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Regular Star Polymers with 64 and 128 Arms. Models for Polymeric Micelles[†]

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ABSTRACT: Carbosilane dendrimers with 64 and 128 surface Si–Cl bonds were used as coupling reagents for monodisperse poly(butadienyl)lithium. Two series of regular star polybutadienes with 64 and 128 arms were prepared. The arm molecular weight was varied between 6400 and 72 000. The dilute-solution properties of the stars were determined in a good solvent (cyclohexane) and in a Θ-solvent (dioxane) for polybutadiene. Measurements of R_G, A_2, D_0, and $[\eta]$ indicate that the isolated stars behave as hard spheres. The ratio of the hydrodynamic radius over the radius of gyration is slightly larger than $(5/3)^{1/2}$. In a comparison which includes previously made stars with lower functionality, it is found that $g = \langle R_G^2\rangle / \langle R_G^2\rangle_{\text{lin}} \propto f^{-0.73}$ in the good solvent and $f^{-0.64}$ in the Θ-solvent. The former result is in good agreement with the Daoud–Cotton scaling model of stars. The latter dependence is stronger than the theory predicts: $g_\Theta \propto f^{-0.5}$. A recent quantitative model developed by Gast et al. for polymeric micelles is in good agreement with the present experimental data. Stars with many arms represent good model polymers for polymeric micelles.

Introduction

Model star polymers are best prepared by coupling of anionic living polymers with multifunctional electrophilic coupling agents. The coupling agents are either multifunctional chloromethylated benzene derivatives or multifunctional chlorosilane compounds. With the former compounds it is difficult to extend the functionality of the star beyond $f = 6$.[1,2] Therefore, multifunctional chlorosilane compounds have become the coupling agents of choice. Originally, incomplete coupling was observed.[3-5] This can now be avoided by limiting the number of chlorine atoms per silicon to two (sometimes three) and by separating the silicon atoms by ethylene spacers. The rate of electrophilic substitution decreases in the order polybutadienyl > polyisoprenyl > polystyryl. Indeed, Zelinski and Wofford described the synthesis of three- and four-arm polybutadienes with methyltrichlorosilane and tetrachlorosilane, respectively.[6] The systematic study of regular star polymers progressed with a series of fractionated and well-characterized four- and six-arm polystyrenes and polyisoprenes.[5,7,8] The synthesis of more complex multifunctional silicon chloride coupling agents led to the preparation of 8-, 12-, and 18-arm polyisoprenes.[9-11] More than 10 years elapsed before higher functionality coupling agents became available. The insights gained in the synthesis of dendritic molecules[12] were used to prepare carbosilane dendrimers with 32 silicon–chloride bonds for the preparation of 32-arm star polybutadienes.[13] In this paper we describe the synthesis and characterization of 64- and 128-arm star polymers.

Star polymers continue to play a significant role in the development of polymer chemistry and physics. Zimm and Stockmayer calculated the unperturbed dimensions of regular and randomly branched star polymers on the assumption that each chain segment adopts a random walk.[14] They showed how regular star polymers constitute the simplest architecture whereby the segment density in a polymer coil can be increased at constant molecular weight. Daoud and Cotton developed a scaling model that describes the radial distribution of the segment density more realistically in isolated stars with many arms.[15] The star polymers described in this paper are of particular interest because high functionalities are needed to check the Daoud–Cotton scaling theory of star polymers.[15] Interestingly, computer simulations on stars with up to 50 arms support the scaling model,[16] but such star polymers have not yet been produced.

It has recently been shown that the arms of a star behave as tethered chains on a (strongly) curved surface.[17] Regular star polymers are also ideal models for polymeric micelles which have been studied for a long time.[18-20] The insoluble block aggregates into a core that is held into solution by the outer soluble block. In many cases the number of chains in the micelles is between 20 and 200.[21]

Due to their high segment density, regular stars with a high functionality are also predicted to have peculiar properties near their overlap concentration in good solvents.[22,23] This paper is limited to the description of the synthesis of the stars and their characterization by their dilute-solution properties. A comparison with the properties of polymeric micelles is also made.

Experimental Section

1. Synthesis of Stars. The synthesis and properties of the vinylcarbosilane dendrimers has been described previously.[13,24] The chlorosilane coupling agents are prepared from the vinyl compounds by hydrosilylation with methyldichlorosilane in the presence of Pt catalyst.[13,24] The third generation dendrimer with 32 vinyl groups yields the 64-arm coupling agent. The fourth generation dendrimer with 64 vinyl groups yields a dendrimer with 128 silicon–chloride bonds for the preparation of the 128-arm star. The coupling agents were freed of excess methyldichlorosilane on a high-vacuum manifold and dissolved in degassed and n-BuLi-treated benzene to make solutions with between 0.15 and 0.25 M in Si–Cl.

Living poly(butadienyl)lithium was prepared in vacuo with *sec*-BuLi in benzene at room temperature. The apparatus was washed with a solution of n-BuLi in benzene and rinsed with benzene. All additions were made by

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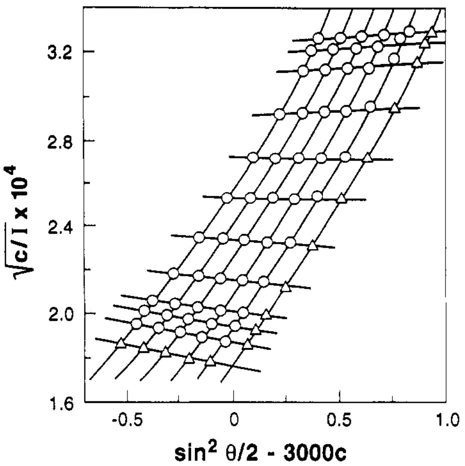


Figure 1. Berry plot of light scattering data for 12880 in cyclohexane at 25 °C. λ_0 = 3650 Å.

fragile break-seals, and removals were done by sealing rinsed constrictions. Prior to the addition of the coupling agent, a sample of the linear arm material is removed and terminated with methanol. The coupling reaction is left for 8 weeks and monitored during that time with SEC. Five μStyragel columns (nominal pore size 500, 10^3, 10^4, 10^5, and 10^6 Å) were used with THF at 1 mL/min as the eluent at 35 °C.

Excess living polymer was terminated with degassed *tert*-butyl alcohol. The star polymer was isolated by repeated fractionation in a benzene–methanol mixture between 30 °C and room temperature. All polymer solutions were protected against oxidation, degradation, and cross-linking by 4-methyl-2,6-di-*tert*-butylphenol.

2. Dilute-Solution Properties. The number-average molecular weight of the single-arm precursor was measured with a Hewlett-Packard 503 osmometer in toluene at 25 °C. Plots of $(\pi/c)^{1/2}$ vs c were used to extrapolate the data to zero concentration.

The weight-average molecular weight of the star polymers was measured by light scattering with a Brookhaven system in the Zimm mode. Flat-bottom sample cells were made from 15- and 25-mm NMR tubes and capped with ground-glass caps. Cyclohexane at 25 °C is the solvent. The Rayleigh ratio of toluene for λ_0 = 632.8 nm light is 14 × 10^{-6} cm^{-1}. The refractive index increment of polybutadiene is 0.108_0 mL/g.[13] For some low-MW star polymers individual values of dn/dc were measured with a Brice–Phoenix differential refractometer.

The general light scattering relation

$$\frac{Kc}{\Delta R(q)} = \frac{1}{M_w P(q)} + 2A_2c + 3A_3c^2 \qquad (1)$$

where K is an optical constant, $\Delta R(q)$ is the Rayleigh ratio of the solution minus that of the solvent, and $P(q)$ is the particle scattering function, is used in the Berry form. At $c = 0$

$$\left(\frac{Kc}{\Delta R(q)}\right)_{c=0}^{1/2} = \left(\frac{1}{M_w}\right)^{1/2}\left(1 + \frac{q^2 R_G^{\,2}}{6} + ...\right) \qquad (2)$$

where $q = (4\pi n/\lambda_0)\sin(\theta/2)$ is the scattering vector, and R_G is the radius of gyration. At $q = 0$

$$\left(\frac{Kc}{\Delta R(q)}\right)_{q=0}^{1/2} = \left(\frac{1}{M_w}\right)^{1/2}(1 + \Gamma_2 c) \qquad (3)$$

where $\Gamma_2 = A_2/M_w$. An example of experimental data is shown in Figure 1. Equation 3 assumes that $A_3 = {}^1/_3A_2{}^2M_w$. It is uncertain whether this relation may be used in the case of highly branched polymers. The numerical coefficient is known to vary with molecular weight between 0.25 and 0.33 for linear polystyrene in benzene[25] and the coefficient takes the value $^5/_8$ for a hard sphere.[26]

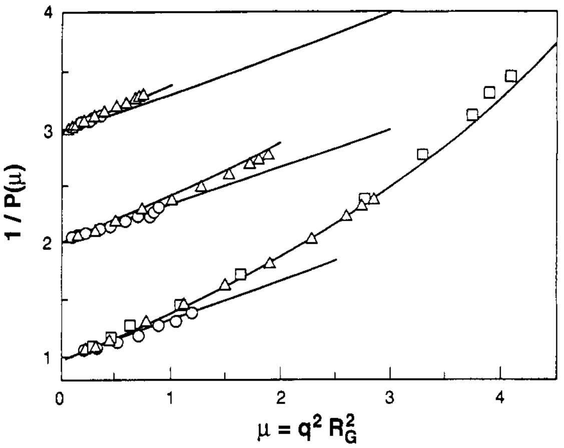


Figure 2. Inverse scattering function (c = 0) as a function of $q^2R_G{}^2$. Solvent: cyclohexane at 25 °C. Top to bottom: 12828, R_G = 216 Å; 12856, R_G = 345 Å; 12880, R_G = 424 Å. The curves are theoretical curves according to the Benoit model.[27,28] The straight lines are the universal asymptotes with slope $^1/_3$. Symbols: (○) λ = 6328 Å; (△) λ = 4358 Å; (□) λ = 3650 Å. The curve for 12828 has been offset by two units. The curve for 12856 has been offset by one unit.

In order to increase the accuracy of $\langle R_G{}^2\rangle$ data, light scattering measurements were also made with a Fica 50 instrument with 435.8- and 365-nm light. In order to improve further the extraction of R_G values from the experimental asymptote at $q = 0$, $1/P(q)$ was plotted against $q^2\langle R_G{}^2\rangle$. $\langle R_G{}^2\rangle$ is then obtained from a best fit to the theoretical scattering curve for a random-walk regular star.[27,28] Although the latter procedure is clearly incorrect at large values of $q^2\langle R_G{}^2\rangle$, it is an acceptable approximation around $q^2\langle R_G{}^2\rangle = 1$. In any case, it should be a better approximation than a simple cutoff of data points at an arbitrary low value of $q^2\langle R_G{}^2\rangle$. Also, this treatment combines all experimental results obtained at different wavelengths into a single curve. Examples are shown in Figure 2. Radii of gyration of the larger stars were also measured in dioxane, the Θ-solvent for the linear polymers at 26.5 °C.

Translational diffusion coefficients, $D = \Gamma/q^2$, of the star polymers were determined in cyclohexane at 25 °C and in dioxane at 26.5 °C. The Brookhaven BI2030AT autocorrelator combined with the BI200SM goniometer and a Spectra-Physics vertically polarized 35-mW He–Ne laser. The same procedure was used as described previously in detail for the 32-arm star polybutadienes[13] and for multiarm stars.[29] The correlation function was fitted to a second cumulant equation

$$\ln\left(\frac{\langle I(0)\,I(t)\rangle}{B} - 1\right)^{1/2} = \ln b^{1/2} - \Gamma t + \left(\frac{\mu_2}{2}\right)t^2 \qquad (4)$$

where B is the base-line reading and b an optical constant. Values of μ_2/Γ^2 were always very low (~0.02) for these narrow MWD polymers. The diffusion coefficient of the multiarm star polymers has a very weak concentration dependence, and accurate determination of k_D in

$$D = D_0(1 + k_D c) \qquad (5)$$

is very difficult. No q dependence of D is found for scattering angles between 15 and 120°.

Intrinsic viscosities were determined in toluene at 35 °C, in cyclohexane at 25 °C, and in dioxane at 26.5 °C. Cannon–Ubbelohde viscometers with a Hewlett-Packard

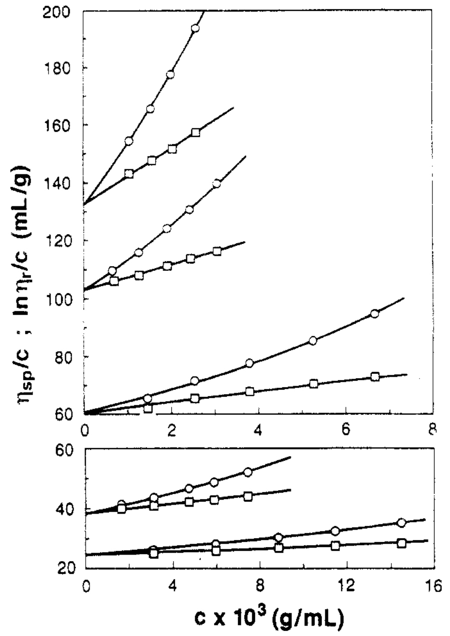
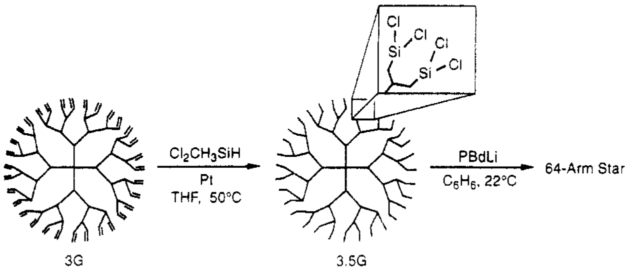


Figure 3. Determination of the intrinsic viscosity of 128-arm star polybutadienes in cyclohexane at 25 °C: (○) η_{sp}/c against c data; (□) ln η_{rel}/c against c data. Top to bottom: 12880, 12856, 12828, 12814, and 12807.

Scheme I. Schematic for the Synthesis of a 64-Arm Star Polybutadiene from a 3rd Generation Carbosilane Dendrimer



automatic timer were used. Flow times of the solvents were typically 150 s or more. Measurements were made at five concentrations. The relative viscosities of the highest concentrations are between 1.4 and 1.6. As observed previously,[13] plots of η_{sp}/c against c are strongly curved for regular star polymers with many arms. Examples are shown in Figure 3. The data were therefore analyzed according to

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c + k_H'[\eta]^3c^2 + 0 \ldots \qquad (6)$$

where $[\eta]$ was first estimated from a (ln η_{rel})/c vs c plot and then used in a plot of ($\eta_{sp}/c - [\eta]$)/c vs c to evaluate k_H and k_H'. The method of Bawn[30] used to derive the third viral coefficient did not improve the data treatment.

Results

1. Polymer Synthesis. The synthesis of the star polymers is based on the complete hydrosilylation and subsequent reaction of the chlorosilane bonds with living poly(butadienyl)lithium as shown in Scheme I. Both reactions seem to be free of side reactions. In particular there is no evidence in the final product of coupling between two or more star polymers. The 64-arm stars have been prepared with 100% excess living ends over Si–Cl. The 128-arm stars have been prepared with 200% excess. Sufficient time for the coupling reaction has to be allowed. Yields of star polymer after 6 days were typically 92–96% of the yield after 8 weeks. SEC samples of crude reaction products are shown in Figure 4. The excess arm material and other low molecular weight impurities are removed by fractionation. It is interesting to note that the SEC spacing between the star and precursor increases with the functionality of the star. This is of course due to the increase in MW of the star with functionality and despite a small drop in $[\eta]$ with increasing functionality (cf. infra).

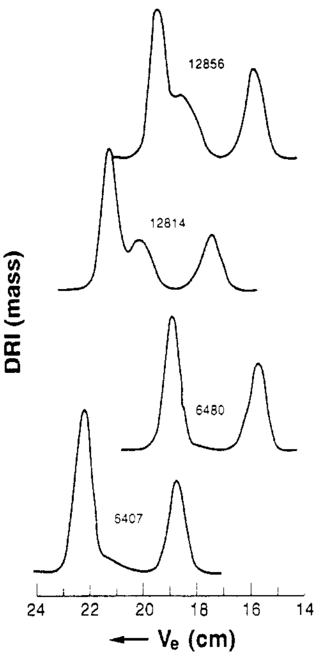


Figure 4. SEC traces of crude reaction products of the star synthesis reaction. The pure star polymers are obtained by repeated fractionation as described in the text.

Table I. Characterization of Regular Star Polybutadienes

sample	$(M_w)_{star}$ × 10^{-5} [a]	$(M_n)_{arm}$ × 10^{-5} [b]	f	A_2 × 10^5,[a] mL mol/g^2	$\langle R_G^2\rangle^{1/2}$,[a] Å
6407B2	3.95[c]	0.0633	62	13.7	[102][g]
6415B2	7.25[d]	0.121	60	11.0	
6430B3	13.4	0.239	56	9.6	185
6460B3	28.9	0.475	61	7.2	280
6480B4	42.0	0.71[e]	59	6.6	341
12807B2	8.4[f]	0.068	124	6.9	
12814B2	16.2	0.130	125	5.1	
12828B2	29.8	0.261	114	4.2	216
12856B4	59.5	0.470	127	3.1	345
12880B4	88.0	0.72[e]	122	3.0	424

[a] From light scattering in cyclohexane at 25 °C. dn/dc = 0.108$_0$ unless otherwise given. [b] From osmometry in toluene at 25 °C. [c] dn/dc = 0.1075. [d] dn/dc = 0.1075. [e] From SEC calibrated with linear polybutadienes. [f] dn/dc = 0.1058. [g] SANS in methylcyclohexane-d_{14}.[35]

The number-average molecular weights of the single arm and the weight-average molecular weight of the star polymers are given in Table I. The functionality of the star calculated by

$$f = (M_w)_{star}/(M_n)_{arm}$$

is also given in Table I. It appears that f is always a little lower than the nominal functionality. Random errors in $(M_w)_{star}$ and $(M_n)_{arm}$ are reflected in the variation of f within each series. The results strongly suggest that there is no steric limitation[31] in the coupling reaction of poly(butadienyl)lithium with chlorosilane dendrimers up to the 4^1/$_2$th generation.

2. Dilute-Solution Properties. It has been shown theoretically[32] and experimentally[7,11,32] that branching can lower the Θ-temperature of a polymer. The Θ-temperature lowering is large in the system polystyrene–cyclohexane[7,32] and less important in polyisoprene–1,4-dioxane[8,11] but has

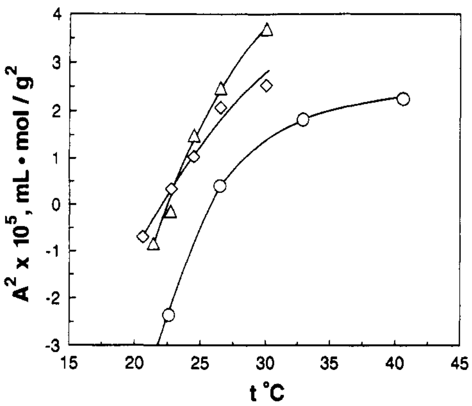


Figure 5. Temperature dependence of A_2 for different star polymers for the determination of θ_{A_2}. The Θ-temperature of linear polybutadiene in dioxane is 26.5 °C.

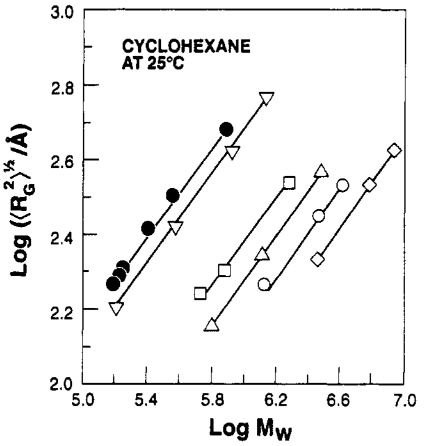


Figure 6. log–log plot of the radius of gyration against molecular weight for linear and star polybutadienes in cyclohexane at 25 °C. Symbols: (●) linear;[34,37] (▽) 4-arm star;[37] (□) 18-arm star;[33] (△) 32-arm star;[13] (○) 64-arm star; (◇) 128-arm star.

not been observed with 18- and 32-arm polybutadienes in dioxane.[13,33] We investigated the dependence of A_2 on temperature in dioxane. The results are shown in Figure 5. Despite the high number of arms in the stars the Θ-temperature lowering is small, approximately 5 °C for the lowest MW stars, and vanishes for high MW stars as expected.[32] Note the crossover of the A_2-temperature curves of PBD6407 and PBD12807. The 128-arm star has the lower Θ-temperature but also the lower value of A_2 in a good solvent (see Table I). Because of the small Θ-temperature lowering, all solution properties in dioxane were determined at 26.5 °C, the Θ-temperature for linear polybutadiene in dioxane.[34]

The values of A_2 and $\langle R_G^2\rangle^{1/2}$ (Table I) of the star polybutadienes in cyclohexane are derived from Berry plots. For the stars with high functionality light scattering can only provide R_G data of the very high MW samples ($R_G > 150$–200 Å). We assume that the measured R_G values are the high-MW limiting values. This means that, for each series, the experimental results are of the form $\langle R_G^2\rangle^{1/2} \propto M^\nu$ where ν is, within experimental error, the value of linear polybutadiene. A few results are available from SANS experiments on low-MW stars in methylcyclohexane-d_{14}.[35] In those cases, positive departures from the high-MW limit are observed, as was previously found for lower functionality stars with very short arms.[36] The molecular weight dependences of R_G and A_2 are shown in Figures 6 and 7, respectively, where a comparison is made with the data obtained with linear,[34,37] 4-arm,[37] 18-arm[33] and 32-arm[13] star polybutadienes. Radii of gyration in dioxane at 26.5 °C were also determined for the high-MW stars. The data are limited to two samples in each series and are collected in Table II.

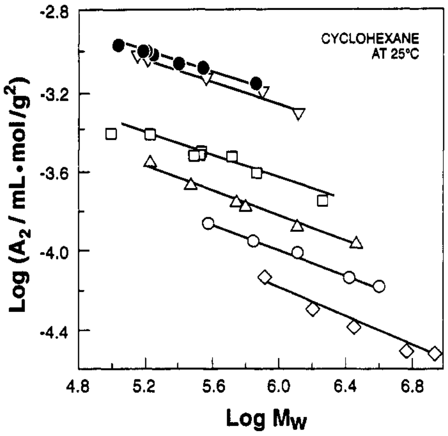


Figure 7. log–log plot of the second virial coefficient against molecular weight for linear and star polybutadienes in cyclohexane at 25 °C. Symbols as in Figure 6.

Table II. Dilute-Solution Properties of 64- and 128-Arm Star Polybutadienes in Dioxane at 26.5 °C

sample	$\langle R_G^2\rangle^{1/2}$, Å	$[\eta]$, mL/g	k_H	$D_0 \times 10^7$, cm²/s	k_D, mL/g
6407		15.8	0.78	1.94	−13.7
6415		21.2	0.78	1.45_5	−19
6430	(118)	29.7	0.81	1.07_9	−51
6460	205	42.8	0.83	0.70_8	−68
6480	225	53.0	0.95	0.58_8	−53
12807		14.8	0.78	1.53_6	−10.4
12814		20.4	0.82	1.12_5	−12.6
12828	(152)	28.8	0.83	0.83_7	−73
12856	238	36.7	1.10	0.58_2	−46
12880	270	45.6	0.97	0.48_5	−57

Table III. Hydrodynamic Properties of 64- and 128-Arm Stars in Cyclohexane at 25 °C

sample	$D_0 \times 10^7$, cm²/s	k_D, mL/g	$[\eta]$, mL/g	k_H	$[\eta]$,[a] mL/g	k_H[a]
6407	2.24	19	26.4	0.91	28.7	0.95
6415	1.54_5	31	41.1	0.88	43.2	1.02
6430	1.09	58	63.3	1.00	70.5	0.88
6460	0.68	90	108.3	0.86	126	0.83
6480	0.53_5	81	144.8	0.92	166	0.90
12807	1.72	20	24.2	0.97	25.8	0.98
12814	1.19	35	38.6	0.95	42.8	0.81
12828	0.83	19(?)	61.0	0.98	69.3	0.81
12856	0.55	100	102.8	0.83	114.9	0.77
12880	0.42_5	130	133.7	0.97	$152._2$	0.94

[a] In toluene at 35.0 °C.

Translational diffusion coefficients, D_0, measured in dioxane at 26.5 °C are given in Table II. The translational diffusion coefficients measured in cyclohexane are given in Table III together with estimates of the coefficient k_D in eq 5. The data are plotted double logarithmically in Figures 8 and 9 for comparison with values of D_0 for linear and other star polybutadienes.[13,29,38] Experimental values of D_0 cover the whole MW range and are more accurate than values of R_G. This is reflected in the parallel lines in Figures 8 and 9.

The intrinsic viscosities of the star polymers in dioxane at 26.5 °C are given in Table II together with the Huggins constants obtained according to eq 6. Values of the intrinsic viscosities of the stars in the good solvents cyclohexane at 25 °C and toluene at 35 °C are given in Table III together with the respective Huggins constants. Plots of the intrinsic viscosities as a function of MW for the different star functionalities are shown in Figures 10–12. Within experimental error the slopes of the lines in

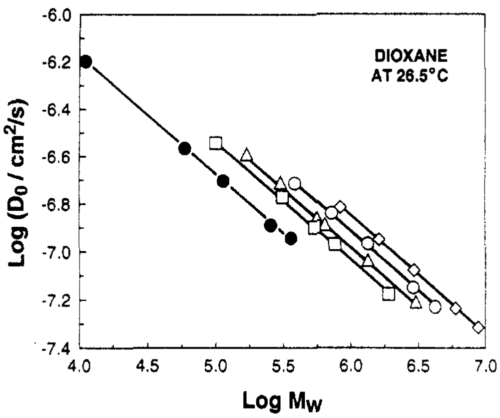


Figure 8. log–log plot of the translational diffusion coefficients against molecular weight for linear and star polybutadienes in dioxane at 26.5 °C (Θ-solvent). Symbols as in Figure 6.

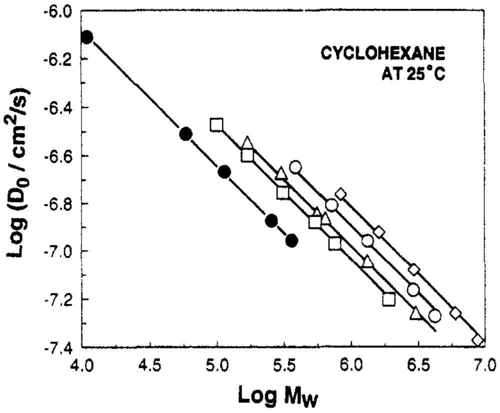


Figure 9. log–log plot of the translational diffusion coefficients against molecular weight for linear and star polybutadienes in cyclohexane at 25 °C. Symbols as in Figure 6.

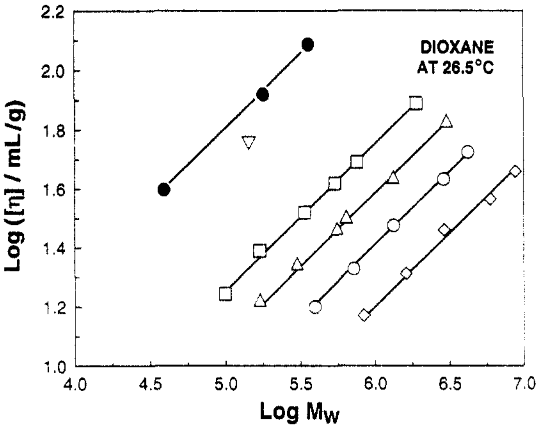


Figure 10. log–log plot of intrinsic viscosities against molecular weight for linear and star polybutadienes in dioxane at 26.5 °C. Symbols as in Figure 6.

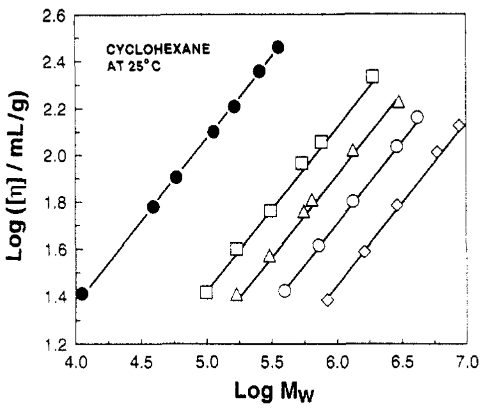


Figure 11. log–log plot of intrinsic viscosities against molecular weight for linear and star polybutadienes in cyclohexane at 25 °C. Symbols as in Figure 6.

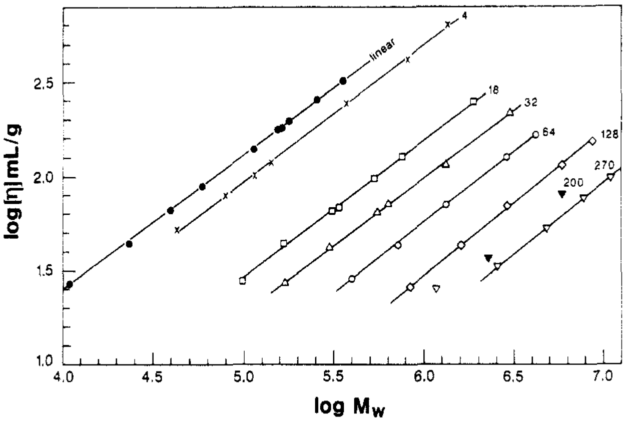


Figure 12. log–log of intrinsic viscosities against molecular weight for linear and star polybutadienes in toluene (good solvent). The number of arms in the stars is indicated on each line. Original data for the multiarm stars with 200 and 270 arms are given in ref 29.

these double-logarithmic plots are identical for all star functionalities and equal to the slope for linear polymers. This allows for the direct evaluation of the dilute-solution properties of regular star polymers as a function of the number of arms in the star.

Discussion

In the discussion we will first consider the interrelation of the different dilute-solution properties of the star polymers. This will lead to a consistent picture of the global dimensions of the stars. The experimentally observed dimensions, normalized with respect to those of the linear polymer of the same molecular weight, are independent of molecular weight and will then be used to test the Daoud–Cotton model for star polymers. Agreement or disagreement will decide the validity of the underlying scaling model for the segment density in the coil. Subsequently, we will relate the star properties to recent results obtained on polymeric micelles. In the final section the concentration dependence of the dilute-solution properties will be discussed. This involves measurements of k_H and k_D.

In Table IV are collected the experimental values of R_G and values of R_H and R_V calculated by

$$R_H = \frac{kT}{6\pi\eta_s D_0} \qquad (7)$$

and

$$R_V = \left(\frac{3}{10\pi N_A}[\eta]M\right)^{1/3} \qquad (8)$$

respectively. R_H is the Stokes radius, η_s is the solvent viscosity (η_s = 0.89 cP for cyclohexane at 25 °C and 1.168 cP for dioxane at 26.5 °C). The viscosity radius R_V is that of the equivalent sphere, and eq 8 is based on the Stokes–Einstein relation for the viscosity of a suspension of spheres: $\eta = \eta_s(1 + 2.5\phi)$, where ϕ is the volume fraction of spheres. From Table IV it can be seen that the ratio of the two hydrodynamic sizes: $R_V/R_H = 1.03 \pm 0.03$. A similar result was previously obtained for linear polymers and stars with fewer arms.[39] It is difficult to attach great significance to R_V/R_H ratios that are occasionally outside the limits of accuracy.[40]

From Table IV it can also be seen that within experimental error $R_H/R_G \approx 1.29 = (5/3)^{1/2}$, the value for the

Table IV. Radii of 64- and 128-Arm Regular Stars (Å)

	dioxane at 26.5 °C				cyclohexane at 25 °C				
sample	R_G	R_V	R_H	R_H/R_G	R_G	R_V	R_H	R_H/R_G	R_T
6407		100	97			118	109		128
6415		135	130			167	158		179
6430	(118)	185	175		185	238	225	1.21	257
6460	205	270	265	1.29	280	364	360	1.29	391
6480	225	328	320	1.42	341	458	458	1.35	487
12807		125	122			148	142		169
12814		174	167			215	206		236
12828	(152)	237	224		216	305	295	1.37	328
12856	238	326	322	1.37	345	459	447	1.30	478
12880	270	399	387	1.43	424	571	576	1.36	613

Table V. Characteristic Ratios of 64- and 128-Arm Polybutadienes

		good solvent		
ratio	Θ-solvent	cyclohexane	toluene	random walk
		64-Arm		
g	0.092	0.068		0.046[a]
g'	0.127	0.090	0.082_7	
h	0.54_9	0.49_3		0.295[b]
		128-Arm		
g	0.060	0.043		0.023[a]
g'	0.080_5	0.049_7	0.044_7	
h	0.47_2	0.41_3		0.211[b]

[a] $g = (3f-2)/f^2$.[14] [b] $h = f^{1/2}[2-f + (2)^{1/2}(f-1)]^{-1}$.[26]

uniform-density hard sphere.[26] A similar ratio has previously been observed for 32-arm stars.[13] For 18-arm stars slightly lower values of 1.24 in cyclohexane and 1.21 in dioxane at the Θ-temperature have been noted.[29,38] The full "hard-sphere" properties are therefore reached for f between 18 and 32. Bauer et al. found a more slowly increasing ratio of $R_V/R_G = 1.0$ at $f \approx 20$ and 1.16 at $f \approx 56$.[40] $R_H/R_G = 1.29$ is a very attractive and simple ratio. However, possible deviations, which have to do with the segment density distribution in the stars, have to be appreciated. In principle at least R_V/R_G may become larger than 1.29. This would be symptomatic of hard spheres with a denser center.[16,41] Indeed, some evidence for this trend exists in dioxane and to a lesser degree in cyclohexane for the highest molecular weight stars. In some dendrimer molecules the opposite has recently be observed. R_H/R_G decreases from about 1.29 for the fourth generation to 1.0 for the eighth generation material[42] and has been ascribed to a higher segment density at the outer edge of the dendrimer sphere.

Values of R_T, the thermodynamic radius, have also been collected in Table IV. They are calculated from A_2 according to[26]

$$R_T = \left(\frac{3A_2M_w^{\,2}}{16\pi N_A}\right)^{1/3} \tag{9}$$

In contrast to R_V and R_H, which are derived from zero concentration intercepts, R_T is derived from the concentration dependence of light scattered. We found that the accurate determination of increasingly small values of A_2 becomes gradually more difficult as f and MW increase. Furthermore, in contrast to R_G, $[\eta]$, and D_0, the $\log A_2 \propto \log M_w$ relation shows gradually increasing negative slopes with increasing f (see Figure 6). This confirms a trend already noted in the study of 32-arm stars[13] and multiarm stars with 270 arms.[29] Values of R_T are systematically approximately 7% larger than values of R_V and approximately 10% larger than R_H. Larger values of R_T/R_V have also been noted by Bauer et al.[40] for stars with $f > 10$. Note that our results lead to $R_T/R_G > 1.29$.

In order to study the dependence of the star dimensions on the functionality of the stars, the shrinkage due to branching can be evaluated by means of dimensionless parameters[14,26]

$$g = \langle R_G^{\,2}\rangle / \langle R_G^{\,2}\rangle_{\text{lin}} \tag{10}$$

$$g' = [\eta]/[\eta]_{\text{lin}} \tag{11}$$

$$h = (D_0)_{\text{lin}}/D_0 \tag{12}$$

where the subscripted property is that of the linear polymer with identical molecular weight. Values of g, g', and h have been calculated with the following relations for linear polybutadienes. In cyclohexane:

$$\langle R_G^{\,2}\rangle_{\text{lin}} = 2.55 \times 10^{-2} M_w^{\,1.18_3}\ (\text{nm}^2) \tag{13a}$$

$$[\eta]_{\text{lin}} = 3.75 \times 10^{-2} M_w^{\,0.69_7}\ (\text{mL/g}) \tag{13b}$$

$$(D_0)_{\text{lin}} = 1.45 \times 10^{-4} M_w^{\,-0.56_1}\ (\text{cm}^2/\text{s}) \tag{13c}$$

In dioxane:

$$\langle R_G^{\,2}\rangle_{\text{lin}} = 1.44 \times 10^{-3} M_w\ (\text{nm}^2) \tag{14a}$$

$$[\eta]_{\text{lin}} = 1.99 \times 10^{-1} M_w^{\,0.5}\ (\text{mL/g}) \tag{14b}$$

$$[D_0]_{\text{lin}} = 6.34 \times 10^{-5} M_w^{\,-0.49_6}\ (\text{cm}^2/\text{s}) \tag{14c}$$

In toluene:

$$[\eta]_{\text{lin}} = 2.85 \times 10^{-2} M_w^{\,0.73}\ (\text{mL/g}) \tag{15}$$

Values of g, g', and h for 64- and 128-arm stars are collected in Table V. Previously similar data have been obtained for 18-,[38] 32-,[13] and 270-arm[29] polybutadiene stars. Another rich source of data on polyisoprene stars is available.[40] Earlier results on lower functionality stars have recently been compiled in Table V of ref 29 and in Table IV of ref 37. Experimental values of g and h are substantially higher than the random-walk calculations given in the last column of Table V. This reflects the chain stretching due to steric crowding. This effect is described by the Daoud–Cotton scaling model for stars with many arms.[15] The model predicts that in the limit of large f and large N (the number of segments per arm)

$$g \propto f^{(1-3\nu)} \tag{16}$$

where $\nu = 0.5$ in the Θ-solvent and slightly less than 0.6 for the self-avoiding chain in a good solvent. Figure 13 shows values of g as a function of f for stars with $3 \le f \le 270$ in a Θ-solvent and in a good solvent. In the Θ-solvent, the f-dependence is stronger than predicted (−0.64 against −0.5). This is in contrast with the original finding which was based on $f \le 12$.[15] The larger experimental than theoretical slope (−0.64 against −0.5) suggests a breakdown of the scaling model under Θ-conditions. It also creates a dichotomy because there is experimental evidence that $R_G \propto N^{\nu}$ at all values of f. In the good solvent, the agreement with theory is excellent because the experimental exponent −0.73 leads to $\nu = 0.57_7$ for polybutadiene in cyclohexane in good agreement with the direct experimental determination of ν from radii of gyration measurements on linear polymers ($R_G \propto M_w^{\,0.59_1}$). Note that the values of g for multiarm stars with a polymeric core are larger than those for the regular stars especially in the Θ-solvent.[29] This was already commented upon in the

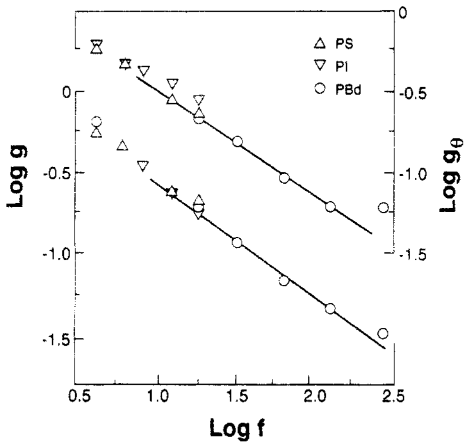


Figure 13. log–log plot of $g = \langle R^2\rangle/\langle R^2\rangle_{\rm lin}$ and $g_\Theta = \langle R^2\rangle_\Theta/\langle R^2\rangle_{{\rm lin},\Theta}$ as a function of the number of arms for regular star polymers. Symbols: (△) polystyrene stars; (▽) polyisoprene stars; (○) polybutadiene stars.

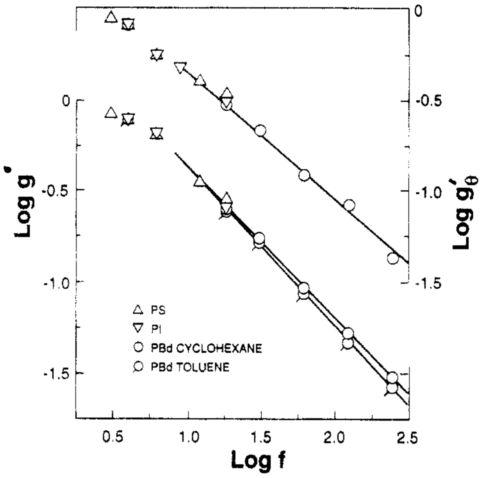


Figure 14. log–log of $g' = [\eta]/[\eta]_{\rm lin}$ and $g_\Theta' = [\eta]_\Theta/[\eta]_{{\rm lin},\Theta}$ as a function of the number of arms of the stars. Symbols as in Figure 13. Data for polybutadiene stars in toluene have been marked with a pip.

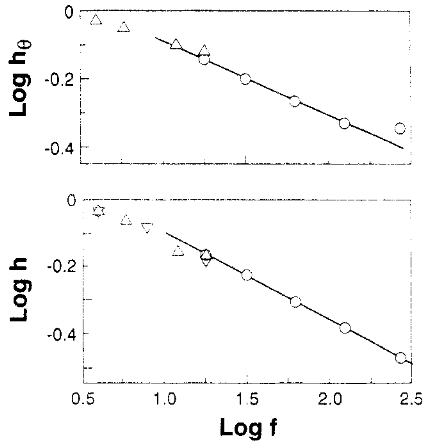


Figure 15. log–log plot of $h_\Theta = (D_0)_{{\rm lin},\Theta}/(D_0)_\Theta$ and $h = (D_0)_{\rm lin}/D_0$ as a function of the number of arms. Symbols as in Figure 13.

study of the 32-arm stars.[17] Star polymers with large divinylbenzene cores show a similar departure.[40] It is possible that R_G is very sensitive to the size of the core. Since experimentally $\langle R_G^2\rangle$ is a z-average, polydispersity may be contributing to the effect.

Plots of g' and h against f are shown in Figures 14 and 15 both in the Θ-solvent and the good solvent. Numerical data for low functionality stars have been collected previously.[37] The good correlations are gratifying as they attest to the quality of the samples. In the case of the g' and h the slopes have no direct physical meaning. Note that g' is much less sensitive than g to polydispersity and the nature of the star core. Indeed the multiarm star polymers with 270 arms fall nicely on the common lines. This is also true for h at least in the good solvent but not in the Θ-solvent. It is interesting to see that g' of stars in toluene are consistently smaller than those in cyclohexane. This reflects the slightly better solvent quality of toluene as can be deduced from the larger exponent in eq 15 than in eq 13b.

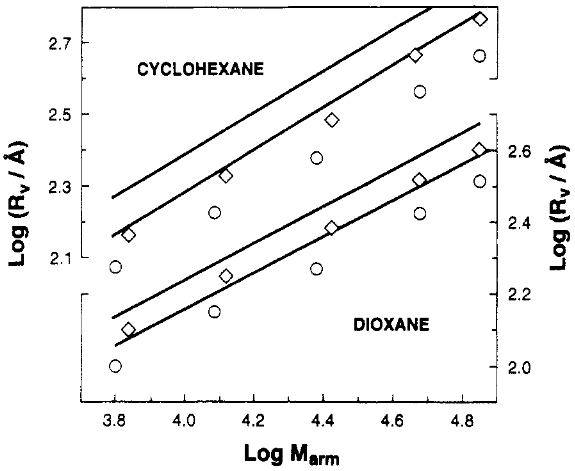


Figure 16. Double-logarithmic plot of the viscosimetric radius of the star against the molecular weight of a single arm of the star. Top: cyclohexane. Symbols for experimental data: (○) 64-arm stars; (◇) 128-arm stars. Lines: calculated with the Gast model, eq 22 with $\nu = 0.58_3$. Bottom: dioxane. Symbols as for cyclohexane. Lines calculated with $\nu = 0.5$.

Gast et al. have recently proposed a quantitative model based on the Daoud–Cotton radial density distribution of polymer segments.[12] The segment density in the star is

$$\rho(r) = A(r/a_s)^{1/\nu} r^{-3} \qquad (17)$$

for $R_c < r < R$ where R_c represents the radius of the core. Beyond R, $\rho(r) = 0$. As in the Daoud–Cotton model the size of the blob is given by

$$\xi(r) = 4r/f^{1/2} \qquad (18)$$

and each blob contains $(\xi/a_s)^{1/\nu}$ monomers.

The coefficient of proportionality in eq 17 is determined by calculating the segment density at R_c

$$A(f) = \frac{3.4^{1/\nu} f^{(3\nu-1)/2\nu}}{32\pi} \qquad (19)$$

and the radius of the star is found from

$$Nf = \int_0^R \rho(r)\, 4\pi r^2\, dr \qquad (20)$$

This yields

$$R = \left[\frac{8Na_s^{1/\nu} f^{(1-\nu)/2\nu}}{3 \times 4^{1/\nu}\nu}\right]^{\nu} \qquad (21)$$

where N is the number of segments with a step length a_s per arm. For polybutadiene $a_s = l_0C_\infty = 1.47$ Å × 5.1 = 7.5 Å[43] and $N = (M/M_0)(3.86/C_\infty)$. Comparison of the experimental R_v data with this model is shown in Figure 16. In general, the calculated radii are about 15% larger than the experimental values in the Θ-solvent. A similar discrepancy has been observed by Gast for polystyrene micelles.[21] In the good solvent the discrepancy increases to 30%. Considering the approximations of the model, the agreement is rather remarkable.

The concentration dependence of the intrinsic viscosity measurements yields the Huggins constant k_H according to eq 6. Values have been collected in Tables II and III. It is interesting to note that k_H increases according to 0.72, 0.77, 0.88, and 0.98 for 18-, 32-,[17] 64-, and 128-arm stars, respectively, in cyclohexane. The Huggins constant for linear polybutadiene in good solvents in typically 0.30–0.35. Values of k_H in dioxane (Θ-solvent) and toluene are not significantly different for the stars. An expansion of Einstein's equation for the viscosity of a suspension of spheres yields $k_H = 6.2/(2.5)^2 = 0.99$.[44] Experimental evidence however suggests that the coefficient of the ϕ^2 term may be larger than 6.2.[45]

It is worth noting that the curvature in η_{sp}/c vs c plots for the star polymers is already apparent at $c = (10[\eta])^{-1}$, i.e., much below the so-called overlap concentration. Similar but less pronounced curvature was also observed for 32-arm stars[13] and multiarm stars with 270 arms.[29]

Finally we have to mention the concentration dependence of D (see eq 5). As for A_2, the initial concentration dependence of D is extremely small and difficult to determine with high precision. The numerical coefficient k_D includes a friction as well as a thermodynamic contribution according to[26]

$$k_D = 2A_2M - k_0\left(\frac{4\pi}{3}N_A\frac{R_H^{\,3}}{M}\right) - \bar{\nu} \qquad (22)$$

where $\bar{\nu}$ is the partial specific volume (1.10 mL/g) and k_0 is a constant. Application of eq 22 to the 64-arm and 128-arm star experimental results yields k_0 between 7 and 11 in cyclohexane and between 1.5 and 4 in dioxane, in remarkable agreement with the Pyun and Fixman calculation of k_0.[26] It appears therefore that k_0 in eq 6 is independent of the chain architecture for linear and all regular star polymers.

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