Osmotic Pressure of Linear, Star, and Ring Polymers in Semidilute Solution. A Comparison between Experiment and Theory

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ABSTRACT: Osmotic moduli from styrene, isoprene, and butadiene polymers of different architectures are compared with new conformational space renormalization group (RG) theory computations that cover a range in concentrations from dilute through semidilute solutions. Three-arm, 12-arm, and ring polystyrenes (PS) are found not to scale with the same power law as linear chains. Theory yields the same power law behavior for linear, star, and ring polymers, but even the linear PS chains exhibit a higher exponent than predicted by RG theory or scaling. Dimensionless osmotic moduli for linear polydiene chains, such as polyisprene (PI) and polybutadiene (PB), are found to be lower than osmotic moduli of PS, thereby raising possible questions of nonuniversality. However, the PI data are nearly exactly represented by theory. The PI stars all show the same power law behavior as linear chains, and differences are nearly negligible in comparison with deviations for different PS architectures. Ring PS are well represented by theory, but differences between three-arm stars and rings are found to be not as strong as predicted by theory. Possible reasons are discussed for the observed apparent nonuniversality and for larger than scaling exponents.

1. Introduction

This paper compares theory with experiment for the normalized inverse osmotic compressibility (or osmotic modulus) $(M/RT)(\partial\pi/\partial c)$ of polymers with different architectures from dilute through semidilute solution. Theoretical predictions are obtained from conformational space renormalization group (RG) methods and predict the osmotic pressure to be a function of reduced concentration c/c^*, where c is the polymer concentration and c^* is the overlap concentration.[1,2] Furthermore, the asymptotic good solvent, high molecular weight limit exponent in a double logarithmic plot of the osmotic modulus vs reduced concentration c/c^* emerges from both scaling and RG theory in three-dimensional space to be $(3\nu - 1)^{-1}$ independent of the architecture, with ν the exponent in the radius of gyration–molecular weight relationship $R_g \propto M_w^{\nu}$.

To our knowledge comparisons between different architectures for the osmotic modulus or osmotic pressure in semidilute solutions have been discussed by Higo et al.,[3] by Burchard,[4,5] and recently by Adam et al.[6] Burchard describes the influence of polymer shape on the osmotic modulus. The osmotic modulus displays a changing characteristic behavior as the polymer shape varies between stiff rodlike polysaccharides, linear flexible chains, such as polystyrene, and more compact structures, such as star-microgels or hard spherical eye lense crystalline. Higo et al. and Adam et al. consider the osmotic pressure power law behavior of star polymers with different numbers of arms. Higo et al. measure the osmotic pressure of three-arm poly(α-methylstyrene) and comb-branched polystyrenes as well as the corresponding linear polymers. Adam et al. report the semidilute scaling limit osmotic modulus of linear, eight-arm, and 18-arm polyisoprenes. Both groups confirm theory for the power law behavior of the osmotic pressure and its derivative. The exponents are found to be independent of the number of arms and are 1.30 ± 0.02, corresponding to $\nu = 0.590 \pm 0.005$, in excellent agreement with the theoretical value $\nu = 0.588$.[7]

We now consider the more general whole variation of the osmotic pressure from dilute to moderately concentrated solutions for various chain architectures in order to compare absolute osmotic moduli with theoretical predictions. New experimental light scattering data for three-arm and ring polystyrenes are also compared with previous measurements. Although it would be desirable to include the osmosis data in our comparison with theory, these data are not included because the data conversion, using the power laws given in the literature, enhance the uncertainities over those in the original data. Thus, the osmosis data are unsuitable for our comparison with theory of absolute osmotic compressibilities.

The Experimental Section describes the light scattering equipment used, the preparation of amino-terminated three-arm polystyrene star polymers, and references where preparation of the other polymers are reported. Section 3 provides a brief description of the RG calculations, focusing primarily on the modifications to the first-order RG calculation by Cherayil et al. Since the integrals in the theoretical expressions can only be evaluated numerically, closed expressions are obtained by fitting the calculated data to a semiempirical series expansion applied by Hager et al.[8] The theoretical calculations are compared with experimental data in section 4. Universality of the osmotic pressure for linear polymers is tested by comparison of data from polystyrenes (PS), poly(α-methylstyrene) (α-PS), polyisoprenes (PI), and polybutadienes (PB) in good solvents. The comparison is then extended to star and ring polymers. Section 5 discusses several

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questions requiring further experimental and theoretical investigations.

2. Experimental Section

Data on the osmotic pressure derivative are either taken from the literature or determined from static light scattering by extrapolating the measured $K_c/(R(\theta))$ to scattering angle $\theta = 0$, where all symbols have their usual meanings. Experiments are carried out with equipment allowing simultaneous recording of static and dynamic light scattering.[9] Both argon and krypton ion lasers (Spectra Physics Model 2020) are used as light sources.

Solutions of linear, three-arm, and ring polystyrenes are prepared by directly weighing the polymer into 2- or 5-mL flasks and filling the flasks with the solvents 1,4-dioxane or toluene. The solvents are p.A. grade quality from Roth and are used after distillation from sodium (toluene) or after purification by eluating from an Al_2O_3-column (1,4-dioxane). The solutions are filtered through 0.2-μm PTFE filters (Nucleopore) into dust-free cylindrical quartz cells. Solutions are restricted to have concentrations less than about 120 g/L in order to keep them semidilute and to avoid complications from high concentrations. This limit is somewhat arbitrary and is mainly based on experimental experience.[10]

Preparation of Amino-Terminated Three-Arm PS. Polymers are prepared by anionic polymerization under slight argon excess pressure[11,12] after initiating the polymerization with [3-(dimethylamino)propyl]lithium (DMAPLi)[13] and coupling the linear carbanions with tris(allyloxy)-1,3,5-triazine (TT).[14] The initiator is prepared according to Thiele et al.[15] but in n-pentane solvent.[16] After filtration of the warm solution and cooling to room temperature, DMAPLi crystallizes as white needles. The initiator content of the supernatent solution is determined with acetanilide and is found to be 0.2 molar, constant, and stable for several weeks at room temperature. Since initiation is found to occur only in hydrocarbons, but the coupling reaction only proceeds in ethers, such as tetrahydrofuran (THF) or mixtures of both, polymerization is performed in benzene (containing 1% THF)[17] and is terminated by a THF solution of TT after adding THF to the carbanionic solution such that the total content of THF is about 15%. During the termination reaction, which takes several hours, the slightly red solution turns from deep red to yellow, which remains even after addition of acids. The star polymer is purified by dissolving in warm cyclohexane and keeping the solution at room temperature where a yellow precipitate contains most of the impurities. Further purification is made by fractional precipitation from a toluene–methanol mixture containing 2% polymer. One fractionation step is sufficient to obtain star-branched polymers without any detectable linear chains (size exclusion chromatography) or colored impurities (UV–visible spectroscopy) from the crude yellow polymers which contain about 30% linear chains. The introduction of a tertiary amino end group does not affect the solution behavior, as shown in a previous paper where monofunctional and telechelic PS chains are compared with untagged PS chains.[18]

Linear PS chains with narrow molecular weight distribution have been purchased from Pressure Chemical Co. Molecular weights and second virial coefficients are listed in Table I. Macrocyclic PS is prepared by anionic polymerization as described previously.[12,19] Data for 12-arm PS are obtained from one star molecule with $M_w = 467\,000$ and a second virial coefficient of $A_2 = 2.09 \times 10^{-4}$ mol mL g^{-2}.[20] PB data are taken from ref 21 where four different linear chains $4.4 \times 10^4 < M_w < 110 \times 10^4$ are investigated in 1,4-dioxane.

3. Theoretical Section

Scaling theory[2,22] dictates that the dimensionless good solvent osmotic pressure $\pi M/cRT$ varies with c/c^* in the semidilute solution scaling limit as $m'(c/c^*)^p$, with a prefactor m' which is inaccessible to scaling theories. The scaling exponent is $p = (d\nu - 1)^{-1}$, where d is the spatial dimensionality and p is also the scaling exponent for the osmotic modulus (≡ inverse osmotic compressibility) $(M/RT)(\partial\pi/\partial c)$. Renormalization group (RG) theory, on the other hand, implies that $(c^*)^{-1} = A_2M$, with A_2 the second virial coefficient. This theory enables computation of the prefactor m' as well as the crossover behavior (for m, p, and c^*) between various asymptotic scaling regimes.[2] The explicit RG computations proceed by use of expansions for equilibrium polymer properties in powers of $\epsilon = 4 - d$ (actually an expansion in $\epsilon/8$). Hence, upon introduction of the ϵ-expansion

$$\nu = \frac{1}{2}\left[1 + \frac{1}{8}\epsilon + O(\epsilon^2)\right] \tag{1}$$

the semidilute solution scaling behavior translates to $(c/c^*)^{[\epsilon/4+O(\epsilon^2)]}$, which must emerge from RG computations in the form of a contribution in $(\epsilon/4)\ln(c/c^*) + O(\epsilon^2)$ as is demonstrated to be the case in Appendix A of ref 1. Thus, in order to be consistent with scaling limits, the $(\epsilon/4)\ln(c/c^*) + O(\epsilon^2)$ terms in the RG computation must be reexponentiated to yield $(c/c^*)^{[\epsilon/4+O(\epsilon^2)]}$. This procedure is followed in ref 1, but because of the complexity of the integral expression for π does not simply separate the ln (c/c^*) portion. Cherayil et al. also reexponentiated the $O(\epsilon)$ contribution to the prefactor m', an approximation later found to be fraught with some difficulties.

Table I. Dilute Solution Properties of Linear PS in Toluene (Left Hand), Three-Arm Star (TRI1 and 2) in Dioxane and Toluene, and Ring PS (CY1 and 2) in Toluene (Right Hand) (Molecular Weights M_w in g/mol and A_2 in mol mL g^{-2})

linear PS			cyclic and three-arm stars		
sample	$M_w \times 10^{-6}$	$A_2 \times 10^4$	sample	$M_w \times 10^{-6}$	$A_2 \times 10^4$
PS-5	0.154	4.2	TRI1	0.105	4.3[a]
				0.107	4.2
PS-45	0.455	3.58	TRI2	0.242	3.2[a]
				0.238	3.6
PS-103	1.04	2.57			
PS-175	1.77	2.51	CY1	0.093	4.4
PS-7	7.60	1.52	CY2	0.189	3.9

[a] In solvent 1,4-dioxane.

While the reexponentiation of the order ϵ contribution to prefactors like m' is consistent with RG computations, simple exactly solvable models provide instances where this incurs rather large spurious errors.[23] Thus, it is our belief that unless general principles or exact limiting situations dictate otherwise, the ϵ-expansion for prefactors should not be reexponentiated. Rather, they should be left as expansions in ϵ as must be done for low-order ϵ-expansions of exponents such as in eq 1. New RG computations have, therefore, been performed for π and for $(M/RT)(\partial\pi/\partial c)$ in order to have comparisons with experiment that are free of this extraneous approximation, which tends to overestimate the prefactor m'. The remainder of this subsection provides technical details on how the scaling behavior can be obtained by the above-described reexponentiation without the need to reexponentiate the $O(\epsilon)$ part of m'. Those readers more interested in predictions and comparison with experiment should skip to section 4.

Equation 18 of ref 1 expresses the renormalized osmotic pressure of star and ring polymers in the expanded form of

$$\frac{\pi M_n}{cRT} = 1 + \frac{c}{c^*}\left[1 - \frac{\epsilon\lambda I}{32(c/c^*)}\right] \tag{2}$$

where $\lambda = (32z/3)[1 + (32z/3)]^{-1}$, z is the excluded volume

Fixman z parameter, I is given by

$$I = 2\int_0^\infty \mathrm{d}y\, y^3 \left\{ \ln\,[1 + 4(c/c^*)g(y^2)] - \frac{4(c/c^*)g(y^2)}{1 + 4(c/c^*)g(y^2)} - \frac{1}{2}[4(c/c^*)g(y^2)]^2 \right\} + O(\epsilon^2) \quad (3)$$

and $g(y^2)$ is an architecture and molecular weight distribution dependent function presented in eqs 19 and 20 of ref 1. The asymptotic large c/c^* limit of I is obtained in (A.11) of ref 1 as $L = -8(c/c^*)^2 \ln\,(c/c^*) + O[(c/c^*)^2]$ and adding and subtracting this limit L from eq 3 yields

$$\frac{\pi M_n}{cRT} = 1 + \frac{c}{c^*}\left[1 + \frac{\epsilon\lambda \ln\,(c/c^*)}{4}\right] - \frac{\epsilon\lambda}{32(c/c^*)}[I + 8(c/c^*)^2 \ln\,(c/c^*)] + O(\epsilon^2) \quad (4)$$

The quantity in the second square brackets on the right-hand side of eq 4 approaches a constant when $c/c^* \to \infty$, so only the preceding square brackets contributes to the exponent p and *must* be reexponentiated. The resultant osmotic pressure is obtained as

$$\frac{\pi M_n}{cRT} = \left(\frac{c}{c^*}\right)^{1+\epsilon\lambda/4} \left\{1 - \frac{\epsilon\lambda}{32(c/c^*)}[I + 8(c/c^*)^2 \ln\,(c/c^*)]\right\} + O(\epsilon^2) \quad (5)$$

The good solvent limit of $z \to \infty$ converts the exponent into the first-order approximation quoted above. The previous treatment of Cherayil et al. unnecessarily reexponentiates the prefactor coefficient $-[\epsilon\lambda/32(c/c^*)][1 + 8(c/c^*)^2 \ln\,(c/c^*)]$ resulting in an overestimation of the scaling limit prefactor coefficient m'. Note that eq 5 depends on two dimensionless variables c/c^* and λ. The latter to order ϵ is proportional to the interpenetration function Ψ. While the general expression (5) may be used for solvents with $z \geq 0.5$, the comparison with experiment in subsequent sections employ limiting $z \to \infty$ good solvent assumption as the use of smaller z does not improve agreement with experiment. These good solvent limit computations of (5) replace the first-order exponent ($\epsilon/4$) by the exact scaling limit $(3\nu - 1)^{-1}$ with $\nu = 0.588$.

4. Results

The following compares the RG computations with experimental data from static light scattering (SLS). The comparison is based on the osmotic modulus $(M/RT)(\partial\pi/\partial c)$, which is directly accessible from SLS since the osmotic compressibility provides the forward scattering intensity as $(1/RT)(\partial\pi/\partial c) = K_c/(R(\theta{=}0)) \equiv 1/M_{\mathrm{app}}$, where M_{app} is the apparent molecular weight at concentration $c \neq 0$. The scaling parameter c/c^* is chosen as $A_2Mc \equiv X$, since it arises naturally from the theory in the regularization of the bare osmotic pressure.[2] Here, A_2 is the osmotic second virial coefficient, M is the molecular weight, and c is the polymer concentration in g/mL. However, the theoretical scaling parameter $X_{\mathrm{th}} = \langle A_2\rangle_w M_n c$ is related to different polydispersity averages than the experimental $X_{\mathrm{ex}} = \langle A_2\rangle_{\mathrm{LS}} M_w c$, where n, w, and LS denote number, weight and LS average, respectively. For monodisperse samples the effect due to this difference is negligible, and in the following we assume $X_{\mathrm{th}} = X_{\mathrm{ex}} \equiv X$.

4.1. Linear Chains. According to scaling ideas,[22] universal behavior is expected for the osmotic modulus of long flexible chains, independent of chain length and chemical structure. This prediction may be considered as confirmed by the examples of PS and α − PS in good solvents. Data for these systems from several independent laboratories[24,25] all follow, within experimental error, one single master curve. These literature data are supplemented by our data on linear PS chains in toluene. The PS data are well represented in Figure 1 by the semiempirical expression

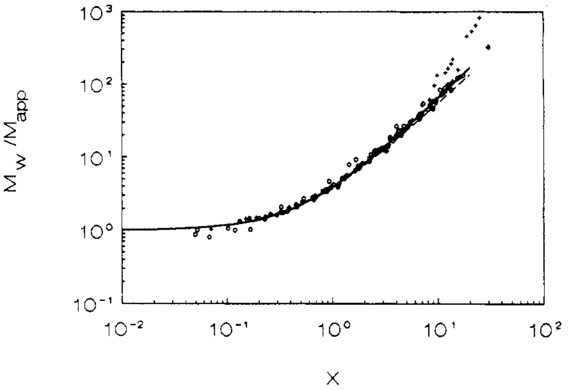

Figure 1. Osmotic modulus of linear chains: dashed line, theory: ●, our data for PS in toluene; ○, literature data for PS and α − PS in toluene; +, data of Koch et al.[32] in concentrated solution; full line, fit to experimental results.

$$\frac{M}{RT}\left(\frac{\partial\pi}{\partial c}\right) = 1 + 2X\left[1 + \left(\frac{q}{p}\right)2X\right]^p J(X) \quad (6)$$

with

$$J(X) = \left(\frac{1 + \left(\frac{q}{p}\right)X}{1 + \left(\frac{2q}{p}\right)X}\right)^p \left(1 + \frac{q}{2}\frac{X}{1 + \left(\frac{q}{p}\right)X}\right) \quad (7)$$

This expression has been introduced by Hager et al.[8] using a series expansion for the osmotic pressure which contains as limiting behaviors the virial expansion for dilute solutions as well as the exponential form at moderate concentrations

$$\frac{\pi M}{RT} = 1 + X[1 + (q/p)X]^p \quad (8)$$

Expanding (8) in powers of X identifies the parameter q as the ratio of the second and third virial coefficients, $q = A_3M/(A_2M)^2$, and for $X \gg 1$ the parameter p corresponds to the exponent in the asymptotic power law $(M/RT)(\partial\pi/\partial c) = mX^p$. Actually, eq 6 only yields the power law behavior for $X > 30$, so all quoted exponents p are obtained from log–log plots. A best least-squares fit to the experimental data is obtained with $q = 0.46 \pm 0.04$ and $p = 0.39 \pm 0.02$. Equation 8 enables the expression of A_3 and all higher virial coefficients in terms of A_2, something which is also possible for hard spheres. In contrast to hard spheres, the physical meaning of the higher coefficients for interpenetrating chains remains questionable. While eq 6 is useful for fitting theoretical computations and experimental data, the physical meaning of the parameter q becomes obscured by this procedure. RG calculations give $q = 0.28$,[26] and this value has been confirmed by experiments for PS in toluene at concentrations for which the series expansion may be truncated at the third virial coefficient,[5] a truncation which enables the description of the osmotic modulus through $X = 3$. However, recent data by Nakamura et al.[27] suggest the q parameter to be $0.25 < q < 0.5$, depending on molecular weight, and therefore to be in the range of earlier theoretical calculations.[28]

The numerically evaluated osmotic moduli from the first-order ϵ expansion are represented in Figure 1 along with the experimental data. This RG computation is well

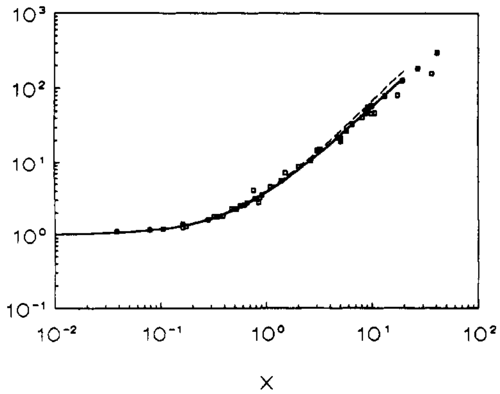

Figure 2. Osmotic modulus of the following: ■, PI; □, PB; full line, theory; dashed line, fit to PS and α – PS data.

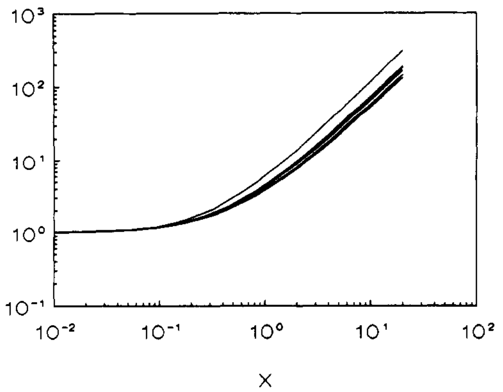

Figure 3. Theoretical results for different architectures. From bottom to top: linear chains, three-arm star, four-arm star, rings, and eight-arm star.

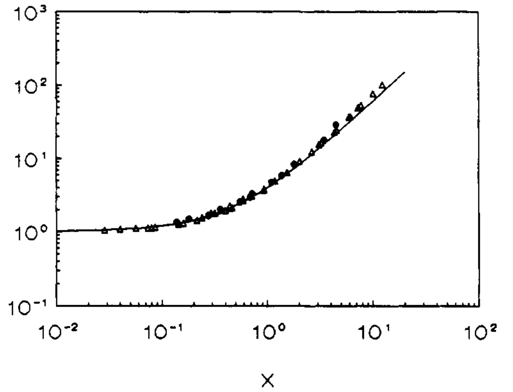

Figure 4. Osmotic modulus of the following: △, 3-arm stars in toluene and 1,4-dioxane; ●, ring PS in toluene as compared with theory for three-arm stars (full line).

described by eq 6 with $q = 0.42$ and $p = 0.32$. The agreement in Figure 1 is excellent for $X < 2$. Differences between experiment and theory become noticable in the region of higher X not only in the prefactor m, but also in the power law exponent p. For $5 < X < 20$ the exponents p are 1.30 and 1.36 ± 0.04 for the theoretical and experimental curves, respectively. It is not completely clear whether the asymptotic limit is actually reached within this range of coil interpenetration as defined by the dimensionless parameter X. The slope of the experimental curve in Figure 1 appears to increase as X becomes larger. The largest value of X yields an exponent $p = 1.42$ from the experimental curve, as also mentioned by Hager et al. Other works likewise report higher exponents than the theoretical scaling limit of 1.32.[5,29]

The influence of moderate and high concentrations is discussed in the literature[10,30,31] and here demonstrated by the data of Koch et al.,[32] who measured the osmotic modulus of PS in dioxane ($M_w = 48\,600$, $A_2 = 8.0 \times 10^{-4}$ mol mL g^{-2}) over the whole concentration range. Deviations from other experimental data occur at $X = 5$ which corresponds to $c = 0.15$ g/mL. Furthermore, contributions of density fluctuations to the total scattering intensity have been found[32] to be important at high concentrations, e.g., 0.7 g/mL, whereas at the concentrations used in this study ($c < 0.12$ g/mL) the concentration fluctuations are dominant.

Data taken from the literature[6] for PI in the good solvent cyclohexane and for PB in 1,4-dioxane[21] are compared with the PS data and with theory in Figure 2. All three linear chain polymers follow the same master curve up to $X \approx 5$. The PI data start to deviate from the PS curve at $X > 8$. At present, no conclusive explanation can be given for this unexpected difference between PI and PS. Both polymers are in the asymptotic good solvent limit, i.e., $z > 3$, based on an estimation of the excluded volume Fixman z-parameter from[33] $\alpha_s^2 = 1.72z^{0.3672}$, where α_s is the radius of gyration expansion factor for which data is taken from the literature.[34,35] One possibility for the difference in behaviors of PS and PI might be due to the influence of the diene chain microstructure, which is neglected in theory, while others are discussed in section 5. Interestingly, the diene exponents p (1.30 ± 0.05 for PI) are closer to theory than that for polystyrene.

4.2. Star and Ring Polymers. RG calculations are expected to be valid for both macrocycles and for stars with $f < 6$, where f corresponds to the number of arms. For many arm stars ($f > 6$) the perturbation from ternary exclused volume interactions in the star center becomes sufficiently large that RG theory no longer provides a useful description.[36] Figure 3 displays the theoretical predictions for some architectures. A common feature is the occurrence of the same exponent as for linear chains, in agreement with scaling expectations.

We first consider three-arm star and ring polymers, since in these cases the best agreement between theory and experiment is anticipated. Dilute solution properties are given in Table I. Based on similarities in molecular weight dependences of radii of gyration, ring polymers are expected to show a behavior similar to four- or five-armed stars. Figure 4 displays the experimental data for three-arm and macrocyclic PS in comparison with the theoretical curve for three-arm stars. The experimental data of both the star and ring polymers follow the same curve with the fitted parameters $q = 0.495 \pm 0.03$ and $p = 0.455 \pm 0.02$, but as for linear PS chains, the osmotic modulus for the three-arm stars is underestimated by theory. An apparent exponent of 1.38 ± 0.04 is found for $5 < X < 10$, which is equal to that obtained for linear PS chains. Since only a limited amount of experimental data is available, it is inadequate to base detailed comparison solely on exponents.

A convenient way to discuss the influence of architecture on the osmotic modulus is to consider universal ratios such as $[M/M_{app}(f)]/[M/M_{app}(\text{lin})] = [M_{app}(\text{lin})/M_{app}(f)]$ for experimental and theoretical data over the available range of X. The purpose of this ratio formation is to eliminate the common power law portion as well as any possible nonuniversal factors which are expected to be almost the same for the linear and star polymers. Figure 5 compares the theoretical and experimental ratios for three-arm star polymers. Up to $X \approx 4$ the ratios are identical in contrast to the absolute values which already start to deviate at $X > 2$. However, at larger X, the experimental data from three-arm stars display a higher apparent exponent than those from linear chains and thus contrast with the

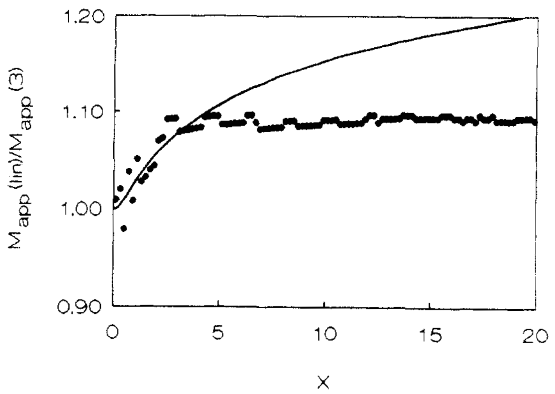

Figure 5. Ratios M_{app}(lin)/M_{app}(3): ●, theory, from numerical evaluation of integrals; full line, from fit to experimental data. For $X > 10$ the experimental line corresponds to an extrapolation, since data are available only for $X < 10$.

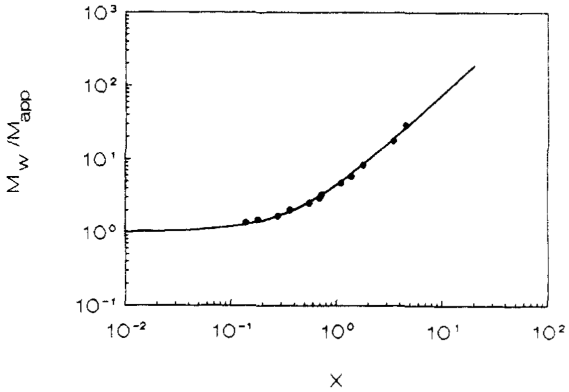

Figure 6. Comparison between theory (full line) and experiment for ● ring PS in toluene.

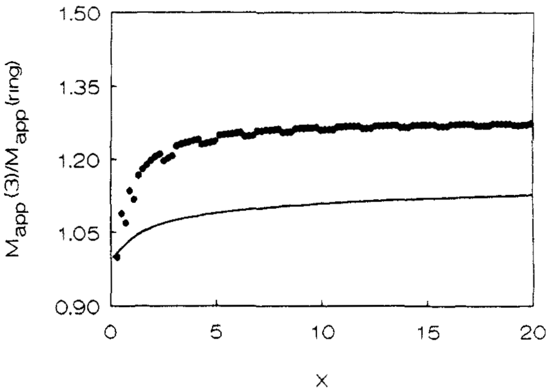

Figure 7. Ratios M_{app}(3)/M_{app}(ring) of osmotic modulus for three-arm stars and ring polymers: ●, calculated from theory; full line, fit to experimental data. Note: Experimental data are available only for $X < 5$.

theoretical curves for M_{app}(lin)/M_{app}(3) which reach their asymptotic limit already at $X > 4$.

Macrocyclic PS yields much better agreement between theory and experiment (Figure 6). Measured and calculated values of the osmotic modulus are nearly identical over the whole experimentally available range ($X < 5$). However, this experimental range is not sufficient to permit making definite statements about the asymptotic power law behavior. Thus, again ratios are formed, but now of M_{app}(3)/M_{app}(ring). Figure 7 reveals differences between the two architectures to be less than predicted by theory. An extrapolation of the ratios to large X further suggests that the apparent exponents p for the two architectures are identical, but different from that of linear chains.

As already mentioned, agreement RG theory and experiment cannot be expected for many-arm stars ($f > 6$). This is demonstrated by Figure 8 for eight-arm PI and 12-arm PS stars. In contrast to architectures with a smaller number of arms, the dimensionless osmotic pressure is now overestimated by theory. The many-arm systems yield theoretical problems mainly from ternary interaction contributions to excluded volume effects,[2] and this is partially reflected in poor predictions of the second virial coefficient A_2. The theoretical A_2 of 12-arm PS is a factor of 1.5 lower than that determined from experiment, and this tendency increases with the number of arms.[36] Therefore, an attempt to correct theory empirically consists in dividing the scaling factor X by this value. The "corrected" theory fits the experimental value reasonably well. However, the fact that the same factor of 1.5 is required for both eight- and 12-arm polymers may reflect the crudeness of such procedure.

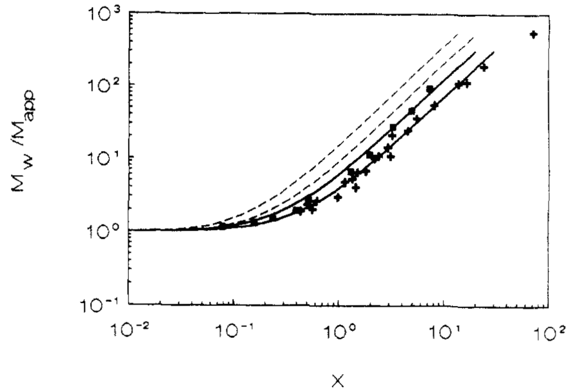

Figure 8. Comparison between eight-arm PI and 12-arm PS: +, eight-arm PS; ■, 12-arm PS; dashed lines, theory; full lines, theory with A_2 "corrected" by a factor 1.5.

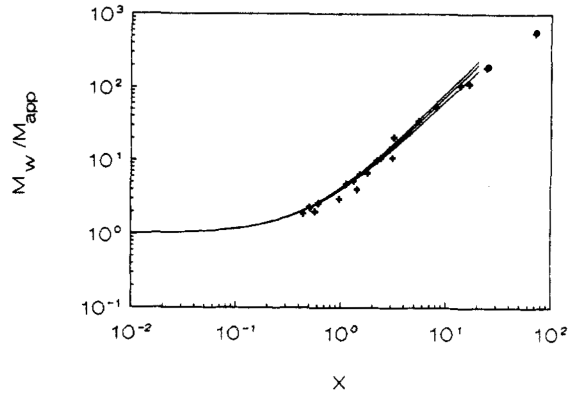

Figure 9. Comparison of + eight-arm PI data with fits to experimental data for PS. From bottom to top the lines are as follows: linear chains, three-arm PS, ring PS.

Another difficulty in comparing data arises from the different chemical structures and is more evident in comparisons between data for PS and PI. The apparent exponent p for the 12-arm PS star is found to be 1.5 ± 0.04 for $1.5 < X < 7.5$, while for the 8-arm PI a value of 1.32 ± 0.05 is reported. The osmotic modulus of the eight-arm PI is generaly lower than would be expected by extrapolating from the styrene star and ring polymers data (Figure 9), a tendency that is also observed for the two types of linear chains. This trend is even more pronounced when literature data for the 18-arm PI are included. Compared to the variations occuring with PS systems, the differences in the osmotic modulus for the isoprene polymers are nearly negligible (Figure 10).

5. Discussion

The osmotic modulus for linear chains of PS, PI, and PB is compared with new renormalization group (RG)

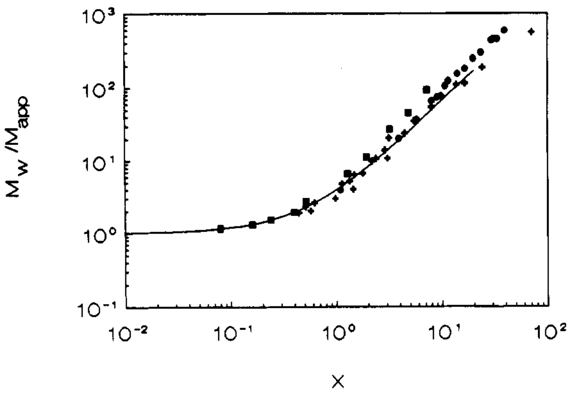

Figure 10. Comparison of + eight-arm PI and ● 18-arm PI with ■ 12-arm PS and fit to linear PS chains in toluene (full line).

computations. The theoretical approach used in this study fits experiment appreciably better than the approximate first-order RG treatment of Ohta and Oono.[37] Nevertheless, the present more complete first-order RG computations do not represent all the experimental data satisfactorily. This observation holds mainly for PS and α − PS in the good solvent toluene, where sufficient data are available from different laboratories. The main discrepancy arises because RG theory (and scaling) yields an exponent p which is lower than that observed for PS. Averaging over a Schultz–Zimm molecular weight distribution for linear chains shows that polydispersity is not strong enough to explain this behavior. In contrast to the available data for PS chains, those for a PI chain exhibit lower osmotic compressibilities and are nearly exactly represented by the new theoretical computations. On the other hand, the PB dimensionless osmotic modulus is still lower, such that it is overestimated by theory for large X. This then poses questions of nonuniversality for linear chains that differ in chemical composition. The origins of this discrepancy remain to be understood, and may arise from the influence of diene chain microstructure or chain stiffness.

Recently, Yamakawa[38] studied the influence of chain stiffness and excluded volume on the penetration function Ψ and second virial coefficient using the Yamakawa–Shimada–Stockmayer theory.[39–41] Although Yamakawa's calculations do not consider the semidilute solution osmotic compressibility, the current lack of renormalization group calculations for excluded volume effects in stiff polymer chains make it useful to use Yamakawa's calculations to guesstimate the influence of chain stiffness on the experimental data. Interestingly, Yamakawa finds that the effective z-parameter has an additional molecular weight dependence for stiff chains that may help to explain the deviation of the experimental apparent PS exponent from scaling and renormalization group predictions, and explicit computations for the osmotic compressibility would be helpful in checking this possibility. Another possible reason may arise from nonuniversalities that are inherent in using M/M_{app} as the dimensionless osmotic modulus. The alternative choice of XM/M_{app} as the basic variable leads to a better, although not universal, scaling of the PS, PI, and PB data.

A difference in apparent exponents is also found for the star molecules. Compared to the data for three-arm, 12-arm, and ring PS, the experimental M/M_{app} for eight-arm and 18-arm PI are lower and not as strongly dependent on architecture. The apparent exponents for PI are all found to be around 1.30, as predicted by theory and in variance to PS.

One feature, which may play an important role in causing the discrepancies between theory and experiment and between PI and PS, involves the lengths of arms in the star polymers. While the arms of the PS stars are relatively short (M_{arm} = 30 000 and 75 000 for the three-arm stars and 12 500 for the 12-arm star), the PI stars have considerably longer arms; they are as large as 220 000 for the eight-arm stars and range from 83 000 to 380 000 for the 18-arm star. Thus, according to the Daoud–Cotton model of star polymers[42] the influence of the central branch portion should be much less pronounced for the long arm stars than for the PS stars which have a relatively high internal density. Thus, the 12-arm PS investigated here is expected to behave much more like a hard sphere than the PI stars with very long and hence flexible arms. Very compact, impenetrable particles, such as hard spheres, are known[4,5,45] to exhibit a much stronger increase in the osmotic pressure with c/c^* than flexible chains or stiff rods.[43,44] Higo et al.[3] have emphasized the influence of the central branch portion on the osmotic pressure of comb-branched PS, and Witten et al.[46] predict a higher apparent exponent for the osmotic presure at intermediate values of X, due to the hard core repulsions. As discussed above, the renormalization group calculations do not include the influence of ternary interactions, which become more significant near the star core and therefore limit the applicability of the RG calculations to stars with $f \leq 6$.[47] In addition, for a fixed number of arms the influence of ternary interactions should diminish as the arm lengths grow. Thus, further careful experiments with higher molecular weights should help to decrease complications from both ternary interactions and chain stiffness.

While all the different PI architectures exhibit the same apparent exponent, this seems not to be the case for PS stars and rings. This exponent variation is not directly apparent from the absolute values of osmotic moduli, but is evident from the universal ratios $M_{app}(\mathrm{lin})/M_{app}(f)$ which clearly demonstrate increased exponents, even for the three-arm stars where p differs very slightly from linear chains. Furthermore, the differences between ring and three-arm PS are evident, but not as strong as predicted by theory. The agreement between experiment and theory for the ring PS may be somewhat fortuitous and appear by virtue of the limited range of experimental data.

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