecular weight results ($\overline{M}_z$, $\overline{M}_w$, $\overline{M}_n$) are compiled in Table V. Good agreement in $\overline{M}_w$ is found for the three samples for which $\overline{M}_w$ was determined both by sedimentation equilibrium (UC) and light scattering (LS) techniques. $\overline{M}_n$ is from osmotic pressure measurements (OP).

The fractions from the highly branched series 9B are broader in molecular weight distribution than those of the lightly branched series 9A. This reflects the increased complexity of the polymer as the molecular weight and conversion increases. There undoubtedly exists in a system like this not only a distribution with respect to molecular weight, but also a distribution with respect to branching. These contribute in different ways to the entropic and enthalpic

TABLE IV
Branched Polystyrene Fractions Characterized

Low conversion series	High conversion series
9A1	9B2-1
9A3	9B2-2
9A5	9B3

TABLE V
Summary of Molecular Weight Data for Branched Polystyrenes

Fraction	$\overline{M}_z$ (UC)	$\overline{M}_w$ (UC)	$\overline{M}_w$ (LS)	$\overline{M}_n$ (OP)	$[\eta]$*
9A5	139,000	88,200	88,400	67,000	0.456
9A3	595,000	400,000	407,000	206,000	0.977
9A1	—	—	572,000	348,000	1.305
9B3	352,000	210,000	228,000	127,000	0.714
9B2-2	—	—	2,230,000	322,000	1.202
9B-1	—	—	5,240,000	681,000	2.109

*THF at 30°C

TABLE VI
Results from Final Curve-Fitted Calibration Curves

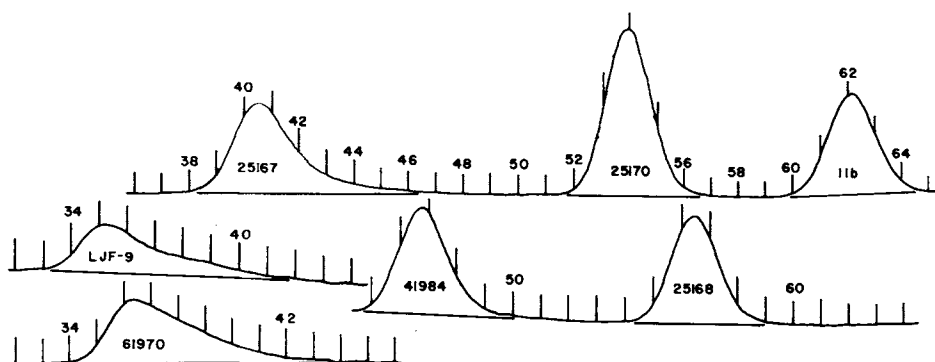| Fraction	$[\eta]$ (dl/gm)	$\overline{M}_z$ (gm/mole)	$\overline{M}_w$ (gm/mole)	$\overline{M}_n$ (gm/mole)
9A5	0.45	121,000	90,100	66,100
9A3	1.01	614,000	372,000	223,000
9A1	1.29	954,000	614,000	328,000
9B3	0.71	361,000	212,000	140,000
9B2-2	1.34	11,500,000	2,010,000	326,000
9B2-1	2.13	15,000,000	5,280,000	920,000

Fig. 1. GPC curves of linear polystyrene standards in Ana-Prep GPC (refractive index vs elution volume counts; sample numbers underneath curve).

variables that govern fractionation by fractional precipitation. This effect has to be recognized in the later GPC analysis. Also contributing to the observed distribution differences is the overall higher molecular weights of the 9B series fractions.

The molecular weight data indicate that the branched fractions are not monodisperse. In order to study the effect of branching on the solution properties, it is necessary to correct for these polydispersities. To do this, the GPC data were used to provide a quantitative picture of the molecular weight distri-
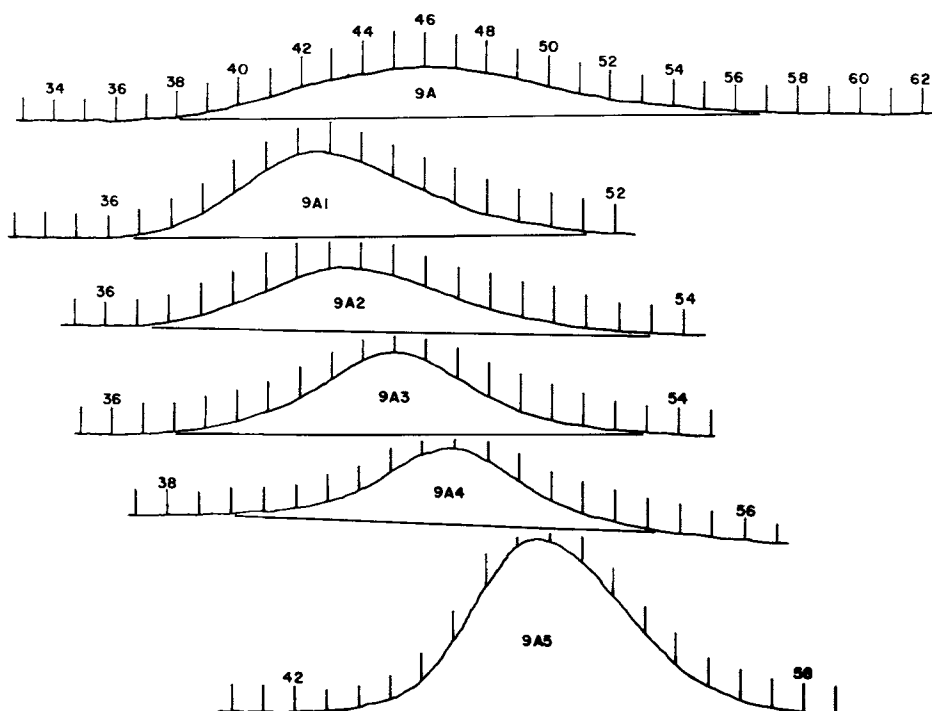

Fig. 2. GPC curves of 9A branched series in Ana-Prep GPC (refractive index vs elution volume counts; sample numbers underneath curve).
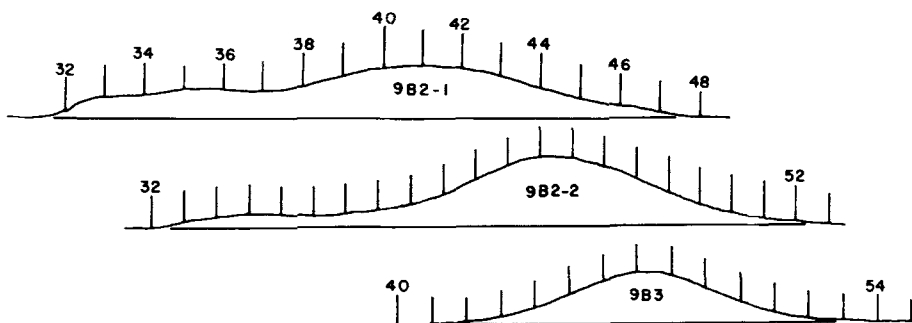
Fig. 3. GPC curves of 9B branched series (refractive index vs elution volume counts; sample numbers underneath curve).

butions. Having previously determined the necessary characterization data on these fractions, calibration of the GPC was done using curve fitting techniques. The basic assumption made was that branching in a whole polymer is a single-valued function. With this assumption, the fractions of one branched series should obey one common calibration curve. An underlying assumption in this approach is, of course, that the chromatogram represents an accurate picture of the molecular size distribution and therefore molecular weight.
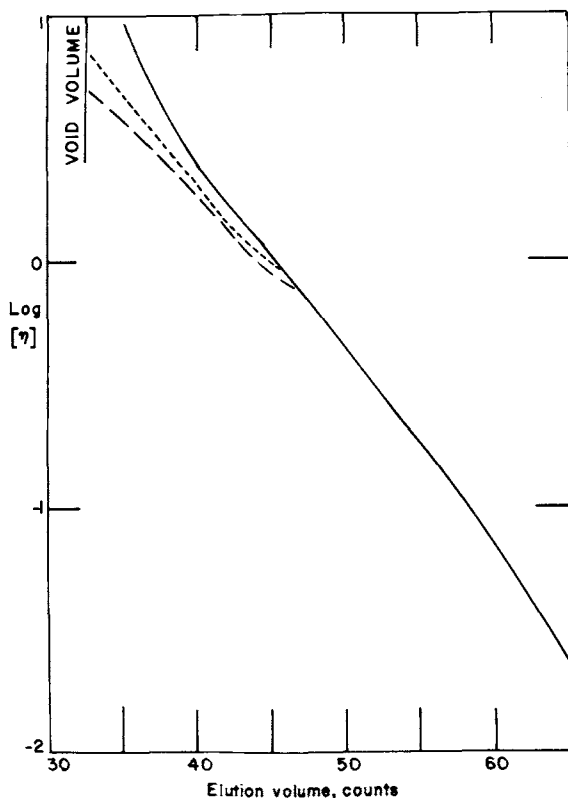

Fig. 4. Final curve-fitted intrinsic viscosity calibration curves for polystyrene in Ana-Prep GPC: (—) linear; (– –) 9B series. (- - -) 9A series.
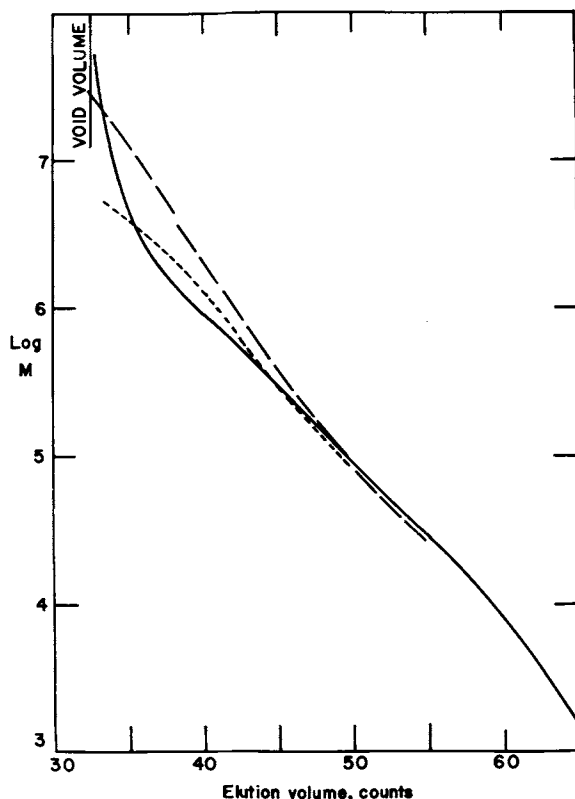
Fig. 5. Final curve-fitted molecular weight calibration curves for branched polystyrene in Ana-Prep GPC: (—) linear; (– –) 9B series; (- - -) 9A series.

The curve fitting analyses were done by using the following equations:

$$M_z = \frac{\Sigma w_i M_i^2}{\Sigma w_i M_i} \qquad (6)$$

$$M_w = \Sigma w_i M_i \qquad (7)$$

$$M_n = \frac{1}{\Sigma w_i / M_i} \qquad (8)$$

$$[\eta] = \Sigma w_i [\eta]_i \qquad (9)$$

The weight fraction data were obtained from the GPC curve in the normal manner, and the $\overline{M}_w$ and $[\eta]$ data were taken from the characterization values shown in Table V. The procedure was to (1) develop a molecular weight calibration curve using $\overline{M}_w$ values for the fractions, (2) develop an $[\eta]$ calibration curve using $[\eta]$ data, and (3) develop an $\langle S^2 \rangle$ calibration curve using the $\langle S^2 \rangle_z$ data for the fractions. All the characterized fractions were used because they eluted at different volumes yet overlapped in volume to define all the elution volume regions of the calibration curve.

The GPC curves of the linear standards and the two branched series (A and B) are shown in Figures 1–3, respectively. Included for reference are the GPC
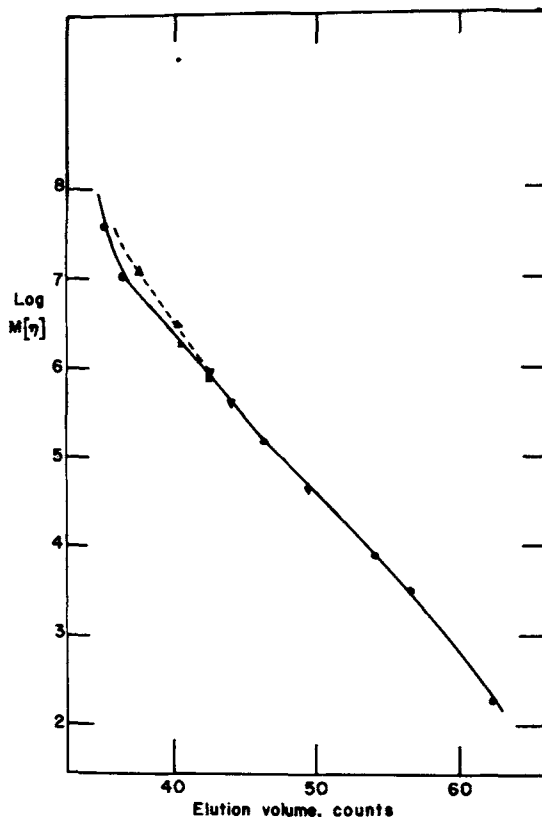
Fig. 6. Curve fitted universal calibration curve ($[\eta]$) in Ana-Prep GPC (points represent experimental data; lines are curve-fitted data): (●) PSty; (▼) series A; (▲) series B.

curves of the fractions not characterized. Whole sample 9B could not be analyzed because plugging of the column occurred when it was injected into the GPC apparatus. Sample 9B1 also plugged the GPC. This was undoubtedly due to a small amount of the microgel present in the polymerized sample and discussed earlier.

A comparison of the GPC curve-fitted results of Table VI to the characterization data of Table V reveals good agreement in all parameters. No corrections for peak dispersion were required to develop a precise calibration curve over the entire molecular weight range. Even though the molecular weight calibration curve was developed using only $\overline{M}_w$ data, the final results for $\overline{M}_z$ and $\overline{M}_n$ agreed quite well with the characterization data. This fortified the original assumption that the chromatogram represented the actual molecular weight distribution. This suggests that for samples of broad molecular weight distribution, peak dispersion is not a problem. However, it must be recognized that just because the calibration curves for the branched series coincides with that of the linear species, especially at low molecular weight, the structure is not necessarily the same. This aspect of the results will be discussed later.

Some justification of the curve-fitting approach should be made. In order to apply curve-fitting to the data, it is assumed that (1) the elution volume is a single-valued function of each of the two parameters M and $[\eta]$, (2) the same

chromatogram is an expression of the two different parameters, (3) there are no double-valued positions along the elution volume space, and (4) both parameters are monotonically decreasing functions. Additionally the solution properties of the polymers in the GPC columns are assumed to be at "infinite dilution." An independent study of the concentraion dependence of both branched series had shown that "infinite dilution" was a good approximation in the GPC analysis.

The final GPC calibration curves derived from the preceding analysis of $[\eta]$, M, and $[\eta]M$ are shown in Figures 4–6. In each case, the calibration curve obtained for linear polystyrene is also shown as a solid curve. It is evident from Figure 4 that for a given $[\eta]$ value, branched samples elute from the GPC sooner than linear polymers, and the deviation from linear polystyrene increases as branching increases from the low-conversion (lightly branched) series 9A to the high-conversion (highly branched) series 9B. Further, at low elution volumes, the rise in $[\eta]$ is less rapid for the branched samples than for the linear samples.

In Figure 5, for a given molecular weight (MW), branched samples elute from the GPC later than linear polymers. Both the $[\eta]$ and MW relations to elution volume for branched polymers show an increasing deviation from the linear polystyrene as branching increases; however, the deviation is in opposite directions. Both deviations are related to the flattening out of the $[\eta]$–M plot for branched polymers.

Some comments regarding the universal calibration parameter $M[\eta]$ shown in Figure 6 must be made. It is obvious that the $M[\eta]$ calibration for the lightly branched series 9A agrees well with that of linear polystyrene, while the corresponding $M[\eta]$ plot for the highly branched series 9B deviates from the linear line. An explanation of this effect involves an extensive analysis of the GPC separation mechanism itself. This will be dwelt on in the succeeding papers. Any GPC analysis of branching must make allowance for the deviation from the linear calibration curve. If there is a significant amount of high-conversion branched polymer in the sample, the error in molecular weights could be as high as a factor of 2. Many commercial samples would have to be corrected by this factor. An analysis of Pannell's GPC data[2] on grafted polystyrene indicates that the deviation in the ln $[\eta]M$ plot even in these samples approaches the factor of 2.

In general, no GPC analysis is better than the calibration curve. In this study the overlap of fractions was required to validate the simplest interpretation of the data, namely that the deviation from the unversal calibration is due to increasing branching. It is always possible to adduce a more ad hoc hypothesis that the deviation is due to adventitious combination of errors. However, it was felt that a better understanding of the deviations from the universal calibration for branched polymers was necessary in order to generalize this observation and apply it to other variants of macromolecular structure. To this end, an extensive study of the solution properties of these branched polymers was undertaken to determine actual sizes and their relation to the mechanism of the GPC separation process.

References

1. C. D. Thurmond and B. H. Zimm, *J. Polym. Sci.*, **8**, 477 (1952).
2. J. Pannell, *Polymer*, **13**, 277 (1972).
3. M. Kurata, M. Abe, M. Iwama, and M. Matsushima, *Polym. J.*, **3**, 729 (1972).

4. M. R. Ambler, R. D. Mate, and J. R. Purdon, *J. Polym. Sci., Polym. Chem. Ed.,* **12,** 1759 (1974).

5. M. R. Ambler, R. D. Mate, and J. R. Purdon, *J. Polym. Sci., Polym. Chem. Ed.,* **12,** 1771 (1974).

6. E. E. Drott and R. A. Mendelson, *J. Polym. Sci. A-2,* **8,** 1361 (1970).

7. E. E. Drott and R. A. Mendelson, *J. Polym. Sci. A-2,* **8,** 1373 (1970).

8. G. Kraus and C. J. Stacey, *J. Polym. Sci. A-2,* **10,** 657 (1972).

9. M. Kurata, H. Okamoto, M. Iwama, M. Abe, and T. Homma, *Polym. J.,* **3,** 739 (1972).

10. A. R. Shultz, *Eur. Polym. J.,* **6,** 69 (1970).

11. L. Westerman and J. C. Clark, *J. Polym. Sci., Polym. Chem. Ed.,* **11,** 559 (1973).

12. E. L. Slagowski, Doctoral Thesis, University of Akron, Akron, Ohio, 1972.

13. H. Fujita, *Mathematical Theory of Sedimentation Analysis,* Academic Press, New York, 1962.

14. J. H. O'Mara and D. McIntyre, *J. Phys. Chem.,* **63,** 1435 (1959).

15. E. F. Jordan, Jr., *J. Polym. Sci. A-1,* **6,** 2209 (1968).

16. H. Utiyama, in *Light Scattering From Polymer Solutions,* M. B. Huglin, Ed., Academic Press, London, 1972, p. 78.

17. C. I. Carr and B. H. Zimm, *J. Chem. Phys.,* **18,** 1616 (1950).

18. B. H. Zimm, *J. Chem. Phys.,* **16,** 1093, 1099 (1948).

19. J. Malinsky, J. Kapban, and K. Dusck, *J. Macromol. Sci., Chem.,* **A5,** 1071 (1971).

20. P. J. Flory, Principles of Polymer Chemistry", Cornell, Ithaca, N.Y., 1953, p. 391.

21. L. H. Tung, *J. Polym. Sci. A-2,* **7,** 47 (1969).