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Dilute Solution Behavior of Asymmetric Three-Arm and Regular Three- and Twelve-Arm Polystyrene Stars

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ABSTRACT: The dilute solution characteristics of regular three- and twelve-arm and asymmetric three-arm polystyrene stars have been studied under Θ conditions (cyclohexane) and in a good solvent (toluene). The parameters evaluated include the intrinsic viscosities and for the regular stars the radii of gyration and the viscometric based radii. The twelve-arm stars show the influence of high segment densities near the star core under Θ conditions; i.e., g_Θ decreases as arm molecular weight increases and approaches the random-walk prediction only at high-arm molecular weight. Additional parameters describing the regular and asymmetric star-shaped polymers are presented and discussed.

Introduction

The equilibrium and dynamic behavior of model nonlinear polymers in dilute solution have received considerable recent attention.[2-20] The common unifying theme relating these materials is that the branched structures, formed via chlorosilane linking reactions, have near-monodisperse chains of identical molecular weight emanating from the branch point (or points). This work reports, in part, on the findings for materials which differ from the structures mentioned above in that chains of differing molecular weight radiate from a common junction.

These branched polymers are three-armed asymmetric stars where one arm differs in molecular weight from the remaining two. Toward this end two series of near-monodisperse stars were studied where two of the arms were of equal molecular weight while the remaining arm had a molecular weight either half or twice that of the two identical arms. These materials are denoted as short-arm stars (SAS) in the case of the former and long-arm stars (LAS) in the case of the latter. An alternative mode of describing these asymmetric stars is to view them as graft polymers where the centrally located single graft of the SAS species has a molecular weight 25% that of the backbone whereas the off-center graft of the LAS series has a molecular weight that is 33% of that exhibited by the backbone. As a counterpoint to these asymmetric three-arm stars, a corresponding series of regular three-armed polystyrene stars were also evaluated. This was done in view of ambiguous results presented elsewhere[21] for three-armed polystyrene stars.

In tandem with the evaluation of the three-armed materials, a study of twelve-arm polystyrenes having the molecular weight range of 6.1×10^4 to 5.5×10^6 was undertaken. The results obtained in this work for the regular star polymers are combined with those previously presented.[12,13,16,19]

Experimental Section

The mode of preparation for the asymmetric three-arm polystyrene stars is available elsewhere.[22,23] The synthetic approach involved the general procedures used for organolithium based anionic polymerizations. The preparation of the symmetric three-armed stars involved, for most samples, the conversion of the styryllithium active center to butadienyllithium prior to reaction with methyltrichlorosilane. (For certain samples this step was eliminated.)[22] The conversion of the active centers was done by adding butadiene in quantities to yield two to three diene units per polystyrene chain. The twelve-armed materials were prepared in the foregoing fashion with the exception that tetrakis((trichlorosilyl)ethyl)silane was used as the linking agent.[24] All star polystyrenes were fractionated to eliminate unlinked linear polymer. The efficiency of the fractionations were checked by size exclusion chromatography (Waters 150C). The linear material was always present as the consequence of carrying out the linking event with an excess of active centers relative to sites on the respective chlorosilane linking agents. Within experimental error the star polymers exhibited the desired functionality.[12,13,16,22]

The techniques used in the dilute solution characterization are given elsewhere.[12,13,19,22,23] Toluene and cyclohexane were the solvents. Intrinsic viscosity was measured with Ubbelhode viscometers under conditions where kinetic energy corrections were unnecessary. Sofica PGD or Fica 50 photometers were used for the weight-average molecular weight determinations and the evaluation of R_G (where $R_G \equiv \langle R_G^2\rangle_z^{1/2}$) for the higher molecular weight regular stars. Other chain dimension data were obtained via neutron scattering by using deuteriated cyclohexane or toluene[19] and by dynamic light scattering to obtain the hydrodynamic radius, R_H.[13]

Branching is known[25] to influence the Θ temperature (defined as where $A_2 = 0$). The Θ temperatures for all samples were determined via light scattering. The intrinsic viscosity measurements in cyclohexane were done at the experimentally determined Θ temperature for each star or at 34.5 °C. This procedure was followed in view of the observed sensitivity of the star intrinsic viscosities to deviations from the Θ temperature of the sample. The chain dimension data and hydrodynamic parameters were obtained from measurements at 35 °C cyclohexane. This was done since mild deviations from Θ do not cause extensive changes in the parameters under investigation, e.g., the radius of gyration, R_G (see ref 13 and 19). Measurements in toluene were done at 35 °C.

The evaluation of the various hydrodynamic and chain dimension data for the star polystyrenes requires the use of the results for the linear analogues. Toward this end, the survey conducted by Schmidt and Burchard[26] regarding the R_H–M_w relationship for linear polystyrene in cyclohexane has been particularly helpful. The linear polystyrene results of Einaga et al.[27] were used for the $[\eta]$–M_w relationship in cyclohexane in view of the wide range of molecular weights covered (4×10^3 to 5.68×10^7) while the toluene relation of Roovers and Bywater[4] was chosen. The R_G–M_w relationships of Roovers et al. for cyclohexane[4,27,28] and toluene[12,28] were used. Unweighted linear regression analysis was used to evaluate all of the data of this work as well as the literature results.

The measurement of the Θ temperature (where $\Theta_{A_2} = 0$) of the branched polystyrenes revealed that for the regular three-arm stars the absence or presence of butadiene units at the star center influenced the value of this parameter. Examples of this can be seen in Table I where sample SS-7, which does not contain butadiene units at the star center, exhibits a higher Θ temperature than SS-8, which is of higher molecular weight and contains butadiene units. Similar behavior is seen for the LAS-2 and LAS-3 asymmetric stars. Thus, the presence of the butadiene segments at the star core can influence the Θ temperature of these materials.

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Table I
Molecular Characteristics of Three-Arm Polystyrene Stars

sample[a]	10^4M_w, g mol^{-1}	Θ, °C	$[\eta]_\Theta$, dL g^{-1}	g'_Θ	$R_{G\Theta}$, nm	g_Θ	$[\eta]_{tol}$, dL g^{-1}	g'	$R_{G\,tol}$, nm	g	10^4A_2, mol cm^3 g^{-2}
SS-1	0.65	12.0	0.060	0.90			0.064	*b*			
SS-2	1.38	24.0	0.085	0.87			0.098	*b*			
SS-3	1.60	28.0	0.092	0.88			0.109	*b*			
SS-4	1.70	28.0	0.094	0.87			0.114	*b*			
SS-5	2.70	31.0	0.120	0.88			0.146	*b*			
SS-6	3.00	32.5	0.128	0.90			0.167	*b*			
SS-7	3.50	33.5	0.135	0.87			0.183	*b*			
SS-8	6.20	31.0	0.175	0.85			0.260	0.85			
SS-9	9.47	32.0	0.214	0.84			0.354	0.85			
SS-10	17.3	34.0	0.290	0.84			0.573	0.88			
SS-11	19.3	34.0	0.306	0.84			0.590	0.84			
SS-12	22.4		0.335	0.85			0.650	0.83			
SS-13	39.2		0.437	0.84	16.0	0.83	0.955	0.81	21.5	0.80	3.5
SS-14	77.5		0.630	0.86	22.4	0.82	1.60	0.83	31.6	0.78	3.0
SS-15	92.0		0.690	0.87	24.4[c]	0.82	1.80	0.82	35.4[c]	0.79	2.8
SS-16	119		0.800	0.89	27.6[c]	0.81	2.15	0.82	40.5[c]	0.77	2.6

[a] Samples SS-1 through SS-7 were prepared without the addition of butadiene prior to linking (see ref 22). [b] These values were not used in the g' evaluation due to the approach to theta condition dimensions in this molecular weight range (see Figure 3). [c] Average values of those measured in this work and those reported in ref 13. In that reference samples SS-15 and SS-16 are denoted as PSI-3 and PSJ-3, respectively.

Table II
Molecular Characteristics of Twelve-Arm Polystyrene Stars

sample	$10^{-4}M_w$, g mol^{-1}	Θ, °C	$[\eta]_\Theta$, dL g^{-1}	g'_Θ	$R_G{}^\Theta$, nm	g_Θ	$[\eta]_{tol}$, dL g^{-1}	g'	$R_{G\,tol}$, nm	g
PS9-12	6.1	21.5	0.092	0.45	3.89[a]	0.31	0.132	*b*	3.83[a]	0.25
PS6-12	14.9	23.5	0.131	0.41	6.97[a]	0.41	0.236	*b*	7.30[a]	0.28
PS4-12	46.7	29.0	0.237	0.42	11.7[a]	0.37	0.461	0.34	12.7[a]	0.23
PS5-12	80.0	31.5	0.310	0.42	14.8	0.35	0.699	0.35	18.1	0.24
PS7-12	111.0	33.0	0.375	0.43	18.0	0.37	0.871	0.35	22.0	0.25
PS10-12	169.0	34.0	0.443	0.41	19.8	0.29	1.15	0.34	28.2	0.25
12PS1B1A[c]	550.0	34.5	0.795	0.41	34.6	0.28	2.71	0.34	57.4	0.28

[a] Neutron scattering.[16,19] [b] These values were not used in the evaluation of g' due to the approach to theta condition chain dimensions in this molecular weight range. [c] Data from ref 12.

For this reason, an evaluation of our Θ temperature findings in terms of the Candau–Rempp–Benoit[25] theory as was done for polyisoprene stars[8] was not attempted.

The presence of butadiene in the higher molecular weight regular three-arm stars, SS-8 through SS-16, is a consequence of the inability of the linking reaction to reach completion when the arm molecular weight exceed ca. 1.4 × 10^4 unless conversion to the butadienyllithium active center is done.[22] All intrinsic viscosity measurements in cyclohexane were thus done at the experimentally determined Θ temperature in order to eliminate any potential influence of the butadiene segments.

Results and Discussion

Star polymers are well-suited for a comparison of the relation between segment density, and their hydrodynamic properties and static dimensions in dilute solution since the former parameter can be changed without a corresponding change in molecular weight. This is accomplished as a consequence of a change in functionality (the number of star arms) while molecular weight remains as the invariant. Thus, regular three- and twelve-armed polystyrene stars were studied as were two series of asymmetric three-arm stars.

Star Polymer Conformation. The molecular parameters of the regular polystyrene stars are given in Tables I and II. The chain dimension results are shown in Figure 1. For the case of the twelve-arm stars in cyclohexane, the measurements (neutron and light scattering) were done at 35 °C. This temperature is not the true Θ temperature for the twelve-arm stars in cyclohexane-d_{12}[30] (the neutron scattering solvent), but as has been shown[13,19] the radii of gyration are only mildly influenced by moderate deviations from Θ conditions. The combination of the light and neutron scattering results for the twelve-arm polystyrene star chain dimensions in toluene and cyclohexane allows coverage over a 90-fold range in molecular weight. This permits the evaluation of the influence of the chain segment density at the core of stars on their respective conformations. The effect of high core segment density would be anticipated to be more pronounced as the arm molecular weight decreased.

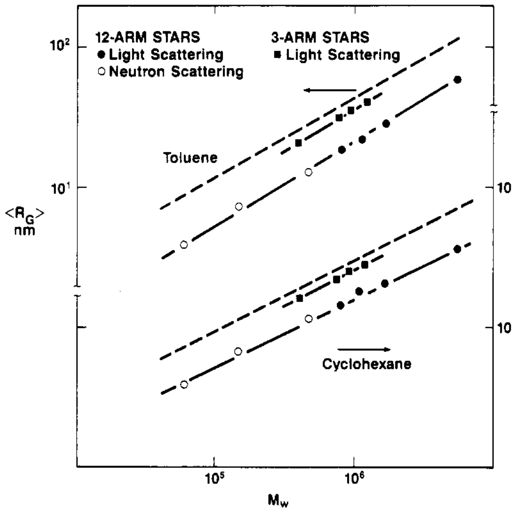

Figure 1. Radii of gyration for regular three- and twelve-arm polystyrene stars in toluene and cyclohexane. The dashed lines denote linear polystyrene.

The conventional fashion used for the comparison of branching on chain dimensions is the comparison of the respective square of the radius of gyration $R_G{}^2$ of the branched material to that of the linear equivalent:

$$g = [R_G{}^2{}_{star}/R_G{}^2{}_l]_M \qquad (1)$$

Table III
Hydrodynamic and Chain Dimension Characteristics of Model Branched Polystyrenes in Toluene

sample	10^5K, g dL^{-1}	a	g'	g	g_{rw}	g_{MC}	m	$gf^{4/5}$	ref
linear	9.96	0.728							4
3-LAS	9.84	0.717	0.87		0.813[a]				this work
3-SAS	7.03	0.745	0.87		0.792[a]				this work
3-SS	10.1	0.712	0.84[b]	0.79	0.778	0.83	0.74	1.90	this work
H shaped	6.38	0.742	0.77	0.70	0.712[a]		0.73		20
4-SS	7.81	0.722	0.73[c]	0.61	0.625	0.67	0.64	1.85	28
6-SS	6.53	0.718	0.58	0.45	0.444	0.50	0.68	1.89	28
12-SS	4.19	0.714	0.34	0.25	0.236		0.77	1.83[d]	this work

[a] Reference 29. [b] An average value for g' of 0.81 is available from ref 21. [c] An average value for g' of 0.70 is reported in: Strazielle, C.; Herz, C. *Eur. Polym. J.* **1970**, *13*, 223. [d] A value of 2.05 is reported[12] for an eighteen-arm polystyrene star.

Table IV
Hydrodynamic and Chain Dimension Characteristics of Model Branched Polystyrenes in Cyclohexane

sample	10^4K, g dL^{-1}	a	g'_Θ	g_Θ	g_{rw}	g_{MC}	m	$g_\Theta f^{1/2}$	α_Θ^2	ref
linear	8.28	0.500								27
3-LAS	7.76	0.494	0.88		0.813[a]					this work
3-SAS	6.31	0.508	0.84		0.792[a]					this work
3-SS	7.66	0.494	0.87[b]	0.82	0.778	0.83	0.53	1.42	1.05	this work
H shaped	5.35	0.516	0.80	0.69	0.712[a]		0.66		0.98	20
4-SS	6.54	0.497	0.76[c]	0.63	0.625	0.67	0.58	1.26	1.01	4, 5, 28
6-SS	5.59	0.496	0.64	0.46	0.444	0.50	0.55	1.13	1.04	4, 28
12-SS	4.19	0.486	0.42	0.28–0.41	0.236		0.60	0.97–1.42	1.18–1.73	this work

[a] Reference 29. [b] An average value for g'_Θ of 0.80 is available from ref 21 when the equation of Einaga et al.[27] is used for linear polystyrene. [c] An average value for g'_Θ of 0.71 is available in the reference of footnote *c* of Table III when the equation of Einaga et al.[27] is used.

Strictly spoken, the values of R_G^2 are controlled by the *z*-average molecular weight. However, no corrections to weight-average values are needed in view of the narrow molecular weight distributions encountered in these regular star polystyrenes. The respective values of R_G^2 for linear polystyrenes are available from the following:

$$R_G{}^2{}_\Theta = 7.90 \times 10^{-4} M_w \ (\mathrm{nm})^2 \qquad (\text{ref } 4) \qquad (2)$$

$$R_G{}^2{}_{\mathrm{tol}} = 1.66 \times 10^{-4} M_w^{1.17} \ (\mathrm{nm})^2 \qquad (\text{ref } 12) \qquad (3)$$

The g and g_Θ values for the regular three- and twelve-arm stars are given in Tables III and IV. Therein it can be seen that $g_\Theta > g_{\mathrm{rw}}$ where g_{rw} is the random walk calculation given as follows

$$g_{\mathrm{rw}} = (3f - 2)/f^2 \qquad (4)$$

where f denotes the star functionality.[31] The Monte Carlo calculations of Mazur and McCrackin[32] involving the ratio of the radii of gyration, g_{MC}, tend to overestimate this parameter. As the combined findings of Table VI show for cyclohexane (the twelve-arm stars excluded), the Zimm–Stockmayer predictions[30] are generally obeyed. The respective relationships between molecular weight and R_G^2 for the regular three- and twelve-arm stars are as follows:

Three-Arm Stars

$$R_G{}^2{}_\Theta = 8.05 \times 10^{-4} M_w^{0.98} \ (\mathrm{nm})^2 \qquad (5)$$

$$R_G{}^2{}_{\mathrm{tol}} = 1.17 \times 10^{-5} M_w^{1.15} \ (\mathrm{nm})^2 \qquad (6)$$

Twelve-Arm Stars

$$R_G{}^2{}_\Theta = 5.12 \times 10^{-4} M_w^{0.95} \ (\mathrm{nm})^2 \qquad (7)$$

$$R_G{}^2{}_{\mathrm{tol}} = 3.50 \times 10^{-5} M_w^{1.18} \ (\mathrm{nm})^2 \qquad (8)$$

The scaling concept leads to the conclusion that $gf^{4/5}$ is a constant[33] in good solvents. The data for toluene solutions in Table III and that of Roovers et al.[12] show $gf^{4/5}$ is indeed a constant within experimental error over the functionality range from 3 to 18. These findings lend support to the Daoud–Cotton proposals[33] relating to star polymer conformation in good solvents. Less success, though, is encountered for Θ condition conformations where a certain degree of non-Gaussian behavior was attributed[33] to the star arms. This led to the prediction that $g_\Theta f^{1/2}$ is a constant. An examination of Table IV demonstrates that for the stars where g_Θ is independent of molecular weight a decrease in the $g_\Theta f^{1/2}$ product is observed as functionality increases (a trend which is also seen if g_{rw} is substituted for g_Θ).

Within experimental error the measured g_Θ values for a given type of branching are invariant for stars having three to six arms. This situation is not encountered for the twelve-arm polystyrene stars. Therein it was observed that g_Θ generally decreased as arm molecular weight increased; g_Θ approaches g_{rw} only at the highest arm molecular weight. This gradual diminuation of g_Θ as arm molecular weight is enhanced is apparently the result of the gradual relative lessening of the influence of the high segment density near the star core. This deviation from Gaussian statistics for the shorter armed stars is a partial cause of the exponent of eq (11) being less than the anticipated value of one.

The apparent Θ temperature expansions

$$\alpha_\Theta^2 = [g_\Theta / g_{\mathrm{rw}}]_M \qquad (9)$$

are given in Table IV. Within experimental error these values are one for the branching types listed with, again, the exception of the twelve-arm stars. Therein it is seen that only the highest molecular weight twelve-arm star exhibits chain dimension behavior reminiscent of that predicted by Zimm and Stockmayer.[31] It should be noted that a value of 1.42 is available[12] for an eighteen-arm polystyrene star with an overall molecular weight of 8.8 × 10^6. This indicates that the degree of chain expansion found for highly branched stars is a function of both the extent of branching as well as arm molecular weight; e.g., the twelve-arm star yields a value of 1.1 for α_Θ^2 at an arm molecular weight of 4.3 × 10^5 whereas the eighteen-arm star yields[12] a value of 1.42 for an arm molecular weight 5.0 × 10^5.

Two additional comments can be made regarding the chain dimensions of the twelve-arm stars. The values of g in toluene show no dependence on arm molecular weight—a finding in accordance for what has been found

Table V
Molecular Characteristics of Long-Arm (LAS) Polystyrene Stars

sample	$10^{-4}M_w$, g mol^{-1}	Θ, °C	$[\eta]_\Theta$, dL g^{-1}	g'_Θ	$[\eta]_{\mathrm{tol}}$, dL g^{-1}	g'
LAS-1[a]	1.0	16.6	0.075	0.91	0.088	b
LAS-2[a]	2.3	29.0	0.110	0.87	0.132	0.89
LAS-3	3.6	26.1	0.135	0.86	0.181	0.90
LAS-4	5.1	26.5	0.164	0.88	0.237	0.89
LAS-5	7.1	27.7	0.191	0.86	0.280	0.83
LAS-6	8.1	27.4	0.208	0.88	0.331	0.89
LAS-7	10.0	29.7	0.237	0.90	0.380	0.87
LAS-8	15.8	28.4	0.280	0.85	0.514	0.85
LAS-9	22.8	30.0	0.341	0.86	0.690	0.87
LAS-10	31.8	30.1	0.415	0.89	0.864	0.86

[a] Butadiene not added prior to linking (see ref 22). [b] See footnote b of Table I.

Table VI
Molecular Characteristics of Short-Arm (SAS) Polystyrene Stars

sample	$10^{-4}M_w$, g mol^{-1}	Θ, °C	$[\eta]_\Theta$, dL g^{-1}	g'_Θ	$[\eta]_{\mathrm{tol}}$, dL g^{-1}	g'
SAS-1[a]	1.1	19.0	0.072	0.83	0.081	b
SAS-2	3.4	28.7	0.127	0.83	0.167	0.84
SAS-3	7.1	28.7	0.182	0.82	0.303	0.89
SAS-4	10.9	27.3	0.224	0.82	0.397	0.86
SAS-5	12.4	28.7	0.245	0.84	0.437	0.86
SAS-6	16.3	30.1	0.289	0.87	0.534	0.86
SAS-7	21.1	30.6	0.320	0.84	0.666	0.89
SAS-8	34.8	29.7	0.415	0.85	0.960	0.89

[a] Butadiene not added prior to linking (see ref 22). [b] See footnote b of Table I.

for the lesser armed stars and H-shaped polystyrenes listed in Table III. Therein the experimental values show general agreement with g_{rw}, although such agreement is perhaps fortuitous since the Zimm–Stockmayer[31] predictions are based on the presence of Gaussian phantom chains. The presence of expanded chain dimensions observed in cyclohexane may account, at least in part, for the Mark–Houwink–Sakurada exponent of 0.486 (Table IV). Some influence would be anticipated since the direct relation between intrinsic viscosity and R_G^2 takes the form[34]

$$[\eta] = \phi'(R_G^2)^{3/2}M^{-1} \qquad (10)$$

where ϕ' is the hydrodynamic constant. If ϕ' is invariant for a given polymer architecture (and we know of no reason to think otherwise), then the segment density contribution would lead to relatively diminishing values of R_G^2 as the star arm approaches Gaussian statistics.

The noninterpenetration function[35]

$$\Psi = A_2M^2/4\pi^{3/2}N_a(R_G^2)^{3/2} \qquad (11)$$

(where A_2 is the second virial coefficient and N_A, the number of Avogadro) is a potential measure of the hard-sphere character of star-shaped polymers. The values obtained in toluene for the three- and twelve-armed stars are given in Tables V and VI (the A_2 values were taken from Table I of this paper and Table I of ref 13).

The values of Ψ for the twelve-arm stars are found to be, in line with expectations, larger than those for the three-arm stars. Recent theoretical calculations[36] yield a value of 0.39 for the Ψ of the three-arm stars whereas our results lead to an average value of 0.41 (Table V).[37] The twelve-arm stars present a somewhat different situation in that Ψ seemingly exhibits some dependency on molecular weight, i.e., samples PS9-12 and 12PS1B1A in Table VII. A decrease in Ψ at high molecular weight has also been observed for linear chains[39] and has also been observed for star-shaped polyisoprenes.[39] An evaluation[12] based on the hard-sphere model described by Yamakawa[35] led to a value of 1.61 for $\lim_{f\to\infty} \Psi$.

Table VII
Noninterpenetration Function and Hydrodynamic Constants for Regular Three-Arm Polystyrene Stars

sample	toluene		cyclohexane
	Ψ	$10^{-23}\phi'$[a]	$10^{-23}\phi'$[a]
SS-13	0.41	0.38	0.42
SS-14	0.43	0.39	0.44
SS-15	0.40	0.38	0.44
SS-16	0.41	0.38	0.45
hard-sphere limit			1.36[b]
linear (theoretical)	0.27[c]		0.39[d]

[a] For [η] in dL g^{-1}. [b] Reference 34, p 351. [c] Reference 35. [d] Reference 34, p 298 (Pyun–Fixman values).

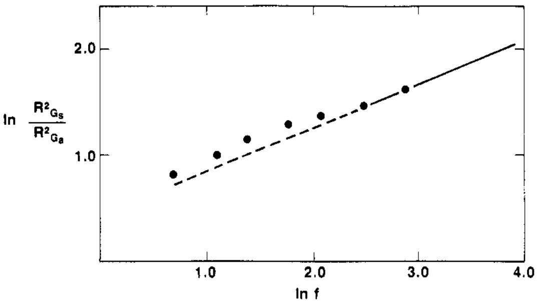

Figure 2. Radii of gyration ratios versus *f* in toluene. The solid line (drawn with a slope of 0.41) denotes the predicted[40] asymptotic power.

A recent simulation study[40] of star polymers with many ($6 \le f \le 50$) arms has evaluated the good solvent behavior of the $R_{G_s}^2/R_{G_a}^2$ ratio, where s denotes the star and a the star arm. The approach used following the scaling procedure first used by Daoud and Cotton[33] for star polymers. The simulation results predict that the ratios of the respective radii of gyration converge at f to a universal function of f:

$$[R_{G_s}^2/R_{G_a}^2] = 1.55f^{0.41} \qquad (12)$$

Within the limits of experimental uncertainty, this prediction is found to hold for the twelve- and eighteen-arm stars (Figure 2) and is independent of the composition of the stars.[40] This agreement between experiment and the scaling analysis[40] serves to fortify the value of the latter as a method for evaluating the dimensions and dynamics of starlike structures.

Hydrodynamic Properties. The hydrodynamic properties of the star polystyrenes are summarized in Tables I through VI for the toluene and cyclohexane results, respectively. Previously published results[4,5,21] for four- and six-armed stars and H-shaped materials are included for comparison. The intrinsic viscosity-molecular weight plots are given in Figures 3–5.

From the intrinsic viscosity data one can calculate

$$g' = [[\eta]_{\mathrm{star}}/[\eta]_{\mathrm{l}}]_M \qquad (13)$$

where l denotes the linear analogue at constant molecular weight (M). As can be seen in Tables VII and VIII, the g' values are, with the exception of the 3-SAS series, are smaller in toluene than under Θ conditions. An additional trend that has been noted[12,21,28,42] previously is that for regular stars $m \simeq 0.58$ in the relation

$$g'_\Theta = g_{\mathrm{rw}}^{\ m} \qquad (14)$$

rather than the proposed[43] exponent of 0.5. This observation holds for regular stars under Θ conditions although mild deviation from this value of m is seen for the three-

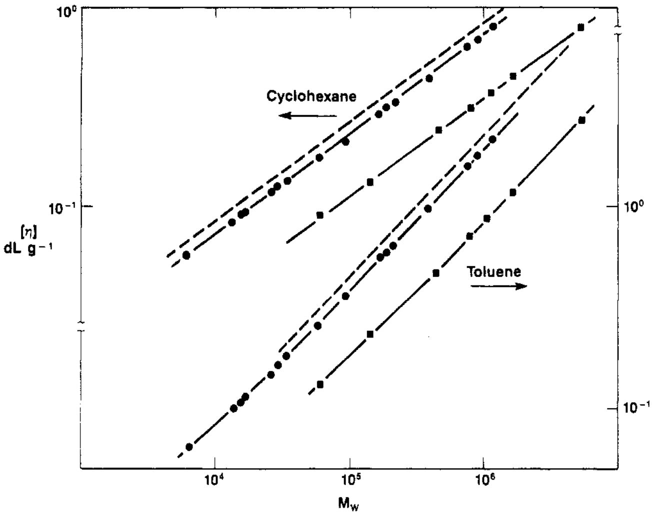

Figure 3. Intrinsic viscosity for regular three- (●) and twelve-arm (■) stars in cyclohexane and toluene. The dashed lines denote linear polystyrene.

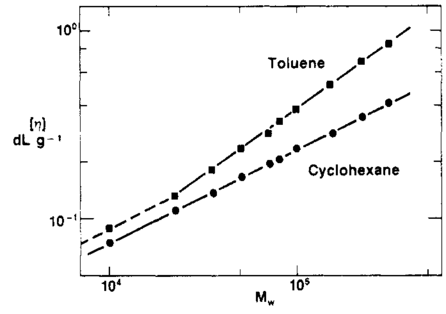

Figure 4. Intrinsic viscosity for three-arm asymmetric (SAS) polystyrene stars in toluene and cyclohexane.

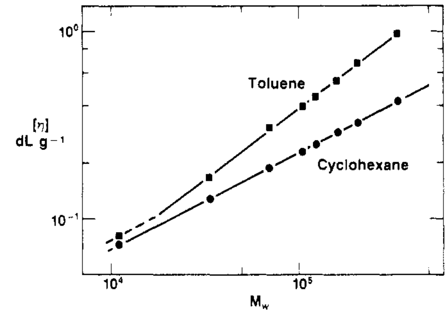

Figure 5. Intrinsic viscosity for three-arm asymmetric (LAS) polystyrene stars in toluene and cyclohexane.

arm polystyrene stars (Table IV). Thus, $m \simeq 0.58$ appears to be the lower limit for branched polymers, i.e., the values for comb- and H-shaped materials range from 0.65 to 1 depending upon the extent of branching.[42] Indeed, values of m in good solvents (Table III), for a given type of branching, are larger than the corresponding Θ condition values and are, for star shaped materials, dependent upon functionality.

The experimental g' values progressively decrease as the branching functionality of the macromolecule increases. In toluene the asymmetric polystyrene stars exhibit identical values of g', whereas under near Θ conditions the 3-SAS stars exhibit a decrease in g' while the 3-LAS materials show, within experimental uncertainty, no change in this parameter (Tables III and IV). Thus, when excluded volume effects are important, the branch point location has little influence on the hydrodynamic behavior, while under Θ conditions differences emerge. Interestingly, the asymmetric 3-LAS and regular 3-SS stars exhibit, within experimental error, equivalent behavior in cyclohexane.

Table VIII
Noninterpretation Function and Hydrodynamic Constants for Regular Twelve-Arm Polystyrene Stars

sample	toluene		cyclohexane
	Ψ	$10^{-23}\phi$[a]	$10^{-23}\phi'$[a]
PS9-12	2.45	1.43	0.96
PS6-12	1.59	0.90	0.88
PS4-12	1.67	1.05	0.69
PS5-12	1.49	0.95	0.81
PS7-12	1.49	0.91	0.71
PS10-12	1.54	0.87	0.96
12PS1B1A	1.10[b]	0.79	1.05[b]
hard-sphere limit			0.39[e]
linear (theoretical)	0.27[d]		0.39[c]

[a] For $[\eta]$ in dL g^{-1}. [b] Data of ref 12. [c] Reference 34, p 351. [d] Reference 35. [e] Reference 34, p 298 (Pyun–Fixman value).

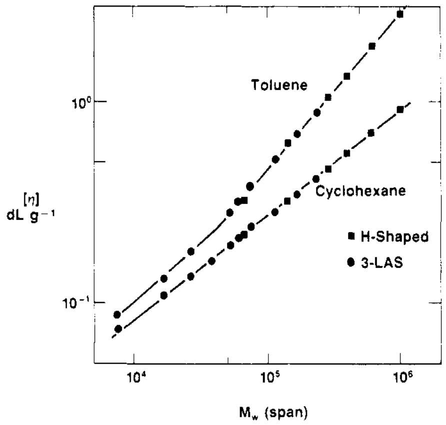

Figure 6. Intrinsic viscosity as a function of span molecular weight for three-arm asymmetric (LAS) polystyrene stars and H-shaped polystyrene in toluene and cyclohexane.

An additional hydrodynamic parameter of interest is the polymer span which can be defined as the distance between the units that are the furthest apart in a given direction. Casassa[44] and Casassa and Tagami[45] have proposed that the polymer span is the parameter that governs the elution characteristics in size exclusion chromatography. There have been various evaluations of the polymer span concept.[46-64] Some general observations can be made from the hydrodynamic behavior—expressed in terms of log $[\eta]$:log span molecular weight plots—for the branched polymers listed in Tables III and IV (where the span molecular weight is equal to twice the arm molecular weight).

Under Θ conditions, the four- and six-arm polystyrene and polyisoprene stars[4-6] show identical log $[\eta]$:log span M_w behavior whereas the same is seen for the six- and twelve-arm stars in toluene. Furthermore, the intercomparison of the H-shaped and 3-LAS polystyrenes show equivalent behavior, when molecular weights are normalized by the span concept, under both Θ and good solvent conditions (Figure 6). The equations available from this treatment are virtually identical with those obtained for linear polystyrenes (where, of course, the span and true molecular weights are identical). The equations for the H-shaped and 3-LAS polystyrenes follow and may be compared to the linear counterparts given in Tables III and IV

$$[\eta]_\Theta = 8.27 \times 10^{-4} M_{\text{span}}^{0.500} \qquad (15)$$

$$[\eta]_{\text{tol}} = 9.01 \times 10^{-4} M_{\text{span}}^{0.744} \qquad (16)$$

where K_Θ was obtained via the Burchard–Stockmayer–

Table IX
Hydrodynamic and Chain Dimension Parameters for Regular Three- and Twelve-Arm Polystyrenes

	toluene					cyclohexane				
sample	R_G, nm	R_V, nm	R_H,[a] nm	R_G/R_H	R_V/R_H	R_G, nm	R_V, nm	R_H,[a] nm	R_G/R_H	R_V/R_H
SS-13	21.5	18.1	...	1.22[b]	...	16.0	13.9	...	1.19[b]	...
SS-14	31.6	27.0	...	1.21[b]	...	22.4	19.7	...	1.17[b]	...
SS-15	35.4	29.7	28.1	1.26	1.06	24.4	21.5	20.4	1.20	1.05
SS-16	40.5	33.6	32.2	1.26	1.04	27.6	24.7	23.4	1.18	1.04
PS9-12	3.83[c]	5.03	4.87	0.79	1.03	3.89[c]	4.46	4.58	0.85	0.97
PS6-12	7.30[c]	8.19	8.25	0.88	1.01	6.97[c]	6.76	7.44	0.94	0.98
PS4-12	12.7[c]	15.0	15.2	0.84	1.01	11.7[c]	12.1	12.4	0.94	0.98
PS5-12	18.1	20.7	20.7	0.87	1.00	14.8	15.8	16.3	0.91	0.97
PS7-12	22.0	24.8	24.8	0.89	1.00	18.0	18.7	18.7	0.96	1.00
PS10-12	28.2	31.3	30.5	0.92	1.03	19.8	22.8	22.3	0.89	1.02
12PS1B1A	57.4[d]	61.8[d]	62.0[d]	0.93	1.00	34.6[d]	41.1[d]	42.6[d]	0.81	1.04
theoretical (linear)				1.56[e]	1.12[e]				1.24[f]	1.23[f]
theoretical (spheres)				0.775[g]	1.0[g]				0.775[g]	1.0[g]

[a] Data of ref 13. [b] R_H taken as $R_V/1.03$.[28] [c] Data from ref 16. [d] Data from ref 12. [e] Reference 67. [f] References 67, 68, and 69. [g] References 34 and 68.

Fixman procedure.[65,66] This observation indicates that the span molecular weight controls the hydrodynamic behavior of these two dissimilar structures in both Θ condition and good solvent environments. This behavior would not be predicted from the available simulations and theoretical work pertaining to the span concept.

The radius of the spherical particle that produces the same increase in intrinsic viscosity as the polymer chain is obtainable from

$$R_V = 5.41 \times 10^{-2}([\eta]M)^{1/3} \text{ (nm)} \tag{17}$$

The equivalent viscometric radii are given in Table IX along with the values of R_G and R_H.[13] Therein it can be seen that within experimental error R_V and R_H are identical for a given solvent. This behavior has been observed previously for linear, comb, and four- and six-armed star polystyrenes[28] and linear polyisoprenes.[70]

The R_G/R_H ratios show a dependence on functionality for the three- and twelve-armed stars in both toluene and cyclohexane. A recent theoretical prediction yields[71]

$$R_G/R_H = \left[\frac{3f-2}{f\pi}\right]^{1/2}\left[\frac{8[2-f+2^{1/2}(f-1)]}{3f}\right] \tag{18}$$

For three- and twelve-arm stars, the predicted values, 1.36 and 1.17, respectively, are higher than the experimental values. The experimental value of this ratio is 1.27 for linear chains under Θ conditions.[26] The Pyun–Fixman prediction[68] of 0.775 is approached as the degree of branching increases while their prediction that R_V/R_H = 1.0 is obeyed (within experimental error) for the twelve-arm stars in both solvents. Values slightly higher than one are seen for the three-, four-, and six-armed polystyrene stars (Table IX and ref 29). This limiting value of one is also seen for an eighteen-arm polystyrene star[12] and a series of twelve- and eighteen-arm polyisoprene stars.[39]

The ratio of the respective hydrodynamic radii

$$h \equiv [R_{H_b}/R_{H_l}]_M \tag{19}$$

yield an additional size comparison for star branched polymers from the theory of Stockmayer and Fixman[72]

$$h_{rw} = \frac{f^{1/2}}{2 - f + 2^{1/2}(f-1)} \tag{20}$$

for species under Θ conditions. These findings are summarized in Table X.

These combined findings show that theory and experiment yield $h_{rw} = h_\Theta$ only for three-armed stars and that $h_\Theta > h_{tol}$ generally holds. This latter trend is also that seen for g' and g'_Θ (Tables V and VI). The data of Table X also show a continuation of the trend remarked upon elsewhere;[12] i.e., $h_\Theta \simeq h_{rw}^{1/2}$. Within experimental error, this relation holds over a functionality range of 3–18. To date, theory does not explain this empirical observation.

Table X
Ratios of Hydrodynamic Radii for Polystyrene Stars

functionality	h_{rw}[a]	h_{tol}[b]	h_Θ[c]	ref
3	0.95	0.91	0.94	13
4[d]	0.89	0.93	0.92	29
6[e]	0.80	0.86	0.88	29
12	0.62	0.73	0.80	13
18[f]	0.53	0.68	0.73	12, 13

[a] Equation 20. [b] $R_{H(\text{linear})} = 9.97 \times 10^{-3} M^{0.586}$ (nm).[28] [c] $R_{H(\text{linear})} = 2.29 \times 10^{-2} M^{0.50}$ (nm).[26] [d] Seven samples. [e] Two samples. [f] One sample.

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