# Assessment of branching in polymers from small angle X-ray scattering (SAXS): SAXS from model comb-branched polystyrenes

**Sunil K. Garg*** **and S. S. Stivala**
*Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, N.J.*, 07030, *USA*

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Comb-branched polystyrenes having both fixed backbone length and number of branches but variable branch lengths were prepared anionically. Small angle X-ray scattering of the model polystyrenes from methyl ethyl ketone (MEK) solutions at 25°C was examined and it is shown that the mass per unit length and cross-sectional radius of gyration increase with increasing branch length. A maximum appears in the Kratky plot for the branched polymers. While the linear polymer displays an essentially Gaussian segment distribution in solution, the branched polymers deviate considerably from the behaviour of the linear polymer under the same conditions.

**Keywords** Polymers; branching; small angle X-ray scattering; polystyrenes; particle scattering factor; cross-sectional properties

## INTRODUCTION

In previous work[1,2], we have shown that small angle X-ray scattering (SAXS) may be used to assess branching in polymers. In particular, it was shown that the mass per unit length, $M_u$, the radius of gyration of the cross-section, $R_q$, and the contour length, $L$, vary in a manner predictable by the topology of branching of the chain. A relation to obtain the Zimm–Stockmayer[3] parameter[3] $g$ from the SAXS data was developed. The samples used in that work, a series of the naturally occurring polysaccharide dextran, were fairly polydispersed and the branching characteristics were known only from secondary evidence to their structure particularly from the work of Wales *et al.*[4,5].

Dextran is dendritic, i.e., has a branched-branch structure, composed of α-D-glycopyranose linked by 1,6 bonds, with branching occurring via non-1,6 bonds, mainly through 1,3 bonds. In contrast with our earlier work on the dextrans, the present investigation examines SAXS data from comb-branched structures, specifically model polystyrenes in 2-butanone or methyl ethyl ketone (MEK) at 25°C. The model compounds were prepared using anionic polymerization techniques[6–9] and, as a result, were nearly monodispersed. Further, their topology could be controlled, and hence their structures were known from the synthetic scheme followed, to allow a better assessment of the SAXS method in estimating branching in polymers.

This paper deals specifically with the comb-branched polystyrenes having both fixed backbone length and number of branches but varying branch lengths. The experimental data are compared to the theoretical expressions for the particle scattering factor developed by Casassa and Berry[10] and by Burchard[11].

## THEORETICAL

The relation governing the angular dependence of the scattered intensity from a dilute polymer solution, when the distribution of segments within the polymer can be assumed to be Gaussian, is the classical Debye expression:

$$\lim_{c=0}\frac{I(Q)}{Kc}=\frac{2M}{(Q^2\langle s^2\rangle)^2}[\exp(-Q^2\langle s^2\rangle)-1+Q^2\langle s^2\rangle] \tag{1}$$

where $\langle s^2\rangle$ is the mean squared radius of gyration, $M$ the molecular weight, $I(Q)$ the scattered intensity as a function of $Q$, $c$ the concentration in g ml$^{-1}$ and $K$ is a constant related to the contrast in electron density between the solute and the solvent in the case of SAXS. $Q$ is related to half of the scattering angle $\theta/2$ by:

$$Q=\frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) \tag{2}$$

where $\lambda$ is the wavelength of the scattered radiation. An expression for $K$ is given later.

It may be shown[12,13] that equation (1) takes three distinct forms depending on the value of $Q$ and various molecular parameters of the polymer chain. Thus,

(a) For $Q<\langle s^2\rangle^{-1/2}$, equation (1) reduces to

$$\frac{Kc}{I(Q)}=M^{-1}\left(1+\frac{Q^2\langle s^2\rangle}{3}\right) \tag{3}$$

This range is usually called the Guinier range and equation (3) enables the calculation of $M$ and $\langle s^2\rangle^{1/2}$ from the experimental data. To extract these parameters from scattering experiments, data on a series of concentrations are usually collected and the apparent values of $M$ and

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* Present address: Celanese Research Company, Box 1000, Summit, N.J. 07901, USA

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$\langle s^2\rangle^{1/2}$ so obtained are extrapolated to infinite dilution to give the true values[1,2,12].

The use of equation (3) to obtain $M$ and $\langle s^2\rangle^{1/2}$ is independent of the restriction of Gaussian segmental distribution and the equation applies for both branched and linear polymers.

(b) For the range $\langle s^2\rangle^{-1/2} \leqslant Q \leqslant q^{-1}$, where $q$ is the persistence length of the polymer chain, equation (1) reduces to

$$\frac{Kc}{I(Q)} = M^{-1}\frac{Q^2\langle s^2\rangle}{2} \tag{4}$$

This is an asymptotic value and equation (4) is valid only for polymers with Gaussian segmental distribution.

(c) In the range $q^{-1} < Q < l^{-1}$, where $l$ is the statistical segmental length of the polymer, the scattered intensity is given by[13,14]:

$$\frac{Kc}{I(Q)} = M^{-1}\frac{nlQ}{\pi} \tag{5}$$

Equation (5) is the characteristic scattered intensity expression for an ensemble of infinitely thin rods of length $nl$, where $n$ is the number of statistical units in the chain (this contribution is not included in equation (1)). Further, $nl = L$ where $L$ is the contour length of the chain. Equation (5) allows for the calculation of the mass per unit length, $M_u = M/L$, for a polymer chain.

Equation (5) is strictly valid only for an infinitely thin rod-like polymer. For rods with a finite cross-section, an additional term $f_q$ has to be included in equation (5)[15], such that:

$$\frac{I(Q)}{Kc} = (\pi M_u/Q).f_q \tag{6}$$

The factor $f_q$, called the cross-section factor, depends on the radius of gyration of the cross-section $R_q$ according to[15,16]:

$$f_q = \exp\left(-\frac{Q^2}{2}.R_q^{\,2}\right) \tag{7}$$

The parameter $R_q$ may be calculated according to:

$$I(Q)Q = Kc\pi\, M_u f_q$$

or

$$\ln[I(Q)Q] = \ln(Kc\pi\, M_u) - \frac{Q^2}{2}R_q^{\,2} \tag{8}$$

A plot of $\ln[I(Q)Q]$ vs. $Q^2$ gives $R_q$ from the slope and $M_u$ from the intercept.

Following a derivation by Kratky[17] it may be shown that

$$K = (Z_1 - \bar{v}_1\rho_2)^2 I_e P_0 N d\, a^{-2} \tag{9}$$

where $Z_1$ is the number of mole electrons per gram of the solute, $\bar{v}_1$ is the partial specific volume of the solute, $\rho_2$ is the number of mole electrons per ml of the solvent, $P_0$ is the energy of the primary beam per cm length, $d$ is the sample thickness, $a$ is the distance in cm between the sample and the plane of registration, $N$ is Avogadro's number and $I_e = 7.9 \times 10^{-26}$, a constant.

The various equations given above apply, in general, to unbranched chain molecules. These have been used to analyse the scattering from branched chains with the implicit and plausible assumption that the resulting values for $M_u$ and $R_q$ should include an averaged contribution from the side chains.

## EXPERIMENTAL

### *Preparation of comb-branched polystyrenes*

A series of four model branched polystyrenes was prepared for this study. In this series, designated by sample numbers **PS9677BR**, **PS9777BR**, **PS83077BR** and **PS12378BR**, the frequency of occurrence of the branches was constant while the length of the branches was varied.

The backbone material was anionically prepared linear polystyrene obtained from ArRo Laboratories, Jolliet, Ill. The weight average molecular weight, $\langle M_w\rangle$, of the backbone material was 37 000. The polydispersity, $\langle M_w\rangle/\langle M_n\rangle$, where $\langle M_n\rangle$ is the number average molecular weight, was less than 1.06 for this material.

Random comb polymers were synthesized by a coupling reaction between polystyryl lithium and chloromethylated backbone material. *Figure 1* shows the reaction scheme followed.

The backbone material was chloromethylated with chloromethylmethyl ether using stannic chloride as the catalyst in carbon tetrachloride as the solvent according to the procedure given by Altares, *et al.*[6] and purified according to methods in the literature[18]. Polystyryl lithium salts of varying molecular weights were prepared in dry benzene from inhibitor-free styrene using n-butyl lithium as the initiator according to procedures given by Altares, *et al.*[6,7] and by Pannell[8,9]. The degree of polymerization ($DP$) of these salts could be obtained from:

$$DP = M_0/a_0 \tag{10}$$

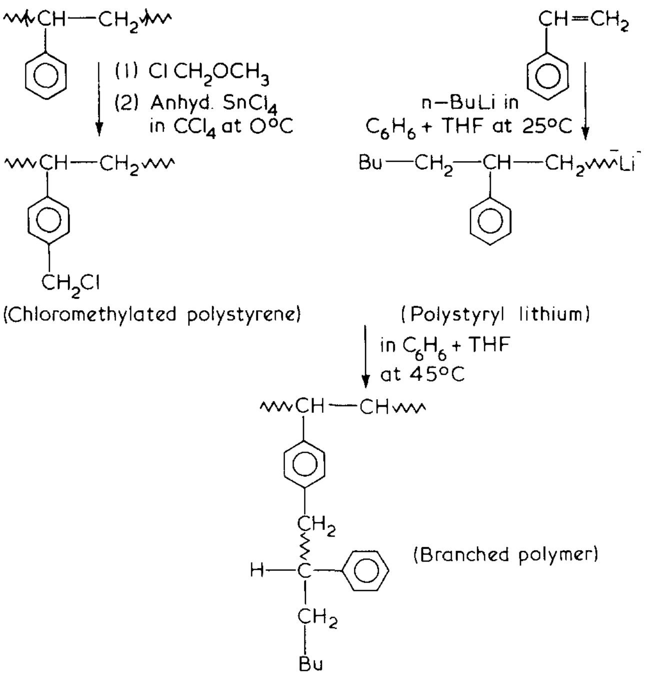

*Figure 1* Reaction scheme for branched polymer preparation

where $M_0$ and $a_0$ are the moles of styrene and n-butyl lithium, respectively, used in a particular reaction. Dry tetrahydrofuran was added to the reaction mixtures to ensure complete consumption of the initiator.

The coupling reaction between the chloromethylated polystyrene and the polystyryl lithium to prepare the model branched systems was carried out in a mixture of benzene and tetrahydrofuran at 45°C following the procedure described by Altares, *et al.*[6]. The concentrations of the polystyryl lithium used were eight to ten times the amount required by the stoichiometry to ensure completion of the coupling reaction.

Due to the large molecular weight difference between the branched polymer and the unreacted side chains, the two were separated from each other by a fractional precipitation scheme. Usually two, but sometimes three, precipitations were carried out with benzene as the solvent and methanol as the non-solvent. Gel permeation chromatography (g.p.c.) was used to assess the purification of the polymers and also to determine the molecular weight of the side chains. To do the latter, a small amount of the anions serving as the branches were terminated in methanol before the coupling was carried out and the recovered polymer analysed by g.p.c. *Figure 2* shows the g.p.c. plots before and after one precipitation for one such reaction. The data on the preparation of the four branched polystyrenes used in this work are presented in *Table 1*. The estimated polydispersity, from g.p.c., for al the final coupled and purified products was generally less than 1.18.

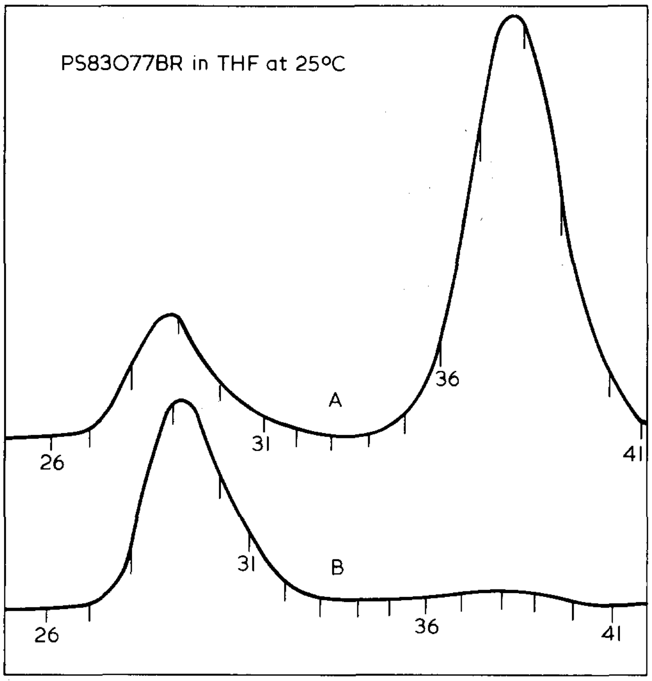

***Figure 2*** G.p.c. curves (A) before and (B) after one precipitation with methanol

*Gel permeation chromatography*

The exclusion or gel permeation chromatography (g.p.c.) of polystyrene was carried out on a system with $10^5$, $10^4$, $10^3$ and 500 Å pore size $\mu$-styragel columns at room temperature with THF as the solvent using a sample injection volume of 25 $\mu$l. A calibration plot was first obtained using standard low polydispersity anionic polystyrenes, obtained from Pressure Chemical Company, Pittsburgh, PA., and was found to be linear from $\langle M_w \rangle = 100\,000$ to 500. The flow rate through the system was maintained at 1.45 ml min$^{-1}$.

To determine the $\langle M_w \rangle$ from g.p.c. for branched polystyrenes obtained after the coupling reaction, a universal calibration plot between $\ln\{[\eta].\langle M_w \rangle\}$ and the elution volume was made according to the method developed by Benoit, *et al.*[19,20]. The $[\eta]-\langle M_w \rangle$ relation used for this purpose was[20]:

$$[\eta]=1.489\times 10^{-3}\langle M_w \rangle^{0.69} \qquad (11)$$

where $[\eta]$ is in ml g$^{-1}$ for the linear polystyrene used as standards, at 25°C in THF. Thus, by obtaining the elution volume $V_e$ and the $[\eta]$ in the THF at 25°C, for the samples of branched polystyrenes, a g.p.c. molecular weight, $M_{\text{g.p.c.}}$, could be obtained since the value for the product $\{[\eta].\langle M_w \rangle\}$ was known from the calibration plot.

*Partial specific volume*

The partial specific volume was measured in MEK at 25°C according to the procedure described elsewhere[1]. A value of 0.91 ml g$^{-1}$ was obtained for all the samples and used in the calculation for the constant $K$.

*Small angle X-ray scattering measurements*

The details of the X-ray measurements are given elsewhere[1,21]. In general, however, 80 000 pulses were counted at each of the 60–80 angles of measurement with high tension voltage and tube current of 45 kV and 24 mA, respectively, using a copper target tube.

Spectral grade methyl ethyl ketone (MEK) was used as the solvent at 25°C. At least three concentrations in the range 0.85 to 4.1% were run for each sample. It may be mentioned that a plot of the apparent radius of gyration *versus* concentration was linear in this range indicating the solutions to be sufficiently dilute for linear extrapolation to infinite dilution.

Since the data were obtained on a Kratky camera[21], the measured intensities are essentially 'smeared' intensities[22]

***Table 1*** Polystyrene preparation data

| | Linear | PS9677BR | PS83077BR | PS9877BR | PS12378BR |
|---|---|---|---|---|---|
| $\langle M_w \rangle_{bb}$ | 37 000 | 37 000 | 37 000 | 37 000 | 37 000 |
| %Cl | – | 2.07 | 2.07 | 2.07 | 2.07 |
| $f$ | – | 22 | 22 | 22 | 22 |
| $M_{br}$ | – | 500 | 950 | 1650 | 2800 |
| $M_K$ | 37 000 | 48 000 | 57 900 | 73 300 | 98 600 |
| $M_{\text{g.p.c.}}$ | 35 400 | 52 600 | 56 200 | 69 200 | – |

bb = backbone; br = branch; $M_K$ = molecular weight from kinetics of the reaction; $M_{\text{g.p.c.}}$ = molecular weight from g.p.c.

and were 'desmeared' according to the procedure by Glatter[23] to give the scattering curves that would have been obtained if a pin-hole collimated beam of sufficient intensity had been used.

The 'smeared' data were refined before the 'desmearing' process according to the following process. Porod has shown[16,24] that the scattering curve of a dilute two phase system where both the solute and the solvent phase are of homogeneous electron density and can be considered to be separated by a sharp boundary, assumes an asymptotic profile given by:

$$\tilde{I}(m) = K_1 m^{-3} \quad \text{or} \quad m^3\tilde{I}(m) = K_1 \tag{12}$$

in the tail end of the curve where $\tilde{I}(m)$ is the 'smeared' scattering curve, $m = a.2\theta$ and $K_1$ is a constant. This implies that the plot of $m^3\tilde{I}(m)$ vs. $m^3$ eventually takes on an asymptotic value. Luzzati, *et al.*[25] have shown that in the event that there is a lack in the homogeneity in the electron density of the solvent or solute or of both, an additional term arising from the electron density variations at atomic orders of dimensions must be added to equation (12). Thus:

$$\tilde{I}(m) = K_1 m^{-3} + K_2 \quad \text{or} \quad m^3\tilde{I}(m) = K_1 + K_2 m^3 \tag{13}$$

where the term $K_2$ represents the additional contributions. A plot of $m^3\tilde{I}(m)$ va. $m^3$ then gives $K_1$ as the intercept and $K_2$ as the slope.

Following the procedure above, plots according to equation (13) were made for polystyrene at each concentration and the term $m^3K_2$ subtracted from the whole scattering curve to eliminate the effects due to electron density variations in the tail end. The data then conformed to Porod's law, equation (12). *Figure 3* shows the 'smeared' data plotted according to equation (13) for one scattering curve and the data were found to conform sufficiently to the equation in the tail end of the curve to allow this correction to be made.

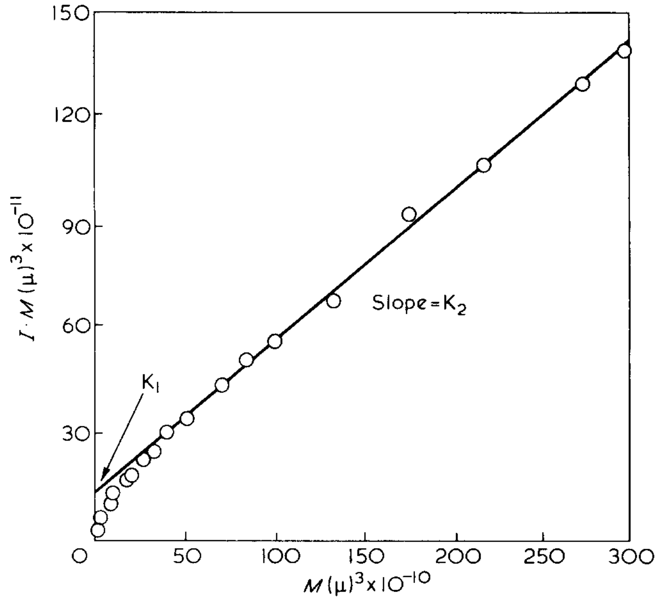

*Figure 3* Porod's law plot for linear polystyrene ($\langle M_w \rangle$ = 37 000) in MEK at 25°C. One concentration only

## RESULTS AND DISCUSSION

*Table 2* lists the data obtained by use of appropriate expressions (see Theoretical section) from small angle X-ray scattering of the model branched polystyrenes in MEK at 25°C. Molecular weights obtained are generally, in agreement with the molecular weights listed in *Table 1* indicating sufficient resolution of the scattering measurements in the inner portion, or Guinier region, of the scattering curve.

*Figure 4* shows plots according to equation (8) for one concentration each of the four branched samples. As the length of branches is increased, it is noticed that the dependence of $\ln[I(Q).Q]$ on $Q$ in the intermediate region changes quite significantly. At large $Q$, however, a reasonable straight line may still be drawn to the initial few points to get $R_q$ from the slope and $M_u$ from the intercept. The intermediate $Q$ region is, as mentioned earlier, sensitive to the statistical segment distribution within the polymer coil or chain.

A Kratky plot, or a plot of $I(Q)Q^2$ vs. $Q$, may be used to study the intermediate $Q$ region more accurately. *Figure 5* shows these plots for the linear as well as branched polystyrenes. The plots have been constructed using the term $\dfrac{I(Q)Q^2}{Kcf_q}$ vs. $Q$ to eliminate the differences due to varying concentrations and cross-section properties of the polymers.

The linear polystyrene used as the backbone material, *Figure 5a*, shows an asymptotic behaviour in the intermediate $Q$ region as predicted by equation (4) for a Gaussian segment distribution. At larger $Q$ values, a

*Table 2* SAXS data from model polystyrenes

| | Linear | PS9677BR | PS83077BR | PS9877BR | PS12378BR |
|---|---|---|---|---|---|
| $M$ | 37 000 | 49 000 | 59 000 | 79 000 | 95 000 |
| $M$ (Branch) | – | 500 | 950 | 1650 | 2800 |
| $R_g$ (Å)[a] | 62 | 65 | 66 | 68 | 72 |
| $R_q$ (Å) | 4.50 | 7.00 | 7.15 | 7.80 | 9.10 |
| $M_u$ (Å$^{-1}$)[b] | 50 | 60 | 61 | 83 | 100 |
| $M_u$ (Å$^{-1}$)[c] | – | 58 | 62 | 80 | 100 |
| $L$ (Å)[d] | 740 | 820 | 965 | 950 | 950 |

[a] $R_g \equiv \langle s^2 \rangle^{1/2}$
[b] From equation (6)
[c] From equation (8)
[d] Calculated from $L = M/M_u$

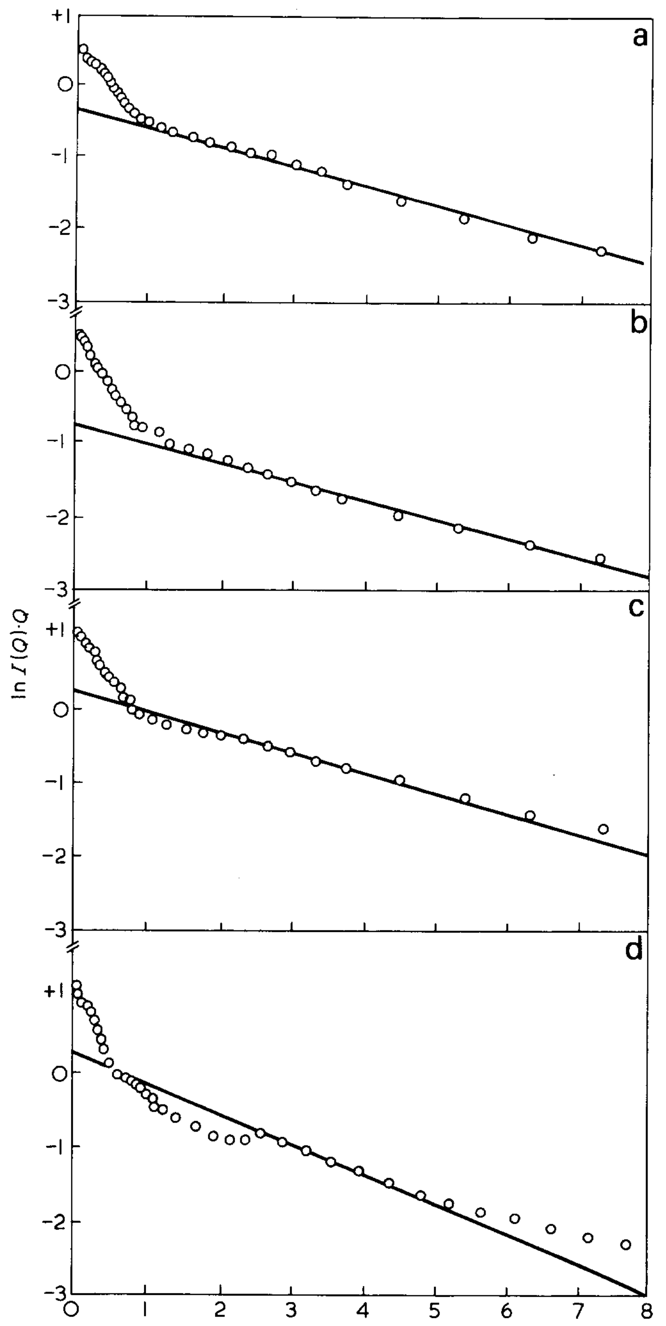

***Figure 4*** **Cross-section factor plots for: (a) PS9677BR at 3.09% concentration, (b) PS83077BR at 2.00% concentration, (c) PS9877BR at 4.10% concentration, (d) PS12378BR at 2.00% concentration**

straight line passing through the origin is observed in keeping with equation (5), since in this region the X-radiation 'sees' essentially stretched and needle-like segments of the polymer[12,26–28]. Sample PS9677BR displays almost a similar behaviour as the linear polymer except for the appearance of a maximum in the function, indicated by an arrow in *Figure 5b*. *Figure 5c*, for sample PS83077BR, shows a pronounced maximum and no asymptotic behaviour in the intermediate $Q$ region. *Figures 5d* and *e* show also considerable deviation from the observed behaviour for the linear material in the same solvent at the same temperature.

It may also be noted in *Figures 5b–e* that, for the branched polymers, the intercept for the linearly rising contribution in the large $Q$ region does not pass through the origin but gives a negative intercept.

The appearance of a maximum in the Kratky plot for the branched polymers in dilute solutions is in keeping with the theory developed for the particle scattering factors of branched polymers by Fedorov[29], and Burchard, Kajiwara and coworkers[11,30–34]. It may be noted that in an earlier paper on SAXS from branched dextrans[1], the appearance of such a maximum in the Kratky plot was not evident. Kajiwara and Ribiero[30] have shown that the appearance of the maximum is evident only in monodisperse or near monodisperse samples. The dextrans had polydispersity in the range 1.5–2.0 which probably obscured the maximum. The samples in this work, prepared by coupling a near monodisperse backbone with near monodisperse side-chains, are of significantly lower polydispersity[10], and as a result, display well pronounced maxima in the Kratky plot.

Burchard[11,31] has shown that the particle scattering factor for $\mathrm{A}\!-\!\!<^{\mathrm{B}}_{\mathrm{C}}$ type non-randomly branched polycondensates is identical with that for polydisperse star branched polymers so long as the branching probability in the polycondensate is much lower than unity. The equation is:

$$P(Q)=\frac{1+u^2/3f}{(1+u^2(f+1)/6f)^2} \tag{14}$$

where $u^2=Q^2\langle s^2\rangle$ and $f$ is the number of branches in the star branched polymer. This observation may be

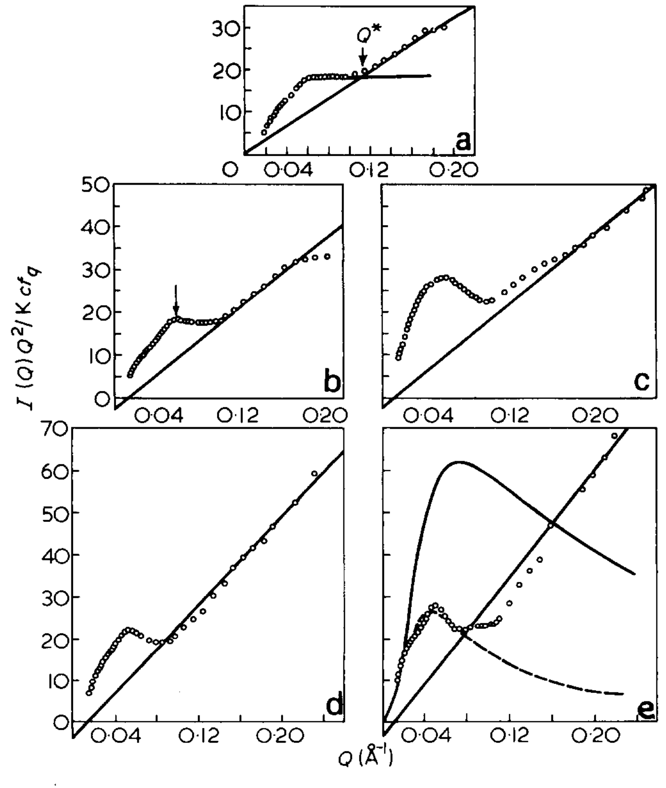

***Figure 5*** **Kratky plots for: (a) Linear polystyrene at 3.93% concentration, (b) PS9677BR at 3.09% concentration. The arrow indicates the maximum in the plot. (c) PS83077BR at 2.00% concentration, (d) PS9877BR at 4.10% concentration, and (e) PS12378BR at 2.00% concentration. The dashed curve was obtained from equation (14) and the solid curve from equation (16)**

intuitively inferred in that for low branching probability in the polycondensate, the radiation discerns the polymer to be made up of star-type segments since the conformations about the branch points are essentially independent of each other. The meaning of $f$—the number of branches in the star-branched molecule—in the case of polycondensates of the $\mathrm{A}{-}{<}^{\mathrm{B}}_{\mathrm{C}}$ type is somewhat different.

Burchard[11] has indicated that

$$f=f_0+f_i \tag{15}$$

where $f_0$ is the number of segments with one end free and the other bound by a branch point and $f_i$ is the number of segments bound on both ends by branch points.

While a comb-branched polymer is topologically not identical with an $\mathrm{A}{-}{<}^{\mathrm{B}}_{\mathrm{C}}$ polycondensate, certain structural features are quite similar in that both contain certain segments bounded either at both or one end by a branch point. The principal difference is that in a comb-branched polymer all the branch points lie on an essentially continuous segment of the molecule, the backbone, while in an $\mathrm{A}{-}{<}^{\mathrm{B}}_{\mathrm{C}}$ polycondensate a branch may appear on an already growing branch. However, for comb-branched molecules the numbers $f_0$ and $f_i$ are easily identified. It is highly probable that for these polymers also, particularly at low branching probabilities such as for the polymers used in this work (branching probability = 0.05), an expression similar to equation (14) may be used to generate the particle scattering factor. Since the number of branches in each of the polymers studied here was 22, $f_0=24$ and $f_i=21$ so that $f=45$. Substituting this value for $f$ in equation (14) together with the appropriate $\langle s^2\rangle$ from *Table 2* one obtains the dotted line in *Figure 5e*. The fit with the measured data is satisfactory, and the important features of the Kratky plot in the regions $Q<\langle s^2\rangle^{-1/2}$ and $\langle s^2\rangle^{-1/2}\leqslant Q\leqslant q^{-1}$ are essentially reproduced by equation (14), and this may indeed be fortuitous, particularly when one allows for the approximations and assumptions implicit in its use for comb-branched polymers as outlined above. The equation does not predict the upturn in the Kratky plot at large $Q$.

As indicated earlier, this upturn is characteristic of the scattering behaviour from rod-like or stretched segments of the molecule[12,16,27].

Casassa and Berry[10] have also developed a theoretical equation for the particle scattering factor from heterogeneous comb polymers. The polymers used in this work are essentially of this type. The equation is:

$$P(Q)=\frac{2}{u^2[1+(1-\lambda)^2/f]}\Bigg\{u-(1-e^{-u\lambda})+(1-e^{-u(1-\lambda)/f})\times\left[f-\frac{2(1-e^{-u\lambda})}{u\lambda/f}\right]+(1-e^{-u(1-\lambda)/f})^2\times\left[\frac{u\lambda-(1-e^{-u\lambda})}{(u\lambda/f)^2}\right]\Bigg\} \tag{16}$$

where $\lambda$ = fraction of material in the backbone and $f$ = number of branches and should not be confused with $f$ in equation (15).

The calculated particle scattering factor from equation (16) is indicated in *Figure 5e* by a solid line. While the equation predicts a maximum in the Kratky plot, there is no agreement with the measured data for this sample except in the initial Guinier region. It may be pointed out that Toporowski and Roovers[35] have shown a good fit of the light scattering data from heterogeneous combs with the calculated function equation (16). However, their measurements were limited to a very narrow range of the function $Q$ ($Q<\sim0.006$) due to the large wavelength of radiation employed and are mostly in the Guinier region. As is evident from *Figure 5e*, the measured data and the computed values from equations (14) and (16) should, and do, satisfactorily agree in this region.

A persistence length $q$[12,36] may be calculated from the point of transition between the intermediate and large $Q$ regions, according to the following procedure. Equations (4) and (5) may be written as:

$$\frac{I(Q)Q^2}{Kc}=\frac{2M}{\langle s^2\rangle} \tag{17}$$

and

$$\frac{I(Q)Q^2}{Kc}=\frac{\pi MQ}{L} \tag{18}$$

respectively. At the transition point $Q^*$, equations (17) and (18) have the same solution so that

$$\frac{2M}{\langle s^2\rangle}=\frac{\pi MQ^*}{L} \tag{19}$$

For a Gaussian chain, it may be shown that[12]:

$$\langle s^2\rangle=\frac{qL}{3} \tag{20}$$

Substituting equation (20) in equation (19) one obtains

$$q=\frac{1.91}{Q^*} \tag{21}$$

For the linear polystyrene equation (21) gives $q=16.0$ Å. Equation (21) may not be used for the branched polystyrenes, however, even though a transition point between the two $Q$ regions can still be identified since these polymers do not conform to the asymptotic behaviour predicted by equation (4).

If the measured values of $\langle s^2\rangle^{1/2}$ and $L$ are used in equation (20) for the linear polystyrene, a persistence length of 15.6 Å may be calculated, in good agreement with the value from equation (21).

The values for the contour length $L$ for linear polystyrene may also be calculated from:

$$L=Pl \tag{22}$$

where $P$ is the degree of polymerization and $l$ the monomer length. From bond angles and lengths in a styrene molecule $l$ may be computed to be 2.52 Å. For linear polystyrene of $M$ equal to 37 000, a contour length $L$ of 900 Å may then be calculated from equation (22). This

*Table 3* Values of the ratio $g$ for model branched polystyrenes

| | PS9677BR | PS83077BR | PS9877BR | PS12378BR | Equation |
|---|---|---|---|---|---|
| $g$ | 0.69 (0.80)* | 0.67 | 0.50 | 0.41 | Eq. (24) |
| $g$ | 0.76 | 0.64 | 0.50 | 0.43 | Ref. 10 |
| $g$ | 0.77 | 0.65 | 0.49 | 0.44 | Ref. 37 |
| $L$ (Å) | 820 | 965 | 950 | 950 | |
| $L_T$ (Å) | 1190 | 1430 | 1900 | 2300 | Eq. (22) |
| $f_b$ | 0.24 | 0.37 | 0.53 | 0.61 | |
| $\langle s^2\rangle^{1/2}$ (Å) | 62 | 63 | 64 | 65 | Ref. 38 |

$f_b$ = Fraction of material in the branches
* The value in parentheses was calculated using $L$ = 950 Å for this sample

value is larger than the 740 Å measured for the linear polymer in this work. Further, the mass per unit length $M_u$ should be 41.3 $Å^{-1}$ from the monomer molecular weight of 104 and with $l = 2.52$ Å. The experimental value is 50 $Å^{-1}$. One explanation for these discrepancies may be that both helical and coil ranges coexist in polystyrene in MEK. This explanation was also offered by Durchschlag *et al.*[15] to explain the SAXS data from poly-*o*-bromostyrene. It is evident[15] that the helical ranges do not extend over large regions of the molecule, since the general impression of a worm-like chain is maintained, to cause this deviation between observed and calculated values. When branches are grafted onto the linear polystyrene, however, the measured length is, in general, close to the calculated length of the backbone, that is ~900 Å.

In an earlier paper[1], we have shown that the Zimm–Stockmayer[3] parameter $g$ given by:

$$g = \frac{\langle s^2\rangle_{\text{br}}}{\langle s^2\rangle_{\text{lin}}} \qquad (23)$$

where the radii of gyration are measured for the same molecular weight in the same solvent at the same temperature, preferably theta temperature, for both the branched (br) and linear (lin) polymers, may be calculated from the SAXS data according to:

$$g = L/L_T \qquad (24)$$

where $L_T$ is the contour length of a linear polymer of the same molecular weight as the branched polymer. Values of $g$ calculated from equation (24) and from theoretical relations for regular comb-branched polymers given by Orofino[37] and Casassa and Berry[10] are listed in *Table 3*.

The agreement, in general, is satisfactory confirming our earlier assumptions regarding dextrans[1]. Values of $\langle s^2\rangle^{1/2}$ calculated according to a relation given by Berry[38] for regular comb-branched molecules at unperturbed conditions are also given in *Table 3*. Values were calculated using $\langle s^2\rangle^{1/2} = 62$ Å for the linear backbone material obtained in MEK at 25°C. This value should be close to the unperturbed value since the polymer displays an essentially Gaussian segment distribution in the Kratky plot, *Figure 5a*. Reasonable correlation is obtained for the calculated and measured $\langle s^2\rangle^{1/2}$ values, at least qualitatively, in that the radius of gyration of the branched polymers depends strongly on the backbone length and not so much on the number of branches and their corresponding lengths, as has also been shown by Orofino[37].

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