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Synthesis and Characterization of Multiarm Star Polybutadienes†

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ABSTRACT: Low molecular weight poly(1,2-butadiene) extensively hydrosilylated with methyldichlorosilane has been used as a coupling agent to prepare multiarm star poly(1,4-butadienes). From a linear poly(1,2-butadiene), stars with 270 arms have been prepared with arm lengths from 4500 to 42 300. From a 18-arm star poly(1,2-butadiene), stars with 200 arms have been obtained. The multiarm stars are characterized by light scattering, intrinsic viscosity, and translational diffusion coefficient measurements in a Θ solvent (dioxane) and in good solvents (cyclohexane and toluene). The exponents of the radius of gyration and intrinsic viscosity molecular weight relations increase with increasing molecular weight to the values observed for linear poly(1,4-butadiene). Values of $g = \langle s^2 \rangle / \langle s^2 \rangle_l$ are 3–5 times larger than the random walk values. Similarly, values of $h = (D_0)_l / D_0$ are 2–3 times larger. The scaling model for star polymers of Daoud and Cotton predicts the size of the multiarm stars reasonably well. The Flory constants ϕ' and P' of these star polymers are essentially those for the hard sphere, and the ratio (Flory–Mandelkern constant) $\phi^{1/3}/P = 9.9 \times 10^6$ ($[\eta]$ in milliliters/gram) gram) is identical with the value for linear and regular star polymers with fewer arms.

Introduction

The study of branched polymers and especially the study of regular star polymers has contributed significantly to our understanding of the relationship between the large-scale molecular structure of polymers and their properties. Moreover, the synthesis and study of the properties of star polymers have led directly to a number of industrial applications, e.g., as melt strength improvers.[1,2] Especially diblock star copolymers have a wide range of applications.[3,4]

Regular stars with 3, 4, 6, 8, and 12 arms have been prepared by means of multifunctional Si–Cl coupling agents and living anionic prepolymers. Their properties are now quite well-known.[5,6] As the number of arms increases, the required purity of the multifunctional Si–Cl coupling agent becomes more difficult to meet. Recently, the synthesis of model star polymers with 18 arms has also been realized,[7–9] and the characterization of the properties of these polymers is progressing.[8,10–12]

A practical method for preparing star polymers with more than 20 arms involves the block copolymerization of a living polymer with divinylbenzene (DVB).[13] The reaction was first exploited by Rempp and co-workers to prepare polystyrene stars with up to 16 arms.[14,15] Polydiene stars with up to 50 arms can be produced by the divinylbenzene method.[16] In general, the number of arms in the star increases with the divinylbenzene/RLi ratio, although it also depends on the reaction time and temperature.[16,17] The divinylbenzene method is more suited to prepare a series of stars with a varying number of arms while keeping the length of the arms constant. The distribution of molecular weight due to a distribution of the number of arms is difficult to assess. Moreover, the divinylbenzene-coupled stars have a rather large central poly(divinylbenzene) nodule because the number of arms, f, appears to increase as $f = [\mathrm{DVB}]/[\mathrm{RLi}] + 10$ when $f > 20$[16] and each arm contributes [DVB]/[RLi] divinylbenzene monomers to the nodule. An extreme case of a large central nodule in a star polymer is produced by the microgel method of Eschwey and Burchard.[18] In this method, n-BuLi is first allowed to form a dense microgel of poly(divinylbenzene) containing numerous C–Li bonds, which are then used to initiate the polymerization of added styrene. Stars with a large number of arms can easily be prepared in this way, but the central nodule carrying e.g. 200 active C–Li bonds has a molecular weight of approximately 1×10^5.[19] Another synthetic possibility leading to stars was described in which a 22 000 poly(methacrylate) macromer was homopolymerized to a polymer with MW $= 1 \times 10^6$ (46 arms).[20]

Table I
Scaling of Star Dimensions

region	condition	R_G[a]	g[b]
hard core	$N \ll f^{1/2}$	$(Nf)^{1/3} l$	$N^{-1/3} f^{-1/3}$
unperturbed	$f^{1/2} \upsilon^{-2} \gg N \gg f^{1/2}$	$N^{1/2} f^{1/4} l$	$f^{-1/2}$
self-avoiding	$N \gg f^{1/2} \upsilon^{-2}$	$N^{3/5} f^{1/5} l$	$f^{-4/5}$

[a] Radius of gyration. [b] $g = R_G^2/(R_G^2)_l$.

There are presently several incentives to study regular star polymers with more than 20 arms. Daoud and Cotton were the first to study the conformation and dimensions of stars by means of the scaling ideas.[21] The picture presented for a star polymer consists of three regions, a central core, a shell with a semidilute segment density in which the arms have the unperturbed chain conformation, and an outer shell in which the arms of the star assume a self-avoiding (good solvent) conformation. The relative importance of each region depends on the number of arms, f; the solvent quality, $\upsilon = 1/2 - \chi$ (χ is the Flory interaction parameter); and the number of monomers per arm, N, each with a statistical length, l. In dilute solution, the radius of gyration scales differently when each of these regions dominates, as shown in Table I. These ideas have been further elaborated.[22,23] Two computer simulations of the conformations of stars with $f \leq 24$[24] and $6 \leq f \leq 50$[25] with $N \leq 100$ and mimicking good solvent conditions have recently provided the first tests of the scaling ideas for stars with more than 18 arms.

Stars with many arms (the critical number of arms is estimated to be of the order 10^2) are expected to form macrocrystal ordered solutions when their concentration is near the overlap concentration.[26] Star polymers with many arms may also be good models for colloidal stabilization by grafted polymers. Indeed, in the Daoud–Cotton picture of star polymers, the arms of a star are contained within an outwardly widening cone, and a similar picture

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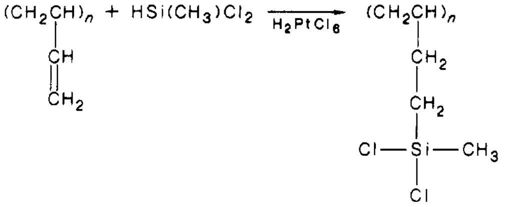
is used to describe colloidal stabilization by grafted polymers.[27,28] Polymers with one ionic end group naturally associate into starlike agglomerates in low dielectric media.[29-31] The degree of association varies with the chain length, the counterion, its concentration, and the overall polymer concentration and is therefore difficult to study. Starlike micelles are the natural structures of diblock copolymers in a selective good solvent for one of the blocks.[28,32,33]

The examples given indicate that there are quite a number of practical situations in polymer science where starlike structures are encountered. For these regular star polymers with a large number of arms constitute a basic model. The synthesis of stars with 270 arms and their dilute solution properties are described in this paper. The dilute solution properties of these stars are compared with those of stars with up to 18 arms and with linear polymer. Where possible, comparison with theoretical proposals is made.

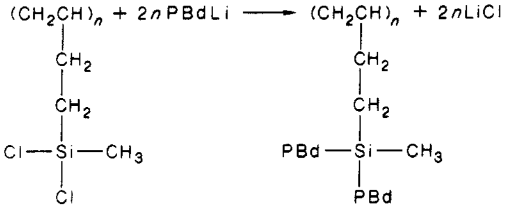
Experimental Section

Synthesis. The multiarm star polybutadienes were prepared by coupling perhydrosilylated poly(1,2-butadiene) with poly(1,4-butadienyl)lithium. Schematically this is



$$(CH_2\underset{\underset{CH_2}{\parallel}}{\underset{|}{C}H})_n + HSi(CH_3)Cl_2 \xrightarrow[H_2PtCl_6]{} (CH_2CH)_n\text{–}CH_2CH_2\text{–}Si(Cl)_2\text{–}CH_3 \qquad (1a)$$

and



$$(CH_2CH)_n\text{–}CH_2CH_2\text{–}Si(Cl)_2\text{–}CH_3 + 2n\,PBdLi \longrightarrow (CH_2CH)_n\text{–}CH_2CH_2\text{–}Si(PBd)_2\text{–}CH_3 + 2n\,LiCl \qquad (1b)$$

The starting poly(1,2-butadiene) (eq 1a) was either a linear polymer (M_n = 9040 by vapor pressure osmometry) or a 18-arm star polymer ($(M_n)_{arm}$ = 1040; M_n = 18 × 1040). The former is the precursor to the LS series, the latter to two SLS samples. These polymers were prepared anionically with *sec*-butyllithium in benzene in the presence of 1,2-dipiperidinoethane (4:1 *s*-BuLi) at 4 °C.[34] The linear polymer was terminated with degassed *tert*-butyl alcohol. For the preparation of the 18-arm star polymer, the living polymer was coupled with $[(Cl_3SiCH_2CH)_3SiCH_2]_2$.[7] After termination with *tert*-butyl alcohol, the excess arm material was removed by fractional precipitation. The purity of the 18-arm star was confirmed by size exclusion chromatography (SEC). The synthesis of the poly(1,2-butadiene) is performed with the usual vacuum techniques.

The hydrosilylation reaction (eq 1a) was performed in benzene with chloroplatinic acid catalyst (Speier). Water was rigorously excluded. The polymer, benzene, and catalyst were first treated overnight with 0.1 mL of $(CH_3)_3SiCl$. Freshly distilled $HSi(CH_3)Cl_2$ was then added and the temperature raised to 75 °C. Darkening of the mixture, vigorous boiling, and refluxing indicated the start of the reaction. (The reaction flask was temporarily withdrawn from the thermostat.) The reaction was continued for 4 h at 75 °C. These conditions are milder than other reported for the hydrosilylation of polybutadienes.[35,36] The hydrosilylated polymer was freeze dried under high vacuum for 2 days. The polymer was dissolved in high-purity, *n*-butyllithium-treated benzene, sealed under vacuum, and subdivided into ampules.

The poly(1,4-butadienyl)lithium used in reaction 1b was prepared with *sec*-butyllithium in benzene at room temperature and added slowly to the stirred hydrosilylated polymer. The coupling reaction was allowed to proceed for 1 week, triethylamine was added, and the reaction was continued for 1–2 weeks more. Excess poly(butadienyl)lithium was then terminated with *tert*-butyl alcohol. The star polymer is protected against oxidation by 2,6-di-*tert*-butyl-*p*-cresol and fractionated in a benzene–methanol mixture. A middle fraction is retained for further study. The polymers were finally precipitated in methanol containing antioxidant, dried to constant weight in vacuum, and stored under vacuum in the dark.

Dilute Solution Characterization. SEC was routinely used to monitor the polymerization and coupling reactions. A series of Waters microstyragel columns of nominal porosity 10^6, 10^5, 10^4, 10^3, and 500 Å was used. THF with a flow rate of 1 mL/min was the solvent.

The microstructure of the polybutadienes was checked by ^1H and ^{13}C NMR spectroscopies in $CDCl_3$. The poly(1,2-butadienes) have more than 99% 1,2 units. The 1:2:1 α-carbon absorption between 113 and 115 ppm from tetramethylsilane indicates that the polymers are atactic. The poly(1,4-butadiene) arm material has typically 8% 1,2 and 50% cis- and 42% trans-1,4 units.

The number-average molecular weights were determined by vapor pressure osmometry with a Wescan 233 in toluene at 50 °C when M_n < 20000 and with a Hewlett-Packard 503 membrane osmometer at 35 °C when M_n > 20000.

Weight-average molecular weights of the star polymers were determined in cyclohexane at 25 °C with a Fica 50 photogoniometer. The wavelength of the vertically polarized light is 436 nm. The Rayleigh ratio of benzene is 49×10^{-6}, and the differential refractive index increment, dn/dc, for polybutadiene in cyclohexane is 0.117_5.[37] Some weight-average molecular weights were also determined in dioxane at 26.5 °C with $dn/dc = 0.117_2$.[37]

The *z*-average radii of gyration, $\langle s^2 \rangle_z$, were determined from the initial slope of the angular dependence, Θ, of the light scattered at λ = 436 and 366 nm. Common plots of $(I_0/I_\Theta)_{c\to 0}$ versus q^2, where $q = 4\pi(n/\lambda)\sin(\Theta/2)$, show little or moderate curvature. n is the refractive index of the solvent. Values of $\langle s^2 \rangle_z$ were also evaluated by the Berry method.

Molecular weight distributions were estimated by analyzing the DRI (mass) and LALLS (molecular weight) traces of a SEC-KMX-6 in-line system. Five ultrastyragel columns (10^6, 10^5, 10^4, 10^3, and 500 Å) were used in these experiments.

Intrinsic viscosities of the multiarm star polymers were determined in toluene at 35 °C, in cyclohexane at 25 °C, and in dioxane at 26.5 °C with Cannon-Ubbelohde semimicroviscometers. Flow times, longer than 150 s, were measured electronically to 0.02 s.

Quasi-elastic light scattering measurements were made with a Spectra Physics Model 164 argon-ion laser operating at 514.5 nm. A floating Newport research table was used for vibration isolation. The scattered intensity was measured with a Brookhaven detection system, using a ITT FW130 photomultiplier tube. After amplification and discrimination, the pulse train was sent to a 256-channel Langley-Ford autocorrelator for analysis. Homodyne intensity autocorrelation functions were collected at 10 scattering angles (10°, 13.0°, 16.9°, 22.1°, 28.8°, 37.8°, 49.6°, 66.3°, 90.6°, and 135°) to ensure that the observed relaxation process was only due to translational diffusion and was not complicated by internal degrees of freedom of the scatterer.

The resultant intensity autocorrelation functions, $C(t) = \langle I(0)I(t) \rangle$, were then fit by using the method of cumulants. To do this, the incoherent baseline had first to be subtracted from $C(t)$. This baseline was determined by two means: using the delayed channels in the autocorrelator to give $C(t\to\infty)$ and *calculating* the baseline from the number of pulses sent to the autocorrelator in the course of the experiment. These estimates of the baseline were always in very good agreement, but in order to be systematic, the calculated baseline was always used. After baseline subtraction, the logarithm of the correlation function was fit to $\log C(t) = a + 2\Gamma t + ct^2$, where Γ is the initial relaxation rate, or first cumulant. This fit was done in a self-consistent fashion to ensure that any errors in Γ would be systematic. In practice, the entire correlation function was first fit to get an initial estimate of Γ. Then only that portion of the correlation function with $t < 1/2\Gamma$ was fit to get an improved estimate of Γ until a condition of self-consistency was achieved; i.e., until the value obtained for $1/2\Gamma$ was equal to the time domain over which the data were fit. The diffusion coefficient was then determined from the relation

Table II
Molecular Weight Characterization of Multiarm Star Polybutadienes

sample	$10^{-6}M_w$[a]	$10^{-3}(M_n)_{arm}$[b] V.P.	$10^{-3}(M_n)_{arm}$[b] OSM	$\bar{f}$[c]	(M_w/M_n)[d]
LS2B4	1.2	4.46		267	1.00_7
LS3B3	2.6	9.3_3		278	1.02_6
LS4B2	4.9	17.3	18.3	267	1.04_6
LS5B2	7.9		29.3	269	
LS6B2	11.2		42.3	263	
SLS1B3	2.3	11.3		202	
SLS2B2	5.9		33.0	180	

[a] By light scattering in cyclohexane at 25 °C. [b] By vapor pressure osmometry or membrane osmometry in toluene. [c] Equation 1. [d] By SEC–LALLS.

$\Gamma = Dq^2$, and the hydrodynamic radius was computed from the Stokes–Einstein relation $D = kT/6\pi\eta_0 R_h$, where η_0 is the solvent viscosity.

Results

The weight-average molecular weights of the multiarm star polybutadienes are collected in Table II together with the number-average molecular weights of the arms. These star polymers contain a small central nodule, M_c, which, if all $HSi(CH_3)$ groups are included, is less than 1.26% of the total mass of LS2 and decreases to 0.13% for LS6. Although the synthesis is similar to that for the preparation of comb polymers, the low backbone content makes these polymers starlike. Some details of this problem are dealt with at the end of the discussion. The molecular weights of Table II permit the calculation of the average number of arms per star according to

$$\bar{f} = \frac{(M_w)_{star} - M_c}{(M_n)_{arm}} \tag{2}$$

Values of $\bar{f}$ are given in Table II. For the LS series, $\bar{f}$ = 269. The small deviations of individual values of $\bar{f}$ can be ascribed to errors in the determination of $(M_w)_{star}$ and/or $(M_n)_{arm}$. A 5% error in either value would change $\bar{f}$ by 13 branches. The SLS polymers have $\bar{f}$ = 200.

The number of arms in the stars is essentially determined by the extent of reaction 1a. Although the yield of this reaction is consistently higher than 30%, we could not obtain complete control over the yield. Reaction 1b goes essentially to completion. This is suggested by the final constant poly(butadienyl)lithium concentration that is reached in reaction 1b. Furthermore, if the living end concentration is less than the Si–Cl concentration, the resulting star polymer contains unreacted Si–Cl bonds (experiment LS1, not quoted in the tables) and slowly develops a distinct high molecular weight tail in its SE chromotogram. This is consistent with the coupling of star polymers through hydrolysis of residual Si–Cl bonds.

The star polymers produced by reactions 1a and 1b have a distribution of molecular weights. This distribution originates in the original molecular weight distribution of the poly(1,2-butadiene) and in a distribution of the number of sites that are hydrosilylated per chain. For the purpose of estimating the polydispersity of the star polymers, it is more convenient to consider them as constructed like comb polymers with branches on a backbone. A good estimate of polydispersity is given by the average number of branches ($\bar{f}$) due to random placement of branches on polydisperse backbones. According to Orofino,[38]

$$\bar{f} = f_n\frac{x_w}{x_n} + \frac{y(x_n - f_n)}{x_n(x_w + f_n y)} \tag{3}$$

where f_n is the number of arms of the monodisperse backbone and x and y refer to the degree of polymerization of the backbone and the arms, respectively. In the case at hand, f_n is the number of branch *sites*, and y is equal to 2 times the degree of polymerization of the arms. The first term in the parentheses of eq 3 can be estimated. The linear polybutadiene of the LS series with M_n = 9040 has a theoretical Poisson molecular weight distribution with $x_w/x_n = 1 + 1/x_n = 1.006$. The 18-arm star poly(1,2-butadiene) precursor of the SLS series has also a narrow molecular weight distribution according to[39] $(x_w/x_n) \approx 1 + (1/18)(x_w/x_n)_{arm} = 1.003$. The second term in parentheses of eq 3 is 0.0014 for the LS series and 0.007 for the SLS series. Therefore, $\bar{f} \approx f_n$ for the stars. A calculation of M_w/M_n for the stars assuming a Gaussian distribution of branch sites confirms the narrow molecular weight distribution for the LS and SLS series.

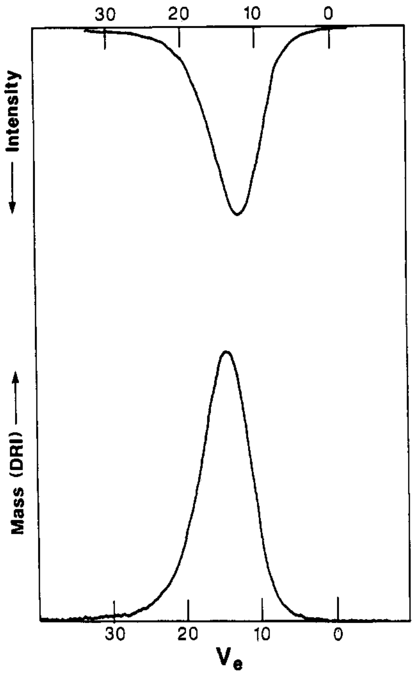


Figure 1. Size exclusion chromatogram of LS3B3. Top: Low-angle laser light scattering signal. Bottom: Differential refractive index signal.

The M_w/M_n ratio of the star polymers can be estimated experimentally from the SEC–LALLS experiment. An example is shown in Figure 1. The molecular weight distribution functions of LS3B3 derived from the data in Figure 1 are shown in Figure 2. The experimental values of M_w/M_n for the LS polymers are given in Table II. The ratios M_w/M_n are less than 1.05. It should be pointed out that these M_w/M_n are minimum values.[40] M_w/M_n is very sensitive to baseline drift and the measurement of the delay between the two detectors. Samples LS5 and LS6 are not completely resolved by the column set used for the SEC–LALLS measurements. As is so often found in polymers prepared by anionic polymerization techniques, the theoretical molecular weight distribution underestimates the real one.

The dilute solution properties of the multiarm polybutadienes in dioxane at 26.5 °C and in cyclohexane at 25 °C have been collected in Table III. The former solvent is a Θ solvent for linear polybutadiene. In the case of the multiarm stars, it is difficult to determine the temperature at which A_2 becomes zero because values of A_2 are extremely low and vary little with temperature. It has been observed, however, that the multiarm star polybutadienes precipitate at 23 °C from the very dilute solution used for the light scattering measurements. Fortunately, no strong

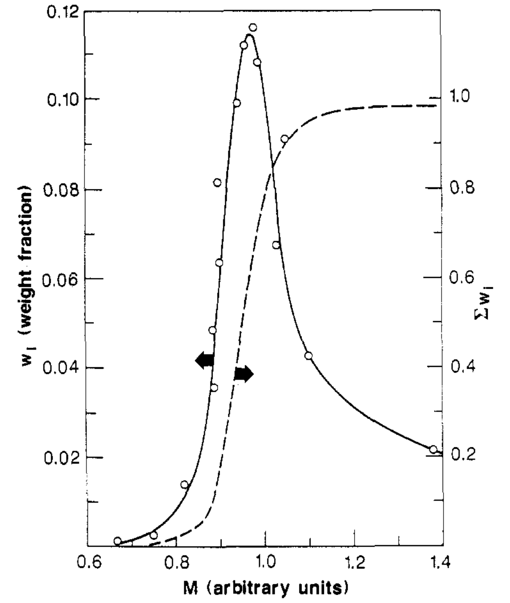


Figure 2. Weight fraction and cumulative weight fraction as a function of molecular weight (arbitrary units) for LS3B3 calculated from the size exclusion chromatograms in Figure 1.

Table III
Dilute Solution Properties of Multiarm Star Polybutadienes

sample	$10^{-6}M_w$	$\langle S^2 \rangle$, nm^2	10^5A_2, mL/g^2	$[\eta]$, mL/g	10^7D_0, cm^2/s
		Solvent: Dioxane at 26.5 °C (Θ Solvent)			
LS2	1.17	137		15.0	1.35
LS3	2.6	216		18.1	0.97_2
LS4	5.0	424		21.8	0.68_5
LS5	9.2	992		27.7	
LS6	12.4	1156		31.4	0.40_0
SLS1	2.2	185		16.9	
SLS2				28.8	
		Solvent: Cyclohexane at 25 °C			
LS2	1.17	159	3.2	24.0	1.50_7
LS3	2.6	296	1.8	33.5	1.04_1
LS4	4.9	600	1.0_5	49.0	0.80_7
LS5	7.9	1350	1.1	73.2	
LS6	11.2	1800	0.9	90.0	0.45_2
SLS1	2.3	282	2.1_4	33.2	
SLS2	5.9	980	1.3	74.0	

dependence of $\langle s^2 \rangle_z$ on temperature near Θ is found. The Θ temperature of 18-arm star polybutadienes in dioxane is also 26 ± 1 °C.[8]

The radii of gyration of the stars in dioxane and cyclohexane are plotted double logarithmically in Figure 3. In cyclohexane, the $\langle s^2 \rangle$ versus M relation changes from approximately 0.85 at low MW to 1.2 at high molecular weight. In dioxane, the slope of logarithmic plot of $\langle s^2 \rangle$ versus M changes from $^2/_3$ to 1. Lines representing data for linear[37] polybutadienes are included as references. Within experimental error, the high MW limiting slopes for the multiarm stars are identical with those for the linear and 18-arm stars. Comparison of $\langle s^2 \rangle$ and $\langle s^2 \rangle_\Theta$ in Table III reveals that the low MW multiarm star polybutadienes expand very little (if at all) from their Θ state when dissolved in a good solvent. Even at $M = 10^7$, $\alpha^2 = \langle s^2 \rangle / \langle s^2 \rangle_\Theta$ is only 1.5_5 compared to more than 4 for a linear polymer with the same molecular weight.

The $[\eta]$–M relations for the multiarm stars are plotted double logarithmically in Figure 4. As for the $\langle s^2 \rangle$–M relation in Figure 3, the data can be joined by upward concave curves. It is observed that the high molecular weight limiting slopes in Figure 4 for the multiarm stars are approximately equal to the Mark–Houwink–Sakurada exponent for linear polybutadienes.

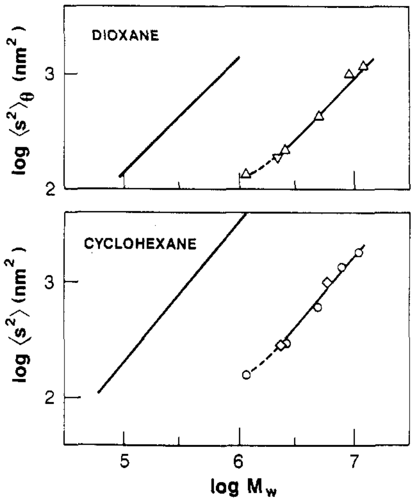


Figure 3. Double-logarithmic plots of the radius of gyration against molecular weight for the multiarm star polybutadienes. Top: Dioxane (Θ). Bottom: Cyclohexane. Lines representing the data for linear polybutadienes are shown for comparison. (○, △) LS series; (◇, ▽) SLS samples.

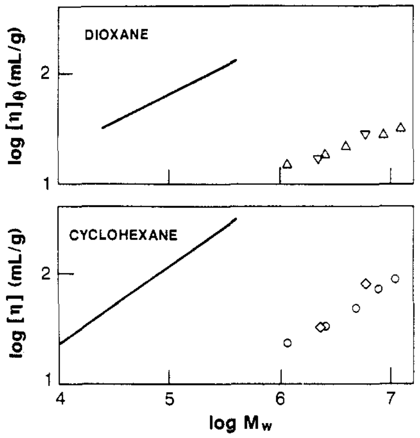


Figure 4. Double-logarithmic plots of the intrinsic viscosity against molecular weight for multiarm polybutadiene stars. Top: Dioxane (Θ). Bottom: Cyclohexane. The lines representing linear polybutadiene are shown for comparison. Symbols as in Figure 3.

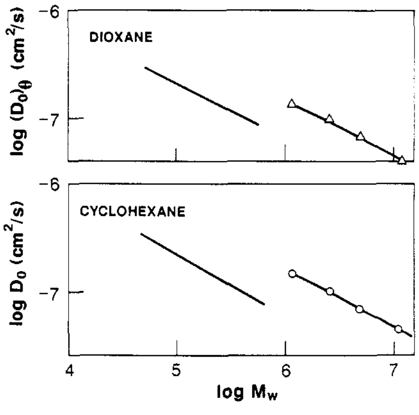


Figure 5. Double-logarithmic plots of the translational diffusion coefficient extrapolated to zero concentration against molecular weight for multiarm polybutadienes. Top: Dioxane (Θ). Bottom: Cyclohexane. Symbols as in Figure 3.

In Figure 5 the translational diffusion coefficients of the star polymers in dioxane and cyclohexane are shown double logarithmically against molecular weight. As has been observed with star polymers with fewer arms, D_0

Table IV
Intrinsic Viscosities and g' of Multiarm Star Polybutadienes in Toluene at 35 °C

sample	$10^{-6}M_w$	$[\eta]$	g'^{a}
LS2	1.17	$25._5$	0.033
LS3	2.6	$36._2$	0.026
LS4	4.9	$53._3$	0.024
LS5	7.9	$76._2$	0.024
LS6	11.2	$97._5$	0.024
SLS1	2.3	$37._0$	0.030
SLS2	5.9	81	0.032

[a] Based on $[\eta]_{lin} = 2.85 \times 10^{-2}M^{0.73}$.[37]

varies less with the number of arms than either $\langle s^2\rangle$ or $[\eta]$. Again, a curve represents best the molecular weight dependence of D_0.

The data for linear polybutadiene in dioxane are based on published results.[41] They are summarized by

$$\langle s^2\rangle_\Theta = 1.44 \times 10^{-3}M_w \quad (\mathrm{nm}^2) \tag{4a}$$

$$[\eta]_\Theta = 1.99 \times 10^{-1}M_w^{0.5} \quad (\mathrm{mL/g}) \tag{4b}$$

The diffusion coefficient of five selected linear polybutadienes has been measured in dioxane at 26 °C. The results can be fitted to

$$D_0 = 6.67 \times 10^{-5}M^{-0.50} \quad (\mathrm{cm}^2/\mathrm{s}) \tag{4c}$$

when the −0.50 exponent is imposed to reflect the Θ-temperature conditions. A least-squares analysis of the experimental data yields $D_0 = 6.34 \times 10^{-5}M^{-0.49_6}$.

The data on linear polybutadienes in cyclohexane which are shown in Figures 3–5 have not been published previously.[41] They are summarized by

$$\langle s^2\rangle = 1.88 \times 10^{-4}M^{1.20_7} \quad (\mathrm{nm}^2) \tag{5a}$$

$$A_2 = 1.32 \times 10^{-2}M^{-0.21_8} \quad (\mathrm{mL/g}^2) \tag{5b}$$

$$[\eta] = 3.75 \times 10^{-2}M^{0.69_7} \quad (\mathrm{mL/g}) \tag{5c}$$

$$D_0 = 1.45 \times 10^{-4}M^{-0.56_1} \quad (\mathrm{cm}^2/\mathrm{s}) \tag{5d}$$

From the intrinsic viscosity–molecular weight relation, it appears that cyclohexane is a slightly less good solvent than toluene ($[\eta] = 2.85 \times 10^{-2}M^{0.73}$),[37] the solvent that has been traditionally used to characterize anionic polybutadienes.[8,37,41–43] The constants in eq 5c agree well with the recent results of Colby et al.[44] ($K = 4.09 \times 10^{-4}$ and $a = 0.69_3$). There is also excellent agreement for eq 5b with the values quoted in Table II of ref 44.

Intrinsic viscosities of the multiarm star polybutadienes in toluene have also been determined. The results are collected in Table IV. These data can be compared with the intrinsic viscosities of linear,[37] 4-arm star,[41] and 18-arm[8] star polybutadienes.

Discussion

Comparison of properties of branched polymers and linear polymers is made by means of three ratios defined for the radius of gyration, the hydrodynamic radius, and the intrinsic viscosity respectively, by

$$g = \langle s^2\rangle / \langle s^2\rangle_l \tag{6a}$$

$$h = R_h/(R_h)_l = (D_0)_l/D_0 \tag{6b}$$

$$g' = [\eta]/[\eta]_l \tag{6c}$$

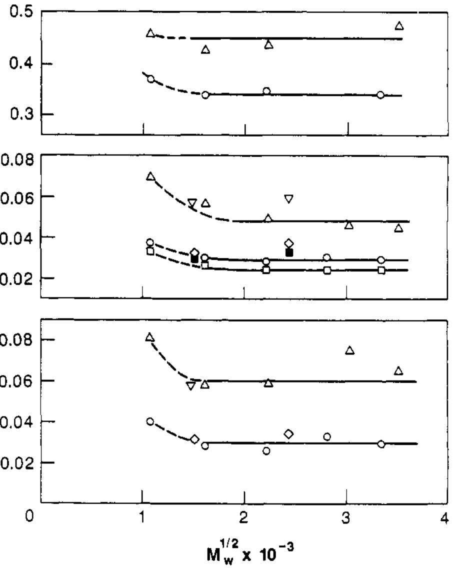


Figure 6. Variation of h, g', and g with molecular weight of the multiarm star polymers. Dioxane: (△) LS series; (▽) SLS series. Cyclohexane: (○) LS series; (◇) SLS series. Toluene: (□) LS series; (■) SLS series.

Table V
High Molecular Weight Limiting Shrinkage Parameters for Multiarm Star Polybutadienes

	g	g'	h
Θ solvent	0.06	0.045	0.45
good solvent			
cyclohexane	0.03	0.029	0.34
toluene		0.025	
random walk	0.011		0.147

Each of these ratios has a Θ condition value indicated by the subscript Θ. Because the experimental Θ condition sometimes depends on the type and number of branches of the polymer,[45] the $A_2 = 0$ Θ condition of the linear polymer is taken as the working reference. The three ratios depend also on the quality of the solvent. The ratios in eq 6 are determined at constant molecular weight. Plots of g, h, and g' against molecular weight are shown in Figure 6. In all cases, g, h, and g' decrease with increasing molecular weight to high molecular weight limiting values. These are summarized in Table V. The values of g, h, and g' are higher in the Θ solvent, dioxane, than in the good solvent, cyclohexane. Values of g' in toluene are 15% lower than in cyclohexane. This is in the direction expected for a better solvent, but the difference may equally well indicate the possible error in these ratios.

The ratio of radii of gyration, g_θ, can be compared with the random-walk value for regular stars.[46] For large f,

$$g_{\mathrm{r.w.}} = \frac{3f-2}{f^2} \approx \frac{3}{f} \tag{7a}$$

Similarly, for regular stars,[47]

$$h_{\mathrm{r.w.}} = f^{1/2}[2 - f + 2^{1/2}(f-1)]^{-1} \approx 1/(2^{1/2}-1)f^{1/2} \tag{7b}$$

The random-walk values are also given in Table V. It can be seen that the random walk is a poor model for these multiarm stars.

For g' no simple theory is available. It has been suggested that $g'_\Theta = g^m{}_{\mathrm{r.w.}}$ where $m \rightarrow {}^1/_2$ for star polymers and $m \rightarrow {}^3/_2$ for combs with large backbones and short branches.[48] For the multiarm stars, $m = 0.69$, which is, considering the long extrapolation, surprisingly close to $m = 0.58$ found for regular stars with $f \leq 18$.[10] Dimensionally, $g' = h^3$.[47] For the stars at hand, $h^3{}_\theta = 0.09$, which is clearly the right order of magnitude.

As pointed out by Daoud and Cotton,[21] comparison of star polymers with many arms with linear polymers within the framework of the random-walk model is not justified because the conformation of the arms is strongly non-

Table VI
g_Θ and g as a Function of Number of Arms in Star

	g_Θ			g		
arms	PS[a]	PI[b]	PBd[b]	PS[c]	PBd[d]	ref
4	0.63_3	0.65		(0.61)	(0.68)	50, 51
6	0.45_8	0.46		(0.46)		52, 51
8		0.41_5				53
12	0.27_6	0.33		0.24_3		8, 53
18	0.22_8		0.20	0.20_3	0.19	8, 6
269			0.06		0.03	this work

[a] Cyclohexane. [b] Dioxane. [c] Toluene; values in parentheses have not been published previously. [d] Cyclohexane, value in parentheses not published previously.

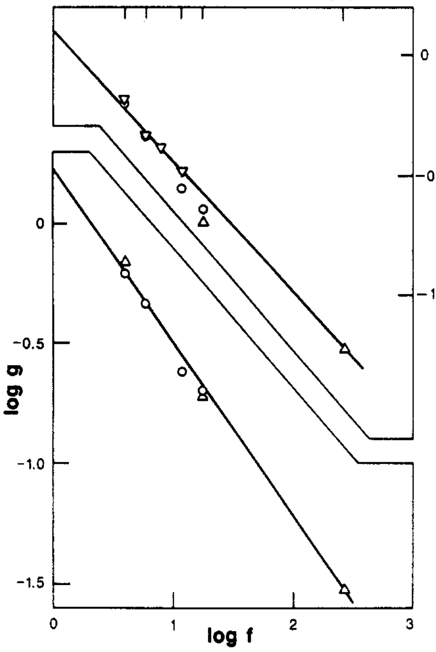


Figure 7. Double-logarithmic plot of the experimental values of $g = \langle s^2\rangle / \langle s^2\rangle_l$ against the number of arms in the star. Top: Θ solvents. Bottom: Good solvents. (○) Polystyrene; (△) polybutadiene; (▽) polyisoprene.

Gaussian. Departures from the random-walk model appear when $f > 8$. They are well documented for 12-arm[10,11,49] and 18-arm star polystyrene[10] and for 18-arm star polybutadienes.[8] For these low functionality stars, the departures from the random-walk model are small (20% and 30%) and, since they are molecular weight dependent, could conceivably disappear as $M \rightarrow \infty$.[11,49] In contrast, the experimental values of g and h for the multiarm polybutadienes are 3–5 times larger than the calculated values and appear to be independent of molecular weight at high molecular weight.

From Table I it can be seen that the scaling theory for star polymers predicts that

$$g_\Theta \approx C_\Theta f^{-1/2} \tag{8a}$$

and in a good solvent that

$$g = Cf^{-4/5} \tag{8b}$$

In Table VI, g_Θ and g data for regular stars have been compiled. Least-squares analyses of double-logarithmic plots of g_Θ and g versus f in Figure 7 yield

$$g_\Theta = 1.27f^{-0.56_6} \tag{9a}$$

$$g = 1.67f^{-0.72_8} \tag{9b}$$

It is therefore concluded that the Daoud–Cotton model holds remarkably well for high values of f. More data on star polymers with $f > 30$ would reduce the uncertainty due to experimental error in the coefficients and exponents in eq 9.

Table VII
ϕ', P', and ψ Ratios for Multiarm Star Polybutadienes

	dioxane		cyclohexane		
sample	$10^{-25}\phi'$	P'	$10^{-25}\phi'$	P'	ψ
LS2	1.1	22	1.4	24	1.6
LS3	1.5	25	1.7	25	1.8
LS4	1.3	25	1.6	26	1.3
LS5	0.8		1.2		1.0
LS6	1.0	26	1.3	24	1.1
SLS1	1.5		1.6		1.8
SLS2			1.4		1.2

It should be noted that the prefactors are not very different from those quoted originally by Daoud and Cotton.[21] Experimental data on 4–12-arm polyisoprenes gave $C_\Theta \approx 1.15$.[21] Data on polystyrene stars yielded $C = 2.2$[21] and 1.8–2.0.[10] A good solvent prefactor, $C = 1.86$, has been calculated by Barrett and Tremain,[24] and $C = 1.55$ has been computed by Grest et al.[25] for stars with 30, 40, and 50 arms. The modified Flory version of the SAW yields $C = 1.94$.[54]

The internal consistency of the $\langle s^2\rangle$, $[\eta]$, and D_0 data for the large stars can be checked through the classic Flory relations[55]

$$\phi' = \frac{[\eta]M}{\langle s^2\rangle^{3/2}} \tag{10a}$$

and

$$P' = \frac{6\pi R_h}{\langle s^2\rangle^{1/2}} \tag{10b}$$

where the primes are introduced to specify the radius of gyration. Values of ϕ' and P' for the multiarm star polybutadienes are given in Table VII. When $[\eta]$ is expressed in milliliters/gram, $\phi' = (1.4 \pm 0.2) \times 10^{25}$ for all the stars in cyclohexane and dioxane. The value of $P' = 25 \pm 2$. These values are identical with those for the hard sphere ($\phi' = 1.36 \times 10^{25}$ and $P' = 24.3$).[56] The Flory–Mandelkern constant $\phi'^{1/3}/P' \equiv \phi^{1/3}/P = (9.9 \pm 0.3) \times 10^6$ compared to 9.8×10^6 for the hard sphere limit (2.1×10^6 when $[\eta]$ is expressed in deciliters/gram). A similar constant was calculated for linear and 4- and 6-arm stars and some combs.[57]

The second virial coefficients in cyclohexane indicate that

$$\psi = \frac{A_2M^2}{4\pi^{3/2}N_A\langle s^2\rangle^{3/2}} \tag{11}$$

for the multiarm stars is equal to the hard sphere limit value (1.61) within experimental error. The values of ψ, given in Table VII, decrease slightly with increasing molecular weight. Whether this is genuine or reflects the errors in measuring small values of A_2 is difficult to judge.

The dilute solution properties studied in this work are global properties of the isolated polymers. They do not provide data to estimate the relative importance of the three regions in the stars as proposed by Daoud and Cotton.[21] The central core, completely occupied by segments of a single polymer, is probably not very large. Very dense star-burst dendritic molecules have seven chemical bonds between branch points[58] compared with approximately eight bonds between the main branch points in the multiarm stars. It is worth noting that Huber et al. place 5 bonds between branch points in a lattice simulation of the core of a 12-arm star.[49] In the multiarm stars, there are four bonds in the core per arm. This is only twice the number of bonds per arm in the low functionality 3-, 4-, 6-, 8-, 12-, and 18-arm stars prepared with Si–Cl coupling agents. Since the starburst molecules have definite hollowness in the fourth generation, the core, in which the monomer concentration is unity, probably does not extend more than a few monomer units. Daoud and Cotton propose the core to have $\bar{f}^{1/2}$ monomer units.[21] A coefficient less than unity is therefore likely. The semidilute to expanded transition should be important in good solvents. The fact that the lowest molecular weight multiarm star does not expand significantly in the good solvents suggests that it is almost entirely made up of the semidilute regime. Such questions could be answered better with results on deutero–proto diblock star polymers for which radii and scattering functions of the individual regions can be determined. We have considered that the central backbone of the LS series acquires an extended (or helical) configuration.[29] For that reason the SLS series was prepared. Unfortunately, the global properties that are measured do not show any effect that can be traced directly to the architecture of the central part of the multiarm stars. On the basis of other core poly(1,2-butadienes), we were able to make polystyrene stars with 75 arms and multiarm poly(butadiene-*block*-styrene) stars.

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