Small-angle X-ray scattering from 12-arm star polystyrene fractions in MEK

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Small-angle X-ray scattering, SAXS, measurements were obtained from 12-arm near-monodisperse star polystyrenes in methyl ethyl ketone at 25°C. Calculations from the SAXS data yielded information on the molecular weight, M_s, the radius of gyration, R_g, mass per unit length, m_u, radius of gyration of the cross-section, R_q, and persistence length, a^*. Values of M_s and R_g from SAXS were in good agreement with values obtained from light scattering. A branching parameter in terms of $a^*, s = a_l^*/a_b^*$ where subscripts l and b refer to linear and branch, respectively, is introduced and related in terms of functionability, f, or g, where $g = (R_g)_b/(R_g)_l$.

(Keywords: polystyrene; star fractions; branching factor; X-ray scattering)

INTRODUCTION

In previous papers[1-4] we have demonstrated the use of small-angle X-ray scattering, SAXS, in assessing branching in polymers. Specifically, SAXS from solution of the dendritic structures (branched-branch) of dextran[1] and levan[2,3] and of the comb structure of model polystyrenes, PS, were examined. It was shown that the mass per unit length, m_u, and the radius of gyration of the cross section, R_q, relate to the topology of branching in the PS chain. A relationship for obtaining the g-factor, a measure of branching, was developed. It was demonstrated from these studies that the g-factor is readily obtained from the m_u, or the total length, L, of the branched polymer without the need of the linear counterpart of the same molecular weight, M, and chemical composition.

The dextrans used in the previous studies were hydrolysed fractions produced from *L. mesenteroides* varying in M from 11 000 to 253 000 whereas the levan samples were fractionated moieties of $M \approx 17 \times 10^6$ and $M \approx 2.7 \times 10^4$ from *S. salivarius*. The comb model polystyrenes were prepared by anionic polymerization methods to yield near-monodispersed samples having both fixed backbone length and number of branches but variable branch lengths.

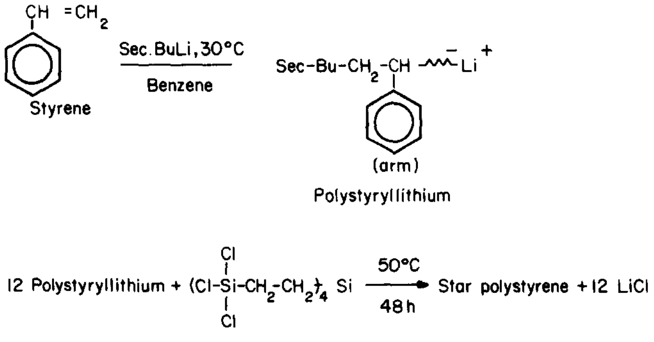
The intent of this paper is to examine the method of SAXS in assessing branching properties in uniform star polymers. Recent papers[5-12] have reported on the conformational and hydrodynamic properties of several star polymers having as few as 3 to as high as 18 arms. Specifically, values of $g = (R_g^2)_b/(R_g^2)_l$, $H = (R)_{hb}/(R)_{hl}$ and $\rho = (R_g)_b/(R)_{hb}$ in various solvents have been reported, where R_g and R_h represent radius of gyration and hydrodynamic radius, and the subscripts h, b and l denote hydrodynamic, branch and linear, respectively. Recently, the conformational and dynamic behaviour of 3, 12 and 18-arm regular polystyrenes were studied[8] by means of static and dynamic light scattering in a good solvent (toluene at 20°C) and a theta solvent (cyclohexane at 34.5°C).

In this paper we report on SAXS measurements from 12-arm near-monodisperse star polystyrenes in methyl ethyl ketone at 25°C. Calculations from SAXS data provided information on M, R_g, mass per unit length, m_u, radius of gyration of the cross-section, R_q, and persistence length, a^*. A branching parameter, $s = a_l^*/a_b^*$, is introduced and related in terms of g or functionality, f.

EXPERIMENTAL

Materials

The four samples of the star polystyrenes used in this study were supplied by Dr L. J. Fetters of the University of Akron, and are similar to those described in ref. 8. The samples were prepared anionically from the reaction between polystyryllithium (as the arm) and tetra-(trichlorosilylethane)silane as the central molecule, as indicated below:



The four samples used in this study are designated as SPS-1.75, SPS-8.2, SPS-12 and SPS-22, having weight average molecular weight of 1.64×10^5, 8.05×10^5, 1.12×10^6 and 2.09×10^6, respectively. These values, obtained from light scattering, were provided by Dr L. J. Fetters.

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Methods

Osmometry. A Mechrolab 501 high speed membrane osmometer was used to determine number average molecular weights, $\bar{M}_n$. The osmotic pressures were determined in toluene at 25°C ± 0.5°C. A regenerated cellulose membrane Model RC 51 from Schleicher and Schuell with a molecular weight retention of 10000 and 43 mm diameter was used.

Light scattering. Light scattering measurements were performed on a Model 5200 light-scattering duophotometer (C. N. Wood, Manufacturing Company) in MEK at 25 ± 0.1°C using a constant temperature compartment. The blue light of mercury source with 436 nm wavelength was used for all measurements with an angle range of 31° to 149°. The z-average radius of gyration, $(\bar{R}_g)_z$, and weight average molecular weight, $\bar{M}_w$, were obtained using the Zimm plot method[13].

Partial specific volume. The partial specific volumes of the polystyrenes, $\bar{v}_1$, were obtained in MEK at 25 ± 0.1°C using a digital precision densimeter model DMA-02C (Anton-Paar Co., Austria). Values of 0.918, 0.917, 0.914 and 0.900 $cm^3\,g^{-1}$ were obtained for SPS-1.75, SPS-8.2, SPS-12 and SPS-22, respectively.

Small-angle X-ray scattering. The procedure used in this work has been described in an earlier work[1]. Detailed procedures, theory and treatment of data may be found elsewhere[14,15]. The entrance slit of 60 μm and counter-slit of 150 μm were used in the Kratky camera for each sample except SPS-22) where 30/75 were used. The collimation error of the raw data was eliminated on a PDP-10 computer according to the method of Glatter[16]. The corresponding corrected data are the desmeared scattering data.

SAXS measurements of the star polystyrene were made at 25 ± 0.2°C at various concentrations ranging from 5.0 to 30×10^{-3} g cm^{-3}. Concentration dependence of the data is eliminated by extrapolation to infinite dilution. It is noteworthy that concentrations higher than the above have been used in SAXS[17,18].

The electron density of the star polystyrene was calculated from the structural formula of its monomer, styrene. The electron density contributed to the overall star polystyrene by its silane core was not included since this is negligible compared with the weight of the entire molecule.

RESULTS

Molecular weight and radius of gyration

The molecular weights, M, of the star polystyrenes, SPS, were obtained according to the equation

$$M = (I_0/p_0)21.0a^2/[(z_1 - \bar{v}_1\rho_2)^2 dc] \qquad (1)$$

where I_0 is the scattering intensity extrapolated to zero scattering angle; a is the distance in cm between the sample and plane of registration; d is the sample thickness ($\approx$0.1 cm); c is the concentration in g ml^{-1}; $\bar{v}_1$ is solute partial specific volume; ρ_2 is the number of mole electrons per ml of the solvent (0.443 for MEK); z_1 is the number of electrons per gram of the solute (0.538 for styrene); and p_0 is the energy of the primary beam per cm length in the plane of registration. The constant 21.0 is equal to $1/I_e N_A$ where I_e is the scattering power of one electron (7.9×10^{-26}, Thomson's constant) and N_A is Avogadro's number. The concentration dependency of M was eliminated by extrapolating the $1/c$ curves to $c = 0$. *Table 1* summarizes M calculated from equation (1). Though the values of M from SAXS are in good agreement with those obtained from light scattering, the former are about 6% lighter than the latter. The M from SAXS also compare favourably with those reported by Khasat[21], cf. *Table 1*. Values of $\bar{M}_n$ from osmometry were 1.52, 7.14, 11.2 and 21.4×10^5 for the SPS-1.75, SPS-8.2, SPS-12 and SPS-22, respectively. The dispersity index, $\bar{M}_w/\bar{M}_n$, calculated from the $\bar{M}_w$ obtained from light scattering, LS, ranged between 1.06 to 1.02.

The radius of gyration was obtained from the Guinier equation,

$$\ln I = \ln I_0 - KR_g^2(2\theta)^2 \qquad (2)$$

or

$$\ln I = \ln I_0 - R_g^2 Q^2/3 \qquad (2a)$$

where $Q = (4\pi/\lambda)\sin\theta$ but at very low angles $Q \approx (2\pi/\lambda)2\theta$, (for $\lambda = 1.54$ Å, $K = 5.55$) and 2θ is the scattering angle in radians. Since decay of the intensity at very small angles (inner portion of the scattering curve) is a Gaussian function of 2θ, a straight line is obtained for the several innermost points according to equation (2) or equation (2a). The slope of this linear portion yields the radius of gyration whereas the intercept gives the intensity at zero angle. *Figure 1* shows the Guinier plot of the SPS-8.2 at four concentrations according to equation (2a). Since R_g is concentration dependent, the apparent values of R_g for each concentration are extrapolated to zero concentration. The R_g of the four star polystyrenes, SPS, at infinite dilution are tabulated in *Table 1*. The M and R_g for the 12-arm SPS obtained from SAXS are, on the average, somewhat higher than those values obtained from LS (cf. *Table 1*).

Radius of gyration of the cross-section

The cross-section radius of gyration, R_q, was obtained from the equation,

$$\ln(I2\theta) = \ln(I2\theta)_0 - K'R_q^2(2\theta)^2 \qquad (3)$$

or

$$\ln(IQ) = \ln(IQ)_0 - R_q^2 Q^2/2 \qquad (3a)$$

where $K' = (2\pi/\lambda)^2/2$, (for $\lambda = 1.54$ Å, $K' = 8.32$). *Figure 2* shows the plot of the cross-section according to equation (3a) of the four samples of the star polystyrenes. The values of R_q, independent of concentration, are obtained from the slopes of the plots shown in *Figure 2*.

Table 1 Comparison of $\bar{M}_w$ and R_g of star polystyrenes in MEK at 25.0°C from light scattering, LS, and small-angle X-ray scattering, SAXS

	$\bar{M}_w \times 10^{-5}$		R_g (Å)	
Sample	LS	SAXS	LS	SAXS
SPS-1.75	1.61 (1.64)[a]	1.70	110	106
SPS-8.2	7.50 (8.05)[a]	8.16 (8.07)[b]	170	210 (216)[b]
SPS-12	11.7 (11.2)[a]	11.6 (11.8)[b]	210	260 (257)[b]
SPS-22	21.9 (20.9)[a]	23.4	300	350

[a] Ref. 21

[b] Independent measurements performed by Dr A. Patel

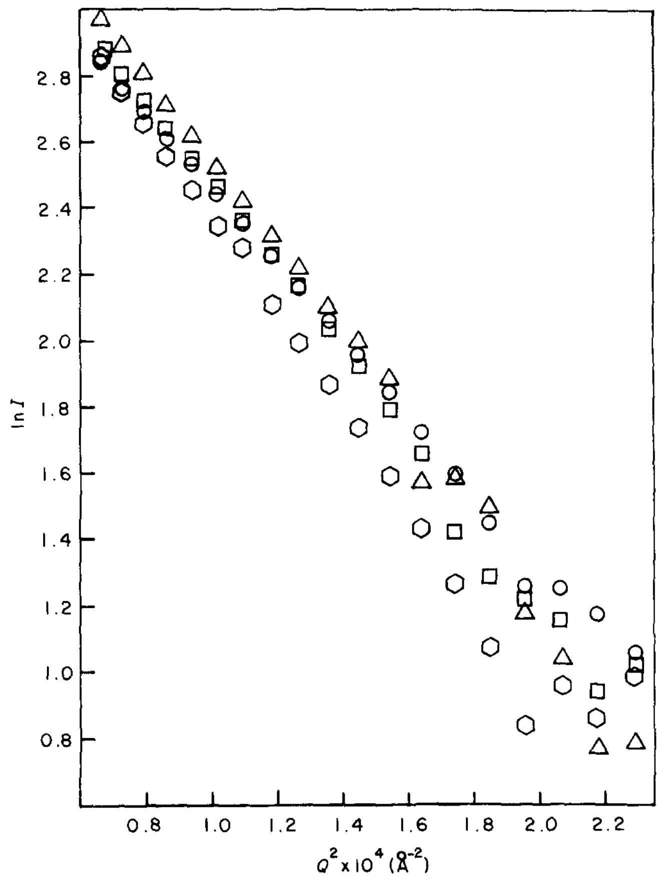

Figure 1 Guinier plots of SPS-8.2 at four concentrations in MEK at 25°C: ○, 3.0%; □, 2.4%; △, 1.8%; ⬡, 1.2%

Mass per unit length and the total length

The mass per unit length, m_u, is calculated from the absolute value of the intensity at zero angle of the cross-section factor, $(I2\theta)_0$ using an equation similar to equation (1), thus,

$$m_u = [(I2\theta)_0/P_0]27.3a^2/[(z_1 - \bar{v}_1\rho_2)^2dc] \qquad (4)$$

where 27.3 is a constant equal to $2/(\lambda I_e N_A)$. The intercepts of the cross-sectional plots (*Figure 2*) yield values of $(I2\theta)_0$ for a given concentration from which the value of $(I2\theta)_0/c$ at infinite dilution is obtained, i.e. $[(I2\theta)_0/c]_{c\to 0}$.

The total length, L, of the molecule is obtained from the division of equation (1) by equation (4), thus,

$$L = M/m_u = 0.77[(I_0/c)/(I2\theta)_0/c]_{c\to 0} \qquad (5)$$

or

$$L = \lim_{c\to 0} 0.77\, I_0/(I2\theta)_0 \qquad (5a)$$

Values of L of the SPS are shown in *Table 2*.

Persistence length

The persistence length, a^*, was calculated from the equation below,

$$a^* = 2.3\lambda/2\pi(2\theta)^* \qquad (6)$$

or alternately,

$$a^* = 2.3/Q^* \qquad (6a)$$

where $(2\theta)^*$ is the transition between the $1/(2\theta)^2$ and the $1/(2\theta)$ portions of the scattering curve. *Figure 3* shows the plot of $\ln IQ^2$ vs. Q of the four star polystyrenes. The persistence length plot is not concentration dependent[19]. The values of a^* of the star polystyrene are shown in *Table 2*.

DISCUSSION

SAXS

The use of equations (1) or (1a) and equations (2) or (2a) in obtaining M and R_g is independent of the restriction of Gaussian segmental distribution, and therefore, these equations should apply to branched as well as to linear polymers. The various other equations given above are applicable, in general, to unbranched structures. These

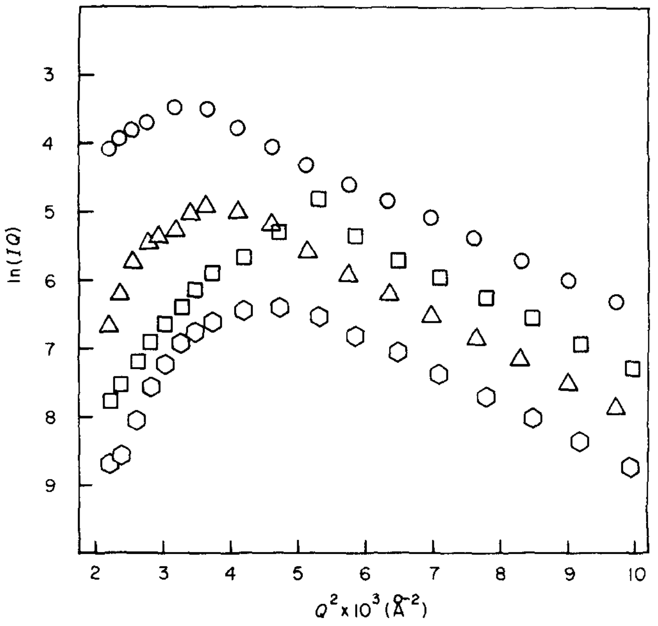

Figure 2 Cross-sectional plots of star polystyrenes in MEK at 25°C: ○, SPS-22 (2.6%); □, SPS-12, (1.3%); △, SPS-8.2 (1.1%); ⬡, SPS-1.75 (2.6%)

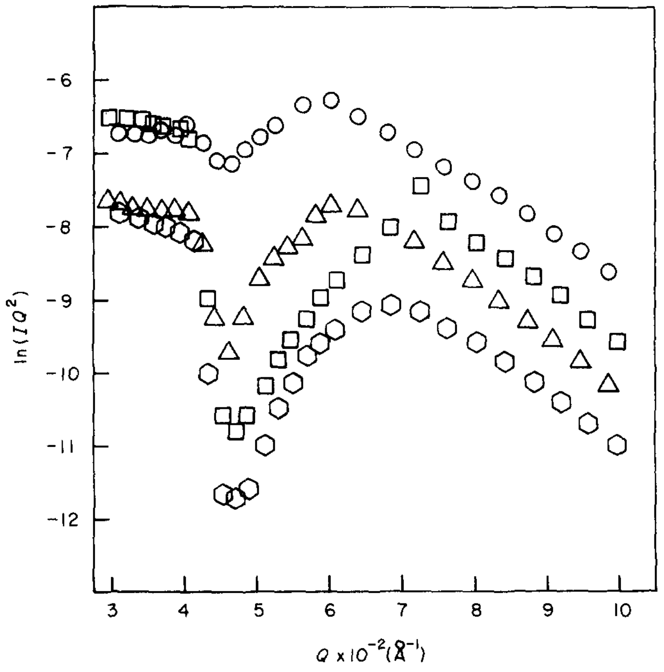

Figure 3 Persistence length plots of star polystyrenes in MEK at 25°C: ○, SPS-22 (2.6%); □, SPS-12 (1.3%); △, SPS-8.2 (1.1%); ⬡, SPS-1.75 (2.6%)

Table 2 SAXS parameters of star polystyrenes in MEK at 25°C

Parameter	SPS-1.75	SPS-8.2	SPS-12	SPS-22
R_q (Å)	18.5	17.9 $(17)^d$	18.7 $(19)^d$	17.9
a^* (Å)	48.4	49.4	49.7	51.1
m_u (Å^{-1})	190	240 $(155)^d$	210 $(187)^d$	220
$(m_u)_{calc}$ (Å^{-1})	247	247	247	247
L_{exp} (Å)	895	3400	5520	10 640
L^a_{calc} (Å)	689	3310	4700	9 490
L'_{calc} (Å)	707	3740	4830	8 980
f^b	9.3	11.7	10.2	10.7
f^c	11.7	11.6	12.4	12.4

^{a}Calculated from LS data
^{b}Calculated from equation (9a)
^{c}Ref. 21
^{d}Independent measurements performed by Dr A. Patel

have been used, however, in previous studies$^{1-4}$ in analysing 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. It is in this context that the SAXS data obtained for the star polystyrenes in this study are applied. In this case it may be convenient, as a point of discussion, to consider a uniform star polymer of f arms as having a 'backbone' defined as consisting of any two arms, to which are attached at its centre the balance of its arms, i.e. $f-2$ number of arms. The molecular weight of an arm, M_a, of the uniform star polymer is readily computed from its molecular weight, M_s, and its functionality, f,

$$M_a = M_s/f \tag{7}$$

Similarly, the length of the arm, l_a, is readily calculated from the molecular weight, M_0, and length, h_0, respectively, of its monomer, and M_s of the regular star polymer, thus

$$l_a = M_s h_0/M_0 f = (DP)_s h_0/f \tag{8}$$

where $(DP)_s h_0$ is the total length of the star polymer if all the monomer units were linked linearly. Alternatively,

$$l_a = (M_a/M_0)h_0 = (DP)_a h_0 \tag{8a}$$

where (DP) is the degree of polymerization. The length of the 'backbone', L, as defined, is

$$L = 2l_a \tag{8b}$$

Table 2 contains the values of L_{exp} for the four star polystyrenes obtained from SAXS data according to equation (5). That these experimental values correspond to the lengths of two arms may be demonstrated by calculating L from information derived from sources other than SAXS using equations (7) to (8b), inclusive. It should be noted that these equations assume identical chemical composition of the core of the star polymer and of its branches. However, for the purpose of computation of L in this work the contribution from the silane core in the star PS may be neglected since it represents a very small fraction of the entire molecule. Taking the values of M_s (from LS), $f = 12$, and $M_0 = 104.15$ daltons and $h_0 = 2.53$ Å^{20} for the styrene monomer, L_{calc} for each sample is obtained, cf. *Table 2*. Values of L were also calculated from measured M_a ($\bar{M}_n$ values) of the polystyryllithium arms used in the synthesis of the star polystyrene^{21}, shown in *Table 2* as L'_{calc}. As may be noted from *Table 2* values of L_{exp}, obtained from equation (5), are, within experimental error, in good agreement with the calculated values of L_{calc} and L'_{calc}. These observations strongly suggest that the total length L from SAXS for the uniform star polymer is, indeed, the length of any two of its arms. In earlier studies it was shown that for various model comb polystyrenes^{4,22,23}, the total lengths obtained from SAXS correspond to the *a priori* known lengths of the backbone. The small differences in the values of L_{exp}, L_{calc} and L'_{calc}, cf. *Table 2*, are attributed to experimental error, neglect of the silane core in the computation, and to some dispersities in l_a, M_s and f of the samples. The value of $f = 12$ used in the calculations was based on the assumption that the coupling reaction in the syntheses of the star PS was complete. In actuality, f was reported to vary from 11.6 to 12.4 (ref. 21), cf. *Table 2*.

The mass per unit length of a long chain molecule is expressed by equation (5). In the case of the uniform star polymer, where two of its arms represent the 'backbone', the m_u is given by

$$m_u = M_s/2l_a = fM_a/2l_a \tag{9}$$

but for linear chains (as is the case for the arms) $M_a/l_a = M_0/h_0 = (m_u)_l$, hence equation (9) is written as

$$m_u = (f/2)(M_0/h_0) = (f/2)(m_u)_l \tag{9a}$$

Hence, the mass per unit length for a uniform star polymer of given functionality is invariant with its molecular weight, i.e. increasing arm length. This is observed to be the case, within experimental error, for the four star polystyrenes, cf. *Table 2*. The averaged value of m_u is 215 Å, which is about 13% lower than that calculated from equation (9a) for $f = 12$, i.e. $(m_u)_{calc} = 247$ daltons Å^{-1}. The unchanged, within experimental error, as M_s or M_a functionality of uniform star polymers from equation (9a). The h_0 may be elicited from available X-ray diffraction data of the monomer, or may be calculated from bond lengths and angles. In the case of the four SPS samples, values of f calculated from equation (9a) are shown in *Table 2*.

The radius of gyration of the cross-section remains unchanged, within experimental error, as M_s or M_a increases. However, Garg and Stivala^1 reported that R_q increases with increasing M of the dendritic dextrans. This was also noted for the comb polystyrenes of fixed backbone length ($M_{bb} = 37\,000$) and fixed number of branches ($f = 22$) but variable branch length^4. Thus, they reported that for branches having molecular weights of 500, 950, 1650 and 2800, the corresponding values of R_q for the comb PS ($f = 22$, $M_{bb} = 37\,000$) were 7.00, 7.15, 7.80 and 9.10 Å, compared with $R_q = 4.50$ Å for the linear PS of $M = 37\,000$. It is expected, in general, that $(R_q)_b > (R_q)_l$. In the case of the SPS, $(R_q)_b > (R_q)_l$ taking R_q for linear PS also to be invariant with M.

Branching factor and the persistence length

Branched molecules are more compact than linear molecules of the same molecular weight and chemical composition. Therefore, at its centre of mass the branched polymer reaches a higher segment density than that of its linear counterpart. Accordingly, the radius of gyration of the branched polymer, $(R_g)_b$, is less than the radius of gyration of the linear polymer $(R_g)_l$ of the same M in the same solvent at the same temperature. The g-factor, defined below by Zimm and Stockmayer[24], may be taken as a measure of branching

$$g=(R_g)_b^2/(R_g)_l^2 \qquad (10)$$

Two sets of values of the branching factor, g, were computed according to equation (10). One set, using values of $(R_g)_b$ from SAXS, and the other set using values of $(R_g)_b$ from LS. The values of $(R_g)_l$, in Å corresponding to the same M as obtained from SAXS for the one set and from LS for the second set, were estimated from the relationship[23] below for linear polystyrene in MEK at 25°C

$$(\overline{R_g^2})_z^{1/2}=0.33\,M_w^{0.51} \qquad (11)$$

It is noted from *Table 3*, taking the averaged values, that $g_{SAXS}=0.38$ compared with $g_{LS}=0.27$. These may be compared with g values computed from the functionality according to the relation[24-26], for uniform star polymers,

$$g=(3f-2)/f^2 \qquad (12)$$

Thus, for $f=12$, $g=0.24$. The value of $g=0.236$ was recently reported[8] for SPS having $M=1.69\times10^6$. It is noted from *Table 3* that the sample SPS-1.75 ($M=1.61\times10^5$) showed g-value considerably higher than the three higher molecular weight samples. It should be mentioned that equation (10) is for theta (θ) solvent. MEK at 25°C is a θ-solvent for linear PS. Values of g computed from LS data are in better agreement with g computed from equation (12) than are those computed from SAXS data.

The weight fraction of the 'backbone', λ', of a uniform star polymer of molecular weight, M_s, may be computed from

$$\lambda'=2M_a/M_s \qquad (13)$$

or

$$\lambda'=(m_u)_l/(m_u)_b \qquad (13a)$$

Equation (13a) follows from equation (13) since $M_s=(m_u)_bL$, $M_a=(m_u)_{l_a}$ and $L=2l_a$. The weight fraction may also be computed, in the case of uniform star polymers, from the functionality, f, from

$$\lambda'=2M_a/M_s=2M_a/fM_a=2/f \qquad (13b)$$

Substituting $f=2/\lambda'$ from equation (13b) into equation (12) we obtain the g-factor in terms of λ',

$$g=\lambda'(3-\lambda')/2 \qquad (14)$$

Table 3 Branching factor, g, for star polystyrenes from SAXS and LS

	SPS-1.75	SPS-8.2	SPS-12	SPS-22	Average[b]
g_{SAXS}	0.48	0.38	0.36	0.41	0.38
g_{LS}	0.54	0.27	0.26	0.28	0.27
g^a	0.24	0.24	0.24	0.24	0.24

[a] Computed from equation (12)
[b] Excluding SPS-1.75

Thus, for a 12-arm uniform star polymer, $\lambda'=2/f=1/6=0.167$, wherein equation (14) yields the expected value of 0.24.

Using the averaged value of $(m_u)_b$, for the four 12-arm PS, of 215 daltons Å^{-1}, (cf. *Table 2*) and $(m_u)_l=41.2$ daltons Å^{-1} for linear polystyrene, we obtain $\lambda=0.19$. Using equation (14) the g value of 0.27 is obtained. That g_{SAXS} is higher than g_{LS} and than that computed from equation (12) reflects the somewhat higher value of $(R_g)_b$ from SAXS, cf. *Table 2*. On the other hand, $g=0.27$ when calculated from equation (14) using λ' evaluated from SAXS (m_u).

The persistence length, a^*, shows small increase with increasing M_s or M_a, cf. *Table 2*. Small increases in a^* with increasing M were also observed for comb polystyrenes in MEK[22,23] and for linear polystyrenes in n-hexane[18]. The $a^*=51.5$ Å for $R_g=350$ Å of SPS-22 is in the same order of magnitude of $a^*=42.8$ Å for $R_g=395$ Å of dendritic levan[2].

Kratky and Porod[27] define the persistence length, a^*, as the mean length of the projection of a sufficiently long thread on its starting direction. Kirste[28] defines a^* as the length of a part of the long thread, which on the average shows a change in direction of $\arccos(1/e)=68.4°$, which for many coil models is identical with the definition of Kratky and Porod. Kirste also refers to 'change in direction' as 'curvature'. It is not realistic for a branched polymer to conform to the model of a long thin thread, particularly a star polymer of high f. Be that as it may, transitions between the IQ^2 vs. Q portions of the scattering curves have been consistently observed for the star polymers in this study; including the dendritic structures of dextran[1] and levan[2,3] and the comb polystyrenes[4,22,23]. Therefore, we might consider that, in the case of branch polymers, the 'curvature' of the backbone of comb structure (or any two arms in regular star polymer) is changing with branching as reflected in the measured values of a^*. Therefore, in this case we may introduce a branching parameter in the form of the ratio of the persistence lengths of linear to branch structures of the same molecular weight and chemical composition, i.e. a_l^*/a_b^*.

Kratky[19] showed that for a Gaussian chain the radius of gyration is related to a^* and L according to the relation

$$R_g^2=a^*L/3 \qquad (15)$$

That this relation is not obeyed by the star polystyrenes may be noted from *Table 4*. Rather, within experimental error, an averaged value of $k_{SAXS}\approx4$, or $k_{LS}\approx5.5$, is obtained for the ratio

$$a^*L/R_g^2=k \qquad (15a)$$

The persistence length of the linear polystyrene in MEK at 25°C having the same molecular weights as those

Table 4 Values of the ratio $a^*L/R_g^2=k$ for star polystyrenes in MEK at 25°C

	SPS-1.75	SPS-8.2	SPS-12	SPS-22	Average
$k_{SAXS}{}^a$	3.86	3.81	4.06	4.44	4.04
$k_{LS}{}^b$	5.49	5.67	5.30	5.39	5.46

[a] Computed from R_g and L obtained from SAXS
[b] Computed from R_g obtained from LS and L_{calc} from LS

Table 5 Ratio $s=(a^*)_l/(a^*)_b$ for star polystyrenes in MEK at 25°C

$\bar{M}_w \times 10^{-5}$	$(R_g^2/L)_l$	$(a^*)_l$ (Å)	$(a^*)_b$ (Å)	s
1.70	5.70	17.10	48.4	0.353
8.16	5.87	17.61	49.4	0.356
11.6	5.93	17.79	49.7	0.358
23.4	6.00	18.00	51.1	0.352
			average:	0.35

of the star PS may be computed from equation (15) using $(R_g^2)_l$ obtained from the relation expressed by equation (11) and $L_l=M/(m_u)_l=Mh_0/M_0$. As noted in *Table 5*, $(a^*)_b>(a^*)_l$. Further, there is a remarkable constancy in the ratio, s, expressed below

$$s=(a^*)_l/(a^*)_b \tag{16}$$

among the samples, with $s_{av}=0.35$.

Equation (16) may be expressed in terms of g and/or f. Thus, $(m_u)_l=M_l/L_l$ and $(m_u)_b=m_b/L_b$, and for the case where $M_l=M_b$ we obtain

$$L_b/L_l=(m_u)_l/(m_u)_b=\lambda' \tag{17}$$

where for the case of uniform star polymer $L_b=L=2l_a$, $M_b=M_s$ and $\lambda=2f$ [cf. equation (13b)]. By dividing equation (15) by equation (15a) and using equation (10), and equation (17) we obtain

$$s=(a^*)_l/(a^*)_b=3\lambda'/kg \tag{18}$$

or for uniform star polymer, from equation (13b), we have

$$(a^*)_l/(a^*)_b=6/kgf \tag{18a}$$

or from equation (12) the above reduces to

$$(a^*)_l/(a^*)_b=6f/k(3f-2) \tag{18b}$$

As the number of arms decreases to the limit where $f \rightarrow 2$ and $k \longrightarrow 3$ in the star polymer, $(a^*)_l/(a^*)_b \longrightarrow 1$. For the case where $f=12$ and taking $s=0.35$ (see *Table 5*), equation (18b) yields $k=6.0$, cf. *Table 4*.

These studies suggest that, for uniform star polymers, the k in equation (15a) is a constant greater than 3 for given f and that it increases with increasing f. Further, the ratio expressed by s in equation (16) may, indeed, be a measure of branching.

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