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Thermodynamic Properties of Dilute and Semidilute Solutions of Regular Star Polymers[†]

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ABSTRACT: The osmotic modulus of solutions of polybutadiene stars with $f = 32$, 64, and 128 arms have been measured from the dilute to the semidilute regime in the good solvent cyclohexane by static light scattering. Some complementary results on low molecular weight stars have been obtained using SANS. Values of the dimensionless virial ratio $g \equiv A_3/A_2{}^2M \approx 0.62$ for these many-arm stars accord well with the hard-sphere value (5/8). The concentration dependence of the osmotic modulus near the polymer coil overlap concentration, $A_2Mc \approx 1$, is characterized by a steep increase. This behavior agrees with arguments by Witten, Pincus, and Cates which indicate a steplike rise in the osmotic modulus where the step height scales as $f^{3/2}$. In the semidilute regime the osmotic modulus becomes identical with that of a homogeneous linear polymer solution. A linear polybutadiene sample was also considered for comparison with the star polybutadiene measurements.

Introduction

The concentration dependence of the osmotic pressure of linear polymer solutions has been studied extensively because it allows for the evaluation of the second and third virial coefficients which are basic measures of the interactions between polymer coils.[1] Alternatively, the same coefficients can be obtained from the osmotic modulus, $\delta\pi/\delta c$, measured by light scattering. In recent years attention has shifted to the scaling properties observed in semidilute solutions where polymers coils overlap while the solvent still constitutes a large volume fraction of the solution.[2,3] The renormalization group theory allows for a description of the crossover between the dilute and semidilute regions,[4,5] and this model has been tested recently by experiment.[6–12]

Less work has appeared on the same subjects for the case of branched polymers. In general, it is observed that regular star polymers with up to 18 arms show only minor differences with the concentration dependence of linear polymers.[10,12–16] When the number of arms is large, regular star polymers should approach hard-sphere behavior and show a strong increase in the osmotic pressure at the concentration of onset of chain overlap not found in linear polymers.[17,18] Some experimental evidence has been found for such behavior e.g. in the case of a star-microgel with 43 arms,[19] for polystyrenes having a dendritic structure,[20] and in the case of a globular protein.[21]

In this work we will describe results on the concentration dependence of light scattered by 32-arm, 64-arm, and 128-arm regular star polybutadienes. In order to determine the effect of molecular weight on the osmotic modulus we also include data obtained by SANS on low molecular weight stars.[22,23] The concentration dependence of the osmotic modulus of the star polymers is compared with the hard-sphere model.[18] In the case of the linear polymer, the third virial coefficient is also derived and the results are compared with the renormalization group theory and exact calculations for "soft" Gaussian spheres.

Experimental Part

The sample preparation and molecular characterization have been described previously.[24–27] The important molecular characteristics of the samples are given in Table 1. Solutions for the static light scattering were prepared by dissolving weighed amounts of polymer in CaH_2-dried and distilled reagent grade cyclohexane. The density of cyclohexane at 25 °C is 0.7738 g/cm^3. All solutions were stabilized with 0.1% 2,6-di-*tert*-butyl-*p*-cresol by weight. Solutions were made dust-free by filtration through 0.2 μm Teflon or silver filters. Higher concentrations were prepared by freeze drying solutions in a dust-free vacuum oven followed by addition of weighed amounts of the filtered base solution. The highest concentrations were obtained by partly freeze-drying solutions and allowing for homogenization. The latter process was slow for solutions above the gel concentration.[28] Homogeneity was checked over time as well as by performing light scattering at various depths in the solution.

Most light-scattering measurements[24] were performed with a Fica 50 photogoniometer with vertically polarized light of 4358 Å. Calibrated neutral density filters were used to keep the scattered light intensity within the linear range of the photomultiplier. Absolute values of light scattered are based on the Rayleigh ratio for benzene equal to 49×10^{-6} cm^{-1} and a polarizability ratio of 1.42. Light-scattering measurements were also performed with a Brookhaven system with vertically polarized light of 6328 Å. The measurements are based on the Rayleigh ratio of toluene at 25 °C equal to 14×10^{-6} cm^{-1}. Measurements with both instruments agreed always within 1%. Light-scattering measurements were performed at different angles between $\theta = 30°$ and $\theta = 150°$. The available q-range is from 1.0×10^{-3} to 4.0×10^{-3} Å^{-1} for 4358 Å light and from 7.4×10^{-4} to 2.7×10^{-3} Å^{-1} for the 6328 Å light, where $q = 4\pi(n/\lambda)\sin(\theta/2)$. The refractive index of cyclohexane is $n = 1.42$ (4358 Å) and 1.43 (6328 Å) at 25 °C. All measurements were extrapolated to the limit $q \to 0^+$.

Theoretical Background

In dilute solution the osmotic pressure is given by

$$\pi = cRT\left[\frac{1}{M_n} + A_2c + A_3c^2 + \ldots\right] \qquad (1)$$

It is often convenient to work with the normalized osmotic pressure

$$\pi/\pi_0 = 1 + A_2Mc + A_3Mc^2 + \ldots \qquad (2)$$

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Table 1. Molecular Characteristics of Polybutadienes in Cyclohexane at 25 °C

sample	f^a	$10^{-6}M_w$	R_G (Å)	10^5A_2 [(mol mL)/g^2]	10^2A_3 [(mol mL^2)/g^3]^b	g^b	ref
PBd300	1	0.256	258	86.9	5.3	0.23 ± 0.03	26,27
3280B3	33.6	3.01	375	11.0	2.4	0.66 ± 0.1	24
6480B4	59	4.2	341	6.6	1.58	(0.79)	25
12880B4	122	8.8	424	3.0	0.48	0.61 ± 0.02	25

[a] f = experimental number of arms in star. [b] This work.

where

$$\pi_0 = cRT/M \tag{3}$$

A_2M has the units of cm^3/g so that A_2Mc serves to define a dimensionless concentration c/c^*. $c^* = (A_2M)^{-1}$ is the "overlap concentration" where excluded volume interferences between the chains begin to give a substantial contribution to the osmotic pressure. Similarly, extrapolation of the absolute excess light scattered by solutions to zero angle yields the virial expansion

$$\frac{Kc}{\Delta R_{\theta=0}} = \frac{1}{RT}\frac{\delta\pi}{\delta c} = \frac{1}{M_{\text{app}}} = \frac{1}{M_w} + 2A_2c + 3A_3c^2 + ... \tag{4}$$

where K contains optical and instrument constants, and $\delta\pi/\delta c$ is the "osmotic modulus" which is the inverse of the osmotic compressibility.

Since $\lim_{c\to0} Kc/\Delta R_{\theta=0} = 1/M_w$, we can also normalize the light scattering data accordingly,

$$\frac{Kc}{\Delta R_{\theta=0}}\bigg/\left(\frac{Kc}{\Delta R}\right)_{\theta=0,c=0} \equiv \frac{M_w}{M_{\text{app}}} = \frac{M_w}{RT}\frac{\delta\pi}{\delta c} = 1 + 2A_2M_wc + 3A_3M_wc^2 + ... \tag{5}$$

In the semidilute concentration range, $c^* \le c \ll c^{**}$ the osmotic pressure π scales as $c^{d\nu/(d\nu-1)}$ where ν is the exponent in the relation $R_G \propto M^{\nu}$. The osmotic modulus is independent of molecular weight at high concentrations and scales as[3,5]

$$\frac{M}{RT}\frac{\pi}{c} \propto \frac{M_w}{RT}\frac{\delta\pi}{\delta c} \propto c^{1/(d\nu-1)} \tag{6}$$

The Flory value of ν equals $^3/_5$ while $^{10}/_{17} \approx 0.588$ is a more precise estimate for $d = 3$ dimensions.[5,29] In the concentrated regime $c > c^{**}$, typically on the order of 10% polymer volume fraction or higher, fluctuation effects are small and mean-field (Flory–Huggins) theory should be applicable. This leads to an exponent of 2 for the osmotic pressure and osmotic modulus.[30-32]

The renormalization group (RG) theory describes the whole dilute to semidilute concentration range[4] of linear flexible polymers. The leading order (*RG*) calculation gives

$$\frac{M}{RT}\frac{\delta\pi}{\delta c} = 1 + \frac{1}{8}\left[9X - 2 + \frac{2}{X}\ln(1+X)\right] \times \exp\left\{\frac{1}{4}\left[\frac{1}{X} + \left(1 + \frac{1}{X^2}\right)\ln(1+X)\right]\right\} \tag{7}$$

with $X = (16/9)A_2Mc$ for narrow molecular weight samples. In the limit of large X eq 7 has the asymptotic variation

$$\frac{M}{RT}\frac{\delta\pi}{\delta c} = 2.309(A_2Mc)^{1.25} \tag{8}$$

The exponent in eq 8 agrees fortuitously with eq 6 with the Flory estimate for ν. It should be appreciated, however, that the leading order *RG* calculation of ν, compatible with the derivation of eq 7, gives $\nu \approx {}^9/_{16} \approx 0.56$.[5b]

Table 2. Virial Coefficients $B_n = A_nM$

	hard sphere[18]	soft Gaussian spheres[33]
B_3/B_2^2	0.625	0.25
B_4/B_2^3	0.28695	−0.125
B_5/B_2^4	0.110254(5)	0.013
B_6/B_2^5	0.38818(55)	0.038
B_7/B_2^6	0.013071(70)	-0.030
B_8/B_2^7	0.00432(10)	

In the case of regular star polymer solutions eqs 1 and 3 are still valid, although the ratio between A_2 and A_3 is different from that of linear polymers.[16] Moreover, eqs 6 and 8 can also be expected to hold, except that the prefactor should depend on branching architecture. The change of the prefactor in eq 8 has been calculated by RG theory,[33] but this leading order estimate seems to predict too large a change of the prefactors with f in comparison with experiment.[10] When the number of arms in the star is large, the transition between the dilute and the semidilute regions should be qualitatively different, however, and can be expected to resemble more the behavior of hard-sphere suspensions. The origin of this difference is the much higher segment density in the star polymer coil than in the linear polymer with the same molecular weight. Near the overlap concentration the interaction between two polymer coils occurs between the coronas, and therefore, the segment density in the coronas should be considered rather than the average segment density of the coil. The osmotic pressure for many-arm stars has been argued to "jump" rapidly from $\pi/kT \sim R_G^{-3}$ to $\pi/kT \sim R_G^{-3}f^{3/2}$ at the overlap concentration.[17] The steep rise in osmotic pressure at the overlap concentration is also compared with the concentration dependence of osmotic pressure of a hard-sphere solution. Up to seven virial coefficients in eq 1 have been computed for the case of hard spheres. (See Table 2.) In closed form, the Carnahan–Starling equation of state is a very good approximation. Accordingly,[18]

$$\frac{\pi}{kT} = \frac{\phi(1 + \phi + \phi^2 - \phi^3)}{(1 - \phi)^3} \tag{9}$$

or in terms of the osmotic modulus

$$\frac{Kc}{\Delta R_{\theta=0}} = \frac{1 + 4\phi + 4\phi^2 - 4\phi^3 + \phi^4}{(1 - \phi)^4} \tag{10}$$

where $\phi = (1/4)A_2Mc$ is the volume fraction of hard spheres. These results correspond to the "good-solvent" regime where there are no attractive sphere–sphere interactions.

Results and Discussion

Linear Polybutadiene. The zero-angle light-scattering data of linear polybutadiene solutions in cyclo-

Table 3. Experimental Light Scattering Data for Linear Polybutadiene (PBd300) in Cyclohexane at 25 °C

10^3c (g/mL)	$10^6Kc/\Delta R_{\theta=0}$ (mol/g)	10^3c (g/mL)	$10^6Kc/\Delta R_{\theta=0}$ (mol/g)	10^3c (g/mL)	$10^6Kc/\Delta R_{\theta=0}$ (mol/g)
0.2329	4.276	2.975	10.38	14.78	51.0
0.4652	4.755	3.054	10.40	21.23	75.5
0.6977	5.219	4.18	13.98	29.21	110.5
0.9301	5.66	5.93	18.7	54.81	228.5
1.168	6.184	6.82_5	22.6	55.31	230.0
2.091	8.22	11.65	40.0	118.1	580

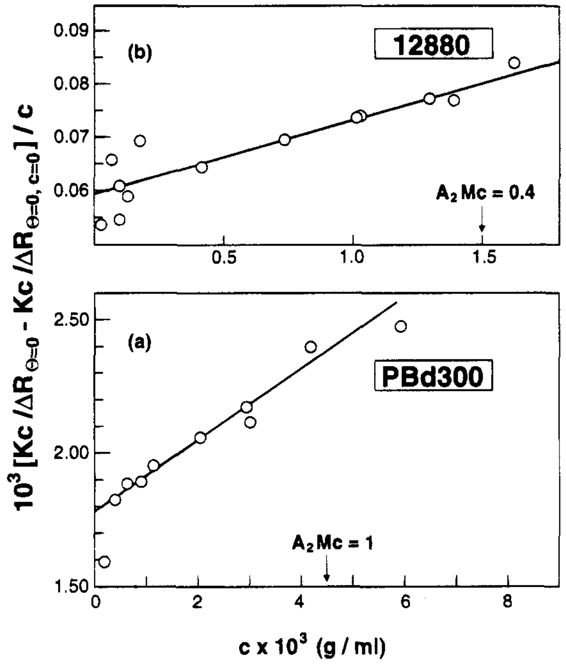

Figure 1. Determination of second and third virial coefficients: (a) linear polybutadiene; (b) 128-arm star polybutadiene. Solvent: cyclohexane, 25 °C.

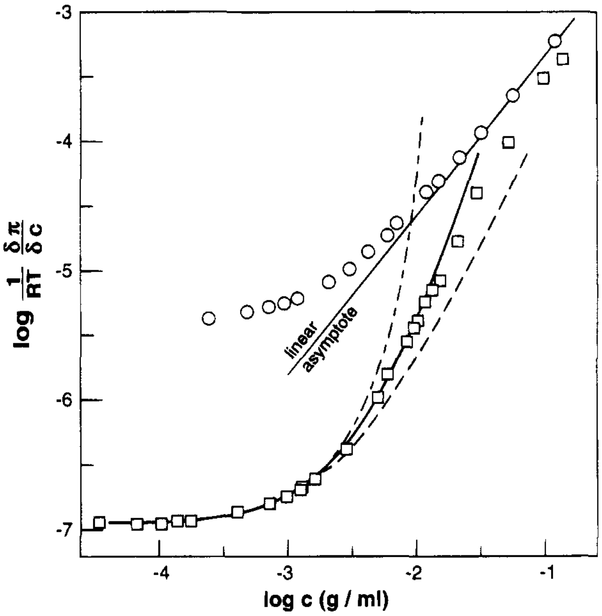

Figure 2. Double logarithmic plot of the osmotic modulus against concentration: (○) linear polybutadiene; (□) sample 12880; (dashed line) eq 3 with the third virial coefficient for hard spheres; (solid line) eq 3 including the fourth virial coefficient; (chain line) Carnahan–Starling eq 10.

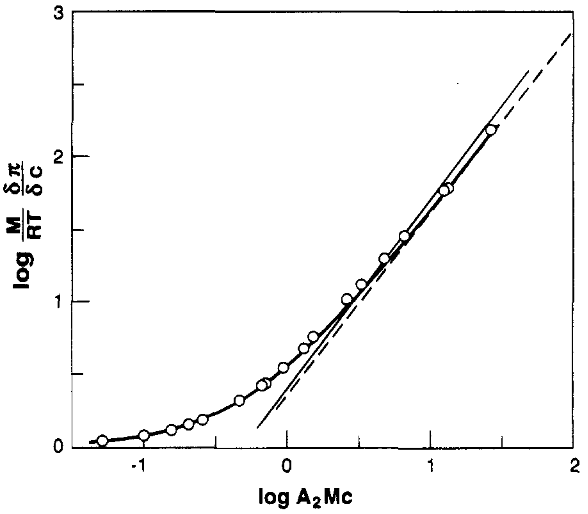

Figure 3. Reduced osmotic modulus against reduced concentration of linear polybutadiene: (○) experimental results; (heavy solid curve) eq 7; (dashed line) asymptote, eq 8; (solid line) asymptote from ref 10 for polyisoprene in cyclohexane.

hexane at 25 °C are given in Table 3. Extrapolation to zero angle is based on plots of $(Kc/\Delta R_\theta)^{1/2}$ against $\sin^2(\theta/2)$ for low concentrations. At high concentrations plots of $Kc/\Delta R_\theta$ versus $\sin^2(\theta/2)$ are linear with positive slopes in agreement with $(\Delta R_\theta)^{-1} \propto (\delta\pi/\delta c)(1 + q^2\xi^2(c))$ where $\xi(c)$ is a concentration dependent correlation length.

The lowest 10 concentrations were used to derive the second and third virial coefficients from a plot of $[Kc/\Delta R_{\theta=0} - 1/M_w]/c$ against c.[34] This is shown in Figure 1a. It can be seen that this plot is linear up to values of $A_2Mc \approx 1$. From the intercept, the second virial coefficient is $8.8_5 \times 10^{-4}$ (cm^3 mol)/g^2, in fair agreement with the original determination which was based on the square root Berry plot.[26,27] (See Table 1.) The value of the dimensionless virial ratio

$$g = A_3/A_2^2M_w \qquad (11)$$

is found to equal 0.23 ± 0.03 in accord with literature values[1] and with the leading order theoretical estimate 0.277 for ideally flexible and long polymer chains in a good solvent.[35] We note that an exact calculation of g for soft (Gaussian) spheres equals g(soft) = 0.256600.[36-38] It seems quite natural that flexible polymer chains are more like soft Gaussian spheres than hard spheres. The use of Bawn plots[39] was not found to give any appreciable change in A_3.

Figure 2 shows the basic double logarithmic plot of $Kc/\Delta R_{\theta=0}$ against c for linear polybutadiene from the dilute to the semidilute concentration regime. The limiting slope at high concentrations is about 1.22, i.e. slightly less than the theoretical minimum value (1.25) and lower than the 1.30 obtained by Adam for linear polyisoprene in cyclohexane.[10] Part of the discrepancy is due to experimental uncertainty. Moreover, with the relatively low molecular weight linear polymer we may not have penetrated far enough into the semidilute regime. Very short chains should lead to larger effective ν in eq 6 which naturally leads to a smaller effective exponent for the osmotic pressure.

In Figure 3 the same data are shown in a reduced plot. The results are compared with the data of Adam

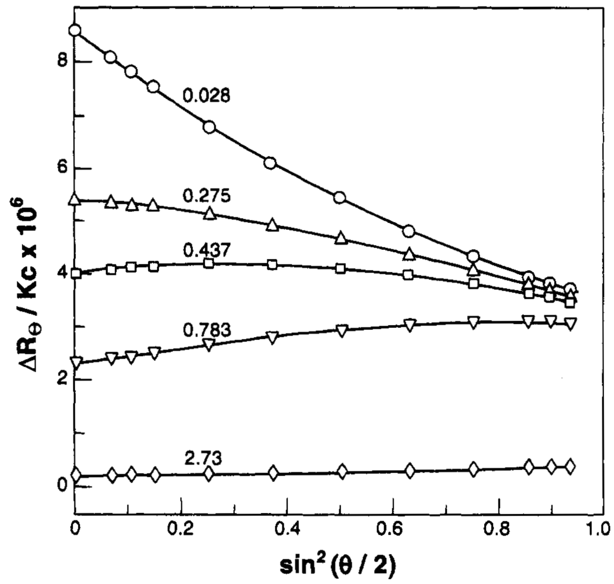

Figure 4. Angular dependence of excess scattered light as a function of reduced concentration for 12880. The number with each curve is the value of A_2Mc.

at high concentrations[10] and with RG estimates from eqs 7 and 8. The slope calculated by this theory between the top two experimental points is about 1.22, confirming that the semidilute region has not been fully reached. Similar conclusions can be drawn by comparison of the experimental results with an equation by Hager et al.[40]

Regular Star Polybutadienes. Examples of the angular dependence of light scattered from solutions of regular star polymers in different concentration ranges are shown in Figure 4. The variety of light intensity patterns can be explained by the general relation

$$\frac{\Delta R_\theta}{Kc} \propto M_w P(\theta) S(\theta) \tag{12}$$

where $P(\theta)$ is the intramolecular scattering function (form factor) and $S(\theta)$ is the intermolecular scattering function (structure factor). At the lowest concentration shown in Figure 4 the decrease of light scattered with angle is a good approximation of $P(\theta)$ since $S(\theta)$ goes to unity in the limit of zero concentration. At intermediate concentrations near the overlap concentration a maximum in the light intensity is observed. The maximum becomes stronger and moves to higher angles with increasing concentration. The maxima occur in $S(\theta)$ and are due to Bragg scattering from preferred distances between polymer coils. At a reduced concentration $A_2Mc = 2.73$ the maximum has moved outside the experimentally available q range and the measured light intensity scattered becomes practically independent of the angle. A detailed SANS investigation of the scattering phenomena in regular star polymers with many arms has been given previously.[22,23]

The zero angle light-scattering data obtained with star polymer solutions are given in Table 4. The evaluation of the second and third virial coefficient of the 128-arm star polymer is shown in Figure 1b. From the intercept, $A_2 = 2.95 \times 10^{-5}$ in good agreement with the earlier determination.[25] Values of A_3 and g are given in Table 1. The value of $g = 0.61$ is in good agreement with the theoretical hard-sphere value 5/8.[18] Evaluation of A_3 must be limited to data obtained under conditions of $A_2Mc \leq 0.5$. At $A_2Mc = 1$ there is already an appreciable contribution from higher terms to the scattered intensity. Values for the 32- and 64-arm stars are also given in Table 1. They have a larger margin of error because fewer experimental data have been collected in the appropriate concentration range. It should be noted that Burchard quotes $g = 0.54$ for a 12-arm star polymer[16] and he notes the tendency of g for many-arm stars to approach the hard-sphere limit $^5/_8$ with increasing f.

The concentration dependence of $Kc/\Delta R_{\theta=0}$ of the 128-arm polybutadiene star in the dilute and semidilute regime is compared with that of linear polymer in

Table 4. Experimental Light Scattering Data for Regular Star Branched Polybutadienes in Cyclohexane at 25 °C

3280		6480		12880	
10^4c g/mL	$10^7Kc/\Delta R_{\theta=0}$ (mol/g)	10^4c g/mL	$10^7Kc/\Delta R_{\theta=0}$ (mol/g)	10^4c g/mL	$10^7Kc/\Delta R_{\theta=0}$ (mol/g)
0.4857	3.329	0.504	2.402	0.3382	1.123_6
0.7306	3.387	1.006	2.420	0.7072	1.152
0.8086	3.481	1.259	2.402	1.0404	1.169
0.9669	3.420	1.538	2.547	1.062	1.163
1.209	3.474	2.050	2.602	1.394	1.188
1.569	3.648	2.522	2.667	1.758	1.224
2.577	3.721	5.027	3.007	4.167	1.373
4.869	4.356	9.743	3.973	7.335	1.616
9.523	5.85	19.78	6.69	10.16	1.858
19.120	10.1	39.49	16.9	10.25	1.866
39.85	25.0	79.13	67.4	12.99	2.116
88.28	110.0	182.4	406	13.83	2.181
151.0	308	340.1	1040	16.17	2.480
195.7	459	754.0	2200	29.00	4.30
321	900			52.56	10.45
				60.57	15.7
				85.45	28.1
				97.4	36.0
				101.2	40.0
				119.2	57.0
				133.3	70.8
				146.1	84.5
				210	170.0
				300	403
				520	980
				950	3110
				1370	4200

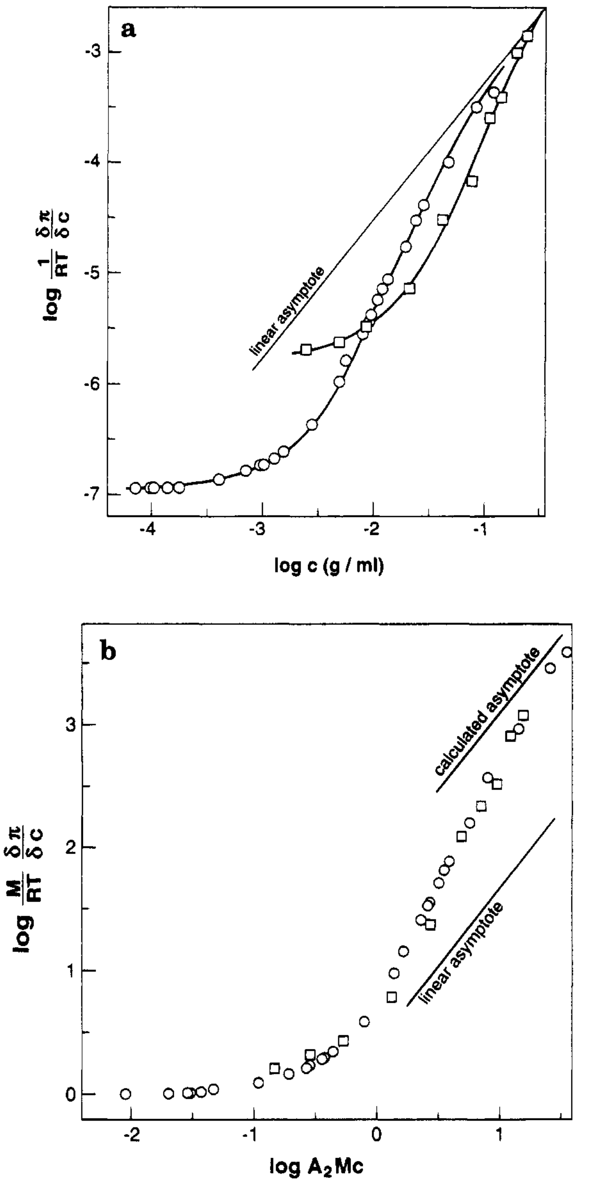

Figure 5. (a) Experimental osmotic modulus as a function of concentration for two 128-arm star polymers: (○) 12880, light scattering: (□) 12807, SANS. (b) Same data in reduced form symbols as in Figure 5a.

Figure 2. The overlap concentrations of the star and linear polymers are 0.0037 and 0.0045 g/mL, respectively. It is first noted that the scattering data of the star polymer fall below the semidilute asymptote line for a linear polymer. Above the overlap concentration the values increase rapidly. In Figure 2 the experimental data of the star are also compared with eq 3 with the exact third- and fourth-order virial expansion (see Table 2) for hard spheres.[18] The data are also compared with Carnahan–Starling eq 10. Note that for concentrations larger than 0.013 g/mL these star polymer solutions have a gel-like character.[28] The light-scattering data of the star polymer almost join but are always slightly lower than the asymptote line of the linear polymer in the semidilute concentration range. This may be due to experimental error because scattering from dust becomes an increasing problem with concentration. This point will be reviewed at the end of the discussion.

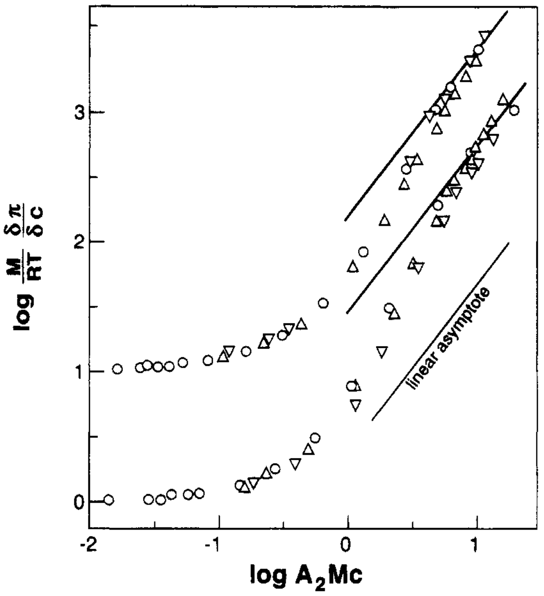

Figure 6. Reduced osmotic modulus as a function of reduced concentration for 64-arm star polybutadienes (lower set of points) and 32-arm star polymers (upper set of points, this set has been shifted vertically by one log unit for clarity).

Dependence on Molecular Weight. The osmotic moduli for two 128-arm polybutadiene stars with widely different molecular weights are shown in Figure 5a. It should be noted that the results of the high molecular weight sample are obtained by light scattering in cyclohexane and the low molecular weight results are from SANS in methylcyclohexane-d$_{14}$. The SANS data are taken from ref 41.[23] It is observed that the data of each sample fall on individual curves and that the star polymers approach the linear semidilute solution asymptote from below. As for linear polymers, the larger star polymer approaches the asymptote at lower concentrations. As a result, the curves for stars with different molecular weights have a crossover point. In the case of the low molecular weight 128-arm star the asymptote is only reached at $c > 0.1$ g/mL, i.e. in a concentration range where departures from the semidilute regime are to be expected.[30-32] In Figure 5b the reduced osmotic modulus is shown to scale with A_2Mc for star polymers with the same number of arms. The semidilute asymptote is indicated. Similar results are shown in Figure 6 for the 32-arm and the 64-arm star polymers. In these cases the semidilute concentration range is reached at lower concentrations. The results in Figure 5a are to be compared with the results of Figure 3 in ref 10 for 8- and 18-arm polyisoprene stars in cyclohexane. For these star polymers a limited number of data points seem to lie a little below the linear chain semidilute asymptote and a crossover between low and high molecular weight samples is not clearly observable.

Dependence on Number of Arms. In order to compare the thermodynamic behavior of star polymers with different numbers of arms, the reduced osmotic moduli are plotted versus the reduced concentration in Figures 5b and 6. The high-concentration asymptotes are reached at different levels of the reduced osmotic modulus. For comparison, the high-concentration data were forced to fit

$$\frac{M}{RT}\frac{\delta\pi}{\delta c} = A(f)\,(A_2Mc)^{1.25} \qquad (13)$$

where the exponent is a reasonable mean value. The prefactors $A(f)$ are given in Table 5. For constant functionality of the star, f, these prefactors vary little

Table 5. Prefactors in $M/M_{app} = A(f)(A_2Mc)^{1.25}$ and $B(f)(C/C^*)^{1.25}$

f	$A(f)$	$B(f)$ (sample)
linear	2.3	3.5
32	14.2	120 (3205); 166 (3210); 214 (3280)
64	26.9	363 (6407); 501 (6415); 661 (6480)
128	58.0	1514 (12807); 1585 (12880)

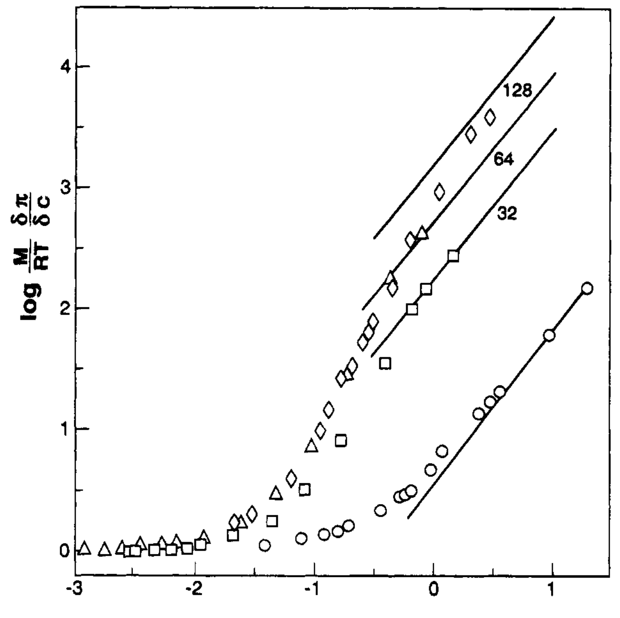

Figure 7. Reduced osmotic modulus against reduced concentration defined in terms of the radius of gyration for (○) linear PBd300; (□) 3280; (△) 6480, and (◇) 12880. The lines are the theoretical asymptotes. The prefactors according to eq 14, $B(f)$, are collected in Table 5.

with molecular weight. Starting from the experimental observation that in the semidilute concentration range all osmotic moduli are independent of polymer architecture, the internal consistency of the reduced plots depends on the consistency and accuracy of the values of M and A_2 for each sample. A plot of $A(f)$ against f indicates a nearly linear f dependence.

The reduced osmotic moduli are plotted in Figure 7 against c/c^* where $c^* = 3M/(4\pi\langle R_G{}^2\rangle^{3/2}N_A)$, i.e. the reduced concentration defined in terms of the radius of gyration. In this case superposition of the samples with different molecular weights is less satisfactory than when scaled by A_2Mc. The individual prefactors in

$$\frac{M}{RT}\frac{\delta\pi}{\delta c} = B(f)\,(c/c^*)^{1.25} \qquad (14)$$

are given in Table 5. A similar situation was encountered for 8- and 18-arm star polyisoprenes, as shown in Figure 5 of ref 10. To some extent this problem can be traced to uncertainties in the values of R_G. For the low molecular weight star polymers values of R_G are derived from Zimm plots and the Ullman correction is applied.[41] In the case of the large stars, light-scattering data have been used (see Table 1). More significantly, the lowest molecular weight star polymers may have slightly modified conformations due to contributions arising from the severe packing interactions within the whole star.[22,42] It is therefore expected that the results of the high molecular weight stars are more representative of the correct asymptotic results for flexible chains. A plot of $B(f)$ against f is shown in Figure 8. Data on 8- and 18-arm star polymers[10] have been included after adjustment to our definition of c^* (a factor of $(3/4\pi)^{1.25}$). As can be seen in Figure 8, a slope of $^3/_2$ is observed in agreement with the prediction of Witten, Pincus, and Cates.[17] The line in Figure 8 does not include the linear polymer, because the Daoud–Cotton star polymer model is valid only for large values of f. It is surprising to us that the prefactor for an 8-arm star polymer fits this scaling dependence so well.

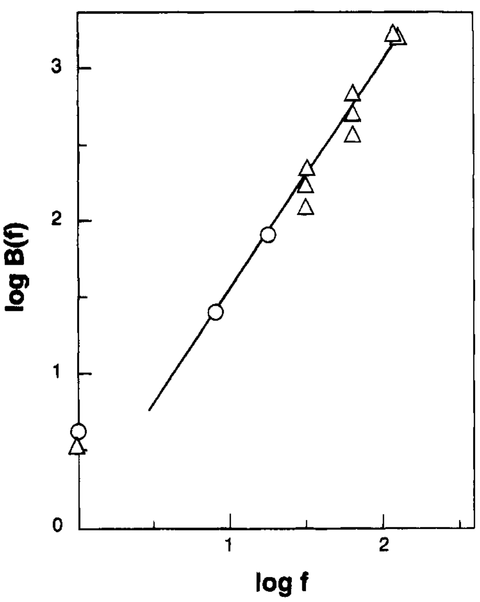

Figure 8. Prefactors in eq 14 plotted logarithmically against the number of arms: (○) data from Figure 5 in ref 10; (△) this work. The slope of the line is 1.5 in agreement with the Witten–Pincus–Cates model.[17]

We comment on the observation that the osmotic moduli obtained by light scattering in a semidilute solution of the stars are consistently below those of the linear polymer. The phenomenon which is perhaps an artifact in the star data strongly resembles the osmotic pressure measurements by Horkay et al. on polymer networks which are also consistently lower than those in the semidilute linear polymer.[43,44] Although star polymers can be considered as a rather special type of cross-linked polymer, the nature of the junction points with 32–128 arms is quite different from network junctions. This is quite clear from the qualitative differences in the structure factors. The stars have a strong Bragg peak that is not seen in the networks.

Conclusions

We have shown that regular star polymers with many arms have rather different equations of state than linear polymers in a good solvent. It has been shown previously that the second virial coefficients of the stars are much lower than those of the linear polymer, testifying to the smaller pervaded volume. We have now shown that the dimensionless virial ratio $A_3/A_2{}^2M_w$ of the stars is larger and corresponds closely with the expected value for the hard sphere. At higher concentrations, however, the osmotic modulus is lower than in the case of a true hard sphere, presumably due to their greater capacity to interpenetrate each other and deform in shape. We have further shown that in the semidilute regime the star polymers approach the same asymptotic scaling with concentration as observed for linear polymers. Somewhat smaller than theoretical exponents are obtained, however. The effect is consistent with the fact that the experimental data are limited to the lower concentration range of the semidilute polymer regime. The osmotic moduli of star polymers approach the asymptote from below in contrast with linear polymers which approach the asymptote from above, and the higher molecular weight stars reach the asymptote at relatively lower concentrations.

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