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Universal Ratios of Characteristic Lengths in Semidilute Polymer Solutions

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ABSTRACT: We use experimental and simulation data from the literature to infer five characteristic lengths, denoted ξ_s, ξ_f, ξ_Π, ξ_ϕ, and ξ_D of a semidilute polymer solution. The first two of these are defined in terms of scattering from the solution, the third is defined in terms of osmotic pressure, the fourth is defined by the spatial monomer concentration profile, and the last is defined by cooperative diffusion. In a given solution, the ratios of any of these five lengths are expected to be universal constants. Knowing these constants thus allows one to use one measured property of a solution as a means of inferring others. We calculate these ratios and estimate their uncertainties for solutions under Θ as well as good solvent conditions. The analysis is strengthened by use of scattering properties of isolated polymers inferred from computer simulations.

1. Introduction

In the 1970s, it was recognized that polymer solutions are a form of critical phenomenon.[1] In the intervening years, a network of powerful consequences of this recognition have been verified. Many measured properties vary with concentration and with molecular weight according to power laws whose exponents are known only approximately, but which are shown to be universal—that is, unchanged under continuous changes in the system properties. Moreover, the coefficients in these power laws are shown to be inter-related by universal ratios. Some of these ratios predict universal properties of dilute solutions. In 1987, Davidson et al. expressed some of this universality in an elegant way by determining characteristic lengths.[2] Several experimental measurements were made on a number of solutions, and each was reduced to a length. Thus, for example, light-scattering measurements were used to determine the radius of gyration. Several different lengths were inferred from different measurements on a given solution. When these lengths were compared, their ratios were found to be independent of the solution studied, thus confirming the anticipated universality. In the process, the experiments obtained well-determined values for the universal ratios that remain as an important part of our knowledge of polymers.

Our aim in this paper is to obtain analogous information for the semidilute regime. Semidilute solutions are commonly characterized by a length derived from small-angle scattering called the correlation length ξ_s.[3] Other common characteristics of these solutions can also be reduced to a length. For instance, the osmotic pressure Π may be expressed in terms of a length ξ_Π (eq 1). Likewise, the cooperative diffusion coefficient D_c can be used to define a hydrodynamic length ξ_D analogous to Stokes' law (eq 2). Like Davidson's dilute lengths,[2] the ratios of these ξ's are expected to be universal in the semidilute limit. The semidilute limit means the limit in which the volume fraction of polymer is at once much larger than the overlap volume fraction, and much smaller than unity. Naturally this limit requires polymers of sufficiently high molecular weight.

In this paper, we determine these semidilute length ratios and several others (Table 2) using data from the experimental literature (Table 1). We expect that knowledge of these ratios should be useful for those who study these solutions. Experimentally, one may use the ratios to predict one experimental quantity such as the cooperative diffusivity from another, such as the scattering correlation length. Conceptually, these ratios give one a clearer picture of the interior structure of the solution. We emphasize that these predictions are not scaling relations with undetermined numerical prefactors. They are quantitative predictions with stringent uncertainly limits.

To demonstrate the utility of these universal ratios, let us study the aqueous polymer solution, poly(ethylene glycol) (PEG) in water at room temperature as an example. The cooperative diffusion coefficient D_c for this system can be inferred simply from the osmotic pressure data and the universal ratios given in Table 2. The osmotic pressure $\Pi \approx 2.95 \times 10^5$ Pa for the case where the PEG molecular weight is 20 000 and the concentration 16 wt %.[4] This Π gives the *osmotic* length $\xi_\Pi \approx 24$ Å (eq 1). By use of Table 2, we obtain the *diffusive* length $\xi_D \approx 11$ Å and hence the cooperative diffusion coefficient $D_c \leq 2 \times 10^{-10}$ m^2/s (eq 2),[5] which agrees with Brown's result.[6] Table 2 thus allows one to use a simple measurement to infer the results of a more difficult measurement.

The universal properties of semidilute solutions have been much explored and tested over the past two decades. The purpose of our work is not to extend the scope of these tests. Instead, we aim to distill known semidilute results into a form that is as useful and simple as possible for one studying a particular semidilute solution. Thus, we define our lengths in a way that does not require a knowledge of the dilute properties of the polymer and solvent in question. Another virtue of our approach is accuracy. Most universal ratios for semidilute quantities reported in the literature require knowledge of dilute quantities with the same polymer and solvent, such as the radius of gyration.

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Table 1. Sources of Experimental and Simulation Data Used in This Work

source[a]	probe[b]	$M_w \times 10^{-6}$	$[[P_\infty]]$	$\{\Omega\}$	ξ_ϕ	ξ_s	ξ_Π	ξ_D	ξ_f
dm1[21]	MC	$N \le 4096$	X	X	–	–	–	–	–
dm2[22]	MC	$N \le 2048$	X	X	–	–	–	–	–
da[24]	LS	8–60	–	X	X	–	–	–	–
sa[15,25,26]	LS	0.4–21	–	–	–	X	–	–	–
sa[25]	LS	1–21	–	–	–	–	X	–	–
sa[15,27]	DLS, CGD	0.4–21	–	–	–	–	–	X	–
db[17]	NS	0.05–1.3	X	X	X	–	–	–	–
sb[9,28]	NS	0.5–1	–	–	–	X	–	–	X
dc[29]	LS	0.2–2	–	X	X	–	–	–	–
sc[30]	XS	0.1–2	–	–	–	X	X	–	–
sc[32]	CGD	0.2–3	–	–	–	–	–	X	–

[a] "d" and "s" stand for "dilute" and "semidilute", respectively. m1: a polyethylene chain model of N C–C bonds. m2: the bond-fluctuation lattice model for a polymer of chain length N. a: PS + cyclohexane at 35 °C. b: PS + CS_2 at 20 °C. c: PS + toluene at 25 °C. [b] MC: Monte Carlo simulation. LS: light scattering. NS: neutron scattering. XS: X-ray scattering. DLS: dynamic LS. CGD: classical gradient diffusion.

These dilute quantities are often sensitive to polydispersity, while the semidilute quantities of interest are not. Thus, recasting the universal information without reference to dilute quantities removes an important source of uncertainty.

Rules about Symbol Usage. To improve the readability of this paper, quantities that depend only on polymer and solvent species but not on concentration or molecular weight are enclosed by curly brackets, for example, $\{A\}$, and quantities that are universal by double brackets, for example, $[[P_\infty]]$. We treat as universal any ratio of two quantities (a) that individually diverge in the semidilute limit defined above and (b) that have the same predicted scaling dependence on a parameter such as concentration, so that their ratio is predicted to be independent of the parameter. The symbol → used in this paper deserves special attention: **a** → **b** means **a** approaches **b** in the asymptotic limit under discussion (for example, dilute or semidilute limit).

Organization of this Paper. This paper is organized as follows: The characteristic lengths for a semidilute polymer solution are defined in section 2. In section 3 we propose two approaches to determining the important quantity $\{C_{\max}A^{3-(1/\nu)}\}$ and express the ratios of the static lengths, ξ_s, ξ_Π, ξ_f, and ξ_ϕ in terms of the basic quantities $[[\beta_2]]$ and $[[\beta_4]]$. In section 4, we describe the experiments and simulations on which our results are based. In section 5, we report our values of the ξ ratios as well as $[[\beta_2]]$ and $[[\beta_4]]$ for both good and Θ solvents. In section 6, we comment on the limitations and implications of these ratios. We also compare our results with those found in the literature. Finally, our work concludes with section 7. Readers not interested in the details of the analysis may skip sections 3, 4, and 5 and look directly at Table 2.

2. Definitions of Characteristic Lengths

Before proceeding, we define explicitly the lengths we will discuss. As noted above, the *osmotic* length ξ_Π is related to the osmotic pressure Π of the polymer solution by

$$\Pi = k_B T/\xi_\Pi^{\,3} \tag{1}$$

where k_B is the Boltzmann constant and T is the temperature. We also define a *diffusive* length ξ_D from the cooperative diffusion coefficient D_c:[3,7]

$$D_c \equiv \frac{k_B T}{6\pi\eta_s\xi_D}, \tag{2}$$

where η_s is the viscosity of the solvent. The *scattering* correlation length ξ_s is inferred from the static structure factor $S(q)$ at wavevector q:[9]

$$S(q) = S_0(1 - \xi_s^{\,2}q^2 + \mathcal{O}(q^4)) \tag{3}$$

where S_0 is the extrapolation of $S(q)$ at $q = 0$. We note that $\xi_s^{\,2} = {}^1/_3\, R_G^{\,2}$ in the dilute limit, where R_G is the radius of gyration of the polymer. A related length ξ_f may be inferred from the scattering in the so-called *fractal* wavevector regime where $1/q$ is much smaller than ξ_s but much larger than a monomer. In this regime $S(q) \sim q^{-1/\nu}$, where the Flory swelling exponent $\nu \simeq 0.588$ for good solvent cases.[8] From this fractal law, we may define the length ξ_f by

$$S(q) \to S_0(q\xi_f)^{-1/\nu} \tag{4}$$

where q is in the fractal regime. Here, as mentioned above, **a** → **b** means that **a** approaches **b** in the asymptotic limit under discussion.

Closely related to ξ_f is a length characterizing the local monomer concentration profile. We define C to be the average monomer concentration and $\langle C(r)\rangle_0$ as the ensemble average of the *local* concentration at distance r from an arbitrary monomer. If this r is much larger than the monomer size $\{a\}$ and much smaller than ξ_s, then $\langle C(r)\rangle_0 \sim r^{1/\nu-3}$.[9] This behavior gives rise to the fractal scattering of eq 4, as discussed below. We define the *concentration* length ξ_ϕ by[10]

$$\langle C(r)\rangle_0 \to C(r/\xi_\phi)^{(1/\nu)-3} \tag{5}$$

where r is in the fractal regime defined above. That is, ξ_ϕ is the distance at which the extrapolated fractal concentration profile meets the solution concentration C, as shown in Figure 1.

We note here that another dynamic length ξ_p can be defined as the radius of a circular pipe with the same solvent permeability as the polymer solution of interest.[11] The solvent permeability P is the ratio of solvent flux to pressure gradient and is usually inferred from the sedimentation coefficient,[12,13] which is rigorously related to the cooperative diffusion coefficient D_c and the osmotic pressure Π.[14,15] Hence, ξ_p can be expressed in terms of ξ_D and ξ_Π:[11]

$$P \equiv \frac{\xi_p^{\,2}}{8} = \frac{(3 - 1/\nu)}{18\pi} \cdot \frac{\xi_\Pi^{\,3}}{\xi_D} \tag{6}$$

3. Relations to Structural Coefficients

In this section, we define a set of structural coefficients that characterize the concentration profile $\langle C(r)\rangle_0$ in a semidilute solution. We found it convenient to relate the static lengths, ξ_s, ξ_ϕ, ξ_f and ξ_Π to these coefficients since all of these lengths can be determined by scattering (eq 10): The leading term S_0 and the q^2 term of the static structure factor $S(q)$ determine ξ_Π and ξ_s respectively (eqs 3 and 18). $S(q)$ in the fractal q regime gives ξ_f as well as ξ_ϕ (eqs 4, 8 and 11). Above, we defined the length ξ_ϕ from the local concentration $\langle C(r)\rangle_0$. We

Table 2. Universal Ratios of the Characteristic Lengths in Semidilute Polymer Solutions

system[a]	$\{A\}$(Å)	$[[\xi_\phi/\xi_s]]$	$[[\xi_\Pi/\xi_s]]$	$[[\xi_f/\xi_s]]$	$[[\xi_D/\xi_s]]$	$[[\beta_2]]$	$[[\beta_4]]$
a	3.21 (±7%)	0.61 (±9%)	2.97 (±5%)	–	4.29 (±10%)	18 (±22%)	968 (±28%)
b	2.79 (±7%)	1.23 (±8%)	–	1.27 (±1%)	–	4.8 (±14%)	64 (±21%)
c	3.16 (±7%)	1.23 (±9%)	3.81 (±6%)	–	1.65 (±7%)	4.3 (±23%)	61 (±29%)

[a] Key: (a) PS + cyclohexane at 35 °C; (b) PS + CS_2 at 20 °C; (c) PS + toluene at 25 °C.

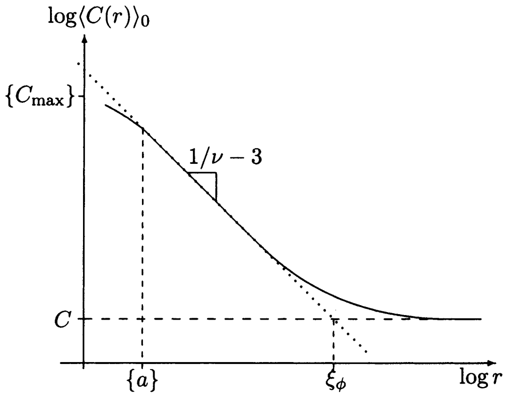

Figure 1. Schematic diagram of the local concentration $\langle C(r)\rangle_0$ (solid line) for a semidilute polymer solution. $C_A(r) \equiv \{C_{\max}A^{3-(1/\nu)}\}/r^{3-(1/\nu)}$ (dotted line). $\{C_{\max}\}$ is the bulk concentration of the polymer in question and $\{a\}$ is the size of a monomer. $\langle C(r)\rangle_0 \approx C_A(r)$, when $\{a\} \ll r \ll \xi_\phi$. ξ_ϕ is such that $C_A(\xi_\phi) = C$. When $r \geq \xi_\phi$, $\langle C(r)\rangle_0$ departs from $C_A(r)$ and approaches the average monomer concentration C.

may express this $\langle C(r)\rangle_0$ in terms of the bulk concentration $\{C_{\max}\}$ for the polymer in question. Here we exploit the fact that $\langle C(r)\rangle_0$ is unaffected by the surrounding solution when r is small. Thus, in the fractal r regime, we may use eq 5 and define the *fractal* length $\{A\}$:

$$\frac{\langle C(r)\rangle_0}{\{C_{\max}\}} \rightarrow \left(\frac{\{A\}}{r}\right)^{3-(1/\nu)}, \quad \text{for } \{a\} \ll r \ll \xi_\phi \tag{7}$$

where $\{a\}$ is the monomer size. This $\{A\}$ is useful because it is independent of concentration. Evidently,

$$\xi_\phi = \left(\frac{\{C_{\max}A^{3-(1/\nu)}\}}{C}\right)^{\nu/(3\nu-1)} \tag{8}$$

Determination of $\{C_{\max}A^{3-(1/\nu)}\}$. The coefficient $\{C_{\max}A^{3-(1/\nu)}\}$ depends only on the polymer and solvent species and is independent of concentration. Although $\{C_{\max}\}$ and $\{A\}$ are two conceptually independent quantities, they go hand in hand in this paper in the form of $\{C_{\max}A^{3-(1/\nu)}\}$, which, moreover, can be measured with scattering experiments. In the following, we present two approaches to determining $\{C_{\max}A^{3-(1/\nu)}\}$, both of which are used in this paper.

The scattering structure–function $S(q)$ in the fractal q regime can also be expressed in terms of $\{C_{\max}A^{3-(1/\nu)}\}$. Here we take the monomer as our elementary scatterer. For a scattering volume V, $S(q)$ may be written as[9]

$$S(q) = \frac{1}{VC}\sum_{j,k=1}^{VC}\langle \exp[i\vec{q}\cdot(\vec{r}_j - \vec{r}_k)]\rangle \tag{9}$$

where $\vec{r}_j$ is the position vector of the jth monomer and $\vec{q}$ the wave vector transfer. In our notation, this reduces to

$$S(q) = \int_V d^3r\, \langle C(r)\rangle_0 \exp(i\vec{q}\cdot\vec{r}) \tag{10}$$

The fractal regime of $\langle C(r)\rangle_0$ gives rise to a complementary behavior in the fractal q regime:[9] The power law regime of eq 7 produces the scattering at the fractal wavevector mentioned in eq 4. By combining eqs 7 and 10, one finds

$$S(q) \rightarrow c_0\frac{\{C_{\max}A^{3-(1/\nu)}\}}{q^{1/\nu}} \quad \text{for } 1/\xi_\phi \ll q \ll 1/\{a\} \tag{11}$$

where

$$c_0 \equiv 4\pi \sin\left(\frac{\pi}{2}(1/\nu - 1)\right)\Gamma(1/\nu - 1) \tag{12}$$

is a numerical constant and $\Gamma(x)$ is the Γ function. We note that eq 11 still holds in the dilute limit, where $\xi_s \simeq R_G$, so the fractal q regime means $1/R_G \ll q \ll 1/\{a\}$.[16] Hence, $\{C_{\max}A^{3-(1/\nu)}\}$ can be determined by scattering experiments on either dilute or semidilute solutions in the fractal q regime. This conclusion also leads into the other approach to determining $\{C_{\max}A^{3-(1/\nu)}\}$.

For a given polymer and solvent, the coefficient $\{C_{\max}A^{3-(1/\nu)}\}$ can also be related to the dilute property of that polymer solution. The chain length N of an isolated polymer is related to the radius of gyration R_G by

$$N \rightarrow (R_G/\{\Omega\})^{1/\nu} \tag{13}$$

We follow the work of Rawiso et al. and define a universal constant $[[P_\infty]]$ for a dilute polymer solution:[17]

$$[[P_\infty]] \rightarrow S(q)/N\cdot(qR_G)^{1/\nu} \quad \text{for } 1/R_G \ll q \ll 1/\{a\} \tag{14}$$

By combination of eqs 11, 13, and 14, $\{\Omega\}$ can then be written as

$$\{\Omega\} = ([[P_\infty]]/c_0)^\nu\{C_{\max}A^{3-(1/\nu)}\}^{-\nu} \tag{15}$$

We note that $[[P_\infty]]$ is just $\bar{P}_\infty$ defined in the paper of Rawiso et al.[17] In this paper we first determine the universal constant $[[P_\infty]]$ using single-chain experiments or simulations (section 4). When $[[P_\infty]]$ is determined, eq 15 can then be used to calculate $\{C_{\max}A^{3-(1/\nu)}\}$ of the system whose $\{\Omega\}$ has been known.

Moments of Local Concentration. Beyond the fractal regime governed by the coefficient $\{C_{\max}A^{3-(1/\nu)}\}$ discussed above, the local concentration $\langle C(r)\rangle_0$ departs from the power-law form and becomes constant (Figure 1). It is convenient to define the reduced moment $[[\beta_n]]$ to characterize this part of the concentration profile:

$$[[\beta_n]] \equiv \frac{\int_0^\infty dr\, r^n(\langle C(r)\rangle_0 - C)}{\int_{C_A>C} dr\, r^n(C_A(r) - C)} \tag{16}$$

where $C_A(r) \equiv \{C_{\max}\}(\{A\}/r)^{3-(1/\nu)}$ (cf. Figure 1), and we use the behavior in the fractal regime to normalize these moments. Several of the ξ ratios can be expressed completely in terms of these reduced moments. By Taylor-expanding eq 10 with respect to q, we show in the appendix that for semidilute polymer solutions (eq 41)

$$[[\xi_s/\xi_\phi]] \to \left(\frac{[[\beta_4]]}{10(1+2\nu)[[\beta_2]]}\right)^{1/2} \qquad (17)$$

The moment $[[\beta_2]]$ may be related to ξ_Π by using the compressibility sum rule:[3]

$$S_0 = k_B T \frac{\partial C}{\partial \Pi} \qquad (18)$$

where S_0 is defined in eq 3. This S_0 can then be expressed in terms of $[[\beta_2]]$, thus yielding a relation between $[[\xi_\Pi/\xi_\phi]]$ and $[[\beta_2]]$ (eq 40):

$$[[\xi_\Pi/\xi_\phi]] \to (4\pi\nu[[\beta_2]])^{1/3} \qquad (19)$$

Finally, by virtue of eqs 4, 11, and 34, we obtain

$$[[\xi_f/\xi_\phi]] \to \left(\frac{4\pi}{3c_0}(3\nu - 1)[[\beta_2]]\right)^{\nu} \qquad (20)$$

where the numerical coefficient c_0 is defined in eq 12. We hence conclude that ξ_f gives no additional information if ξ_ϕ and ξ_Π are known.

4. Sources of Data

Our results are based on the experimental data of solutions of polystyrene(PS) in the good solvents, toluene and carbon disulfide(CS_2), and the solvent cyclohexane at its Θ temperature. A few terms such as C and $\{C_{\max}\}$, though having the merit of theoretical simplicity, are not particularly convenient for experimentalists. Hence, we quote experimental results from literature without converting them into terms used in preceding sections, so that audience can easily double-check our calculations if needed.

For nondeuterated PS, the molecular weight $\{m_s\}$ of the monomer ($CH_2CHC_6H_5$) is 104 and the bulk density $\{\rho_{\max}\}$ is 1.05 g/cm^3,[18] so that $\{C_{\max}\} = 6.08 \times 10^{-3}$ Å^{-3}. In this paper, we assume the value of $\{C_{\max}\}$ is invariant, regardless of whether the polymers are deuterated or not. Thus, we have ignored possible effects of tacticity of the molecules or of processing to obtain the neat (glassy) state of the polymer. Such effects introduce insignificant uncertainties compared to other uncertainties. Table 1 summarizes the sources of data and the quantities we derive from the associated sources.

The Values of $[[P_\infty]]$. The determination of ξ_ϕ requires the knowledge of $\{C_{\max}A^{3-(1/\nu)}\}$, which can be obtained from the scattering data in the fractal q regime (eq 11). However, data of this sort are rare. Measurements of $\{\Omega\}$ (eq 13) are much more accessible and provide the same information if the universal coefficient $[[P_\infty]]$ is known (eq 15). We may determine $[[P_\infty]]$ using polymer simulations or theory. Under Θ conditions $[[P_\infty]]$ may be determined analytically by treating the polymers as ideal random walks.[20] It is straightforward to show that $[[P_\infty]] = 2$ for Θ cases.[17] Destrée et al. obtained $S(q)$ for a single polyethylene under Θ and good solvent conditions using Monte Carlo techniques.[21] From their results, we determine $[[P_\infty]] = 2$ (±4%) for the Θ cases where the number of C−C bonds $N \leq 4096$, and $[[P_\infty]] = 1.26$ (±22%) for the good solvent cases where $N \leq 1024$. Müller et al. reported $S(q)$ in their Monte Carlo simulation of a single chain,[22] which yields $[[P_\infty]] = 1.23$ (±4%). $[[P_\infty]] = 1.20$ (±14%) was also obtained using the scattering data for dilute PS in the good solvent CS_2.[17] These values are consistent with the renormalization group estimate of $[[P_\infty]] = 1.29$ to first order in $\epsilon \equiv$ (4 minus the dimension of space).[8,23] In the following sections, $[[P_\infty]] = 2$ and 1.23 (±4%) are adopted to calculate ξ_ϕ for Θ and good solvent cases, respectively.

PS + Cyclohexane at 35 °C. Although for many purposes, polymers in Θ solvents may be considered as ideal random walks, Θ polymers interact, and their semidilute solutions differ from a solution of noninteracting polymers. Thus, not all of the universal ratios we seek for Θ solutions can be found analytically. Here we make use of several studies of PS in cyclohexane at 34.5 °C (or 35 °C), a well-known Θ solvent. Hayward and Graessley reported $R_G \to 0.28$ (±4%) $M^{0.5}$Å,[24] which implies (eq 13)

$$\{\Omega\} = 2.86\ (\pm 4\%)\ \text{Å} \qquad (21)$$

The behavior of ξ_s is given in Adam and Delsanti's paper,[15] where they summarized the results of neutron- and light-scattering experiments:[25,26]

$$\xi_s = \frac{5.5}{\rho}\ (\pm 5\%)\ \text{Å} \qquad (22)$$

where ρ is measured in g/cm^3. They also reported

$$D_c = 1.25\ (\pm 8\%) \times 10^{-6}\rho\ \text{cm}^2/\text{s}, \quad \text{for } \rho \leq 0.08\ \text{g/cm}^3 \qquad (23)$$

We note that the viscosity η_s of cyclohexane at 35 °C is 0.762×10^{-2} P.[32] Their result is consistent with the classical gradient diffusion measurement done by Roots and Nyström.[27] Stepanek et al. measured the osmotic compressibility using a light-scattering technique.[25] They obtained

$$\frac{1}{\rho}\frac{\partial\Pi}{\partial\rho} = 2.93 \times 10^7 \rho, \quad \text{for } 3 < \rho/\rho^* < 11 \qquad (24)$$

where $\partial\Pi/\partial\rho$ is expressed in dyn·cm/g and ρ is in g/cm^3.

Perdeuterated PS + CS_2 at 20 °C. CS_2 is known to be a good solvent for PS at 20 °C. Rawiso et al. measured the radius for dilute perdeuterated PS in CS_2 and reported $R_G \to 0.133$ (±4%) $M_w^{0.588}$(above eq 46 of the paper by Rawiso et al.[17]). Since the molecular weight $\{m_s\}$ of a perdeuterated monomer is 112, according to the definition of $\{\Omega\}$ (eq 13), we infer

$$\{\Omega\} = 2.13\ (\pm 4\%)\ \text{Å} \qquad (25)$$

Here M_w is identified with M without further concern about the polydispersity, which is justified if the polydispersity is small. Rawiso et al. also reported $S(q)$ in the fractal q regime (above eq 46 of the paper by Rawiso et al.[17]):

$$S(q)\cdot q^{1/\nu} \to 0.330\ (\pm 8\%)\ \text{Å}^{-1/\nu}$$

which, in view of eq 11, gives

$$\{C_{\max}A^{3-(1/\nu)}\} = 2.27\ (\pm 8\%) \times 10^{-2}\text{Å}^{-1/\nu} \qquad (26)$$

Farnoux et al. measured ξ_s for semidilute perdeuterated PS in CS_2 also using neutron scattering:[28] $\xi_s = 44$ Å (ρ

$= 0.025$ g/cm^3, $M_w = 1.1 \times 10^6$), 29.8 Å ($\rho = 0.04$, $M_w = 5 \times 10^5$), 18.3 Å ($\rho = 0.075$, $M_w = 5 \times 10^5$) and 10.5 Å ($\rho = 0.15$, $M_w = 5 \times 10^5$). We note that since they used perdeuterated PS, the monomer concentration C and the chain length N are related to ρ and M by $C = N_a\rho/112$ and $N = M/112$, respectively, where N_a is Avogadro's constant. Des Cloizeaux and Jannink reported in their book (below eq 15.4.37) that

$$\frac{S_0}{S(q)}\cdot(q\xi_s)^{-1/\nu} = 1.51\ (\pm 1\%) \quad \text{for } q\xi_s \geq 2.6 \qquad (27)$$

from which we can calculate ξ_f.

PS + Toluene at 25 °C. Higo et al. summarized the results of several light-scattering experiments and reported $R_G{}^2 = 1.38 \times 10^{-2}\ M^{1.19}$ Å^2.[29] This implies (eq 13)

$$\{\Omega\} = 1.95\ (\pm 5\%)\ \text{Å} \qquad (28)$$

The small-angle X-ray scattering experiment done by Hamada et al. gives ξ_s and S_0:[30]

$$\xi_s = 2.67\rho^{-0.77}\ (\pm 5\%)\ \text{Å} \qquad (29)$$

and

$$S_0 = 2.65\rho^{-1.30}\ (\pm 10\%) \qquad (30)$$

where $\rho \leq 0.1$ is measured in g/cm^3. The cooperative diffusion constant is given in Schaefer and Han's review article:[32]

$$D_c = 93.0\left(\frac{C}{\{C_{\max}\}}\right)^{0.75} (\pm 5\%) \times 10^{-7}\text{cm}^2/\text{s}, \quad \text{for } 0.02 \leq C/\{C_{\max}\} \leq 0.08 \qquad (31)$$

We note that the viscosity η_s of toluene at 25 °C is 0.552 $\times 10^{-2}$ P.[32]

5. Results

We report in this section the ratios of ξ_s, ξ_ϕ, ξ_Π, ξ_f, and ξ_D, as well as the reduced moments $[[\beta_2]]$ and $[[\beta_4]]$ for polymer solutions under Θ and good solvent conditions. ξ_f is rigorously related to a combination of ξ_ϕ and ξ_Π (eq 20), and ξ_p can be determined using eq 6. For PS + cyclohexane and PS + toluene solutions, we are able to determine all ξ's except ξ_f. For PS + CS$_2$ solution, we obtain ξ_ϕ, ξ_s, and ξ_f, but find no data in the literature helpful in determining ξ_Π and ξ_D. The results are also summarized in Table 2 for clarity's sake. The quoted uncertainties are those claimed in the original references. When our quantity involves more than one number from these references, we have propagated the quoted uncertainties, presuming that these are independent.

PS + Cyclohexane at 35 °C. Equations 15 and 21, together with the assumption that $[[P_\infty]] = 2$, yield

$$\{C_{\max}A^{3-(1/\nu)}\} = 1.95 \times 10^{-2}(\pm 7\%)\text{Å}^{-2} \qquad (32)$$

where $\nu = 0.5$. Hence $\{A\} = 3.21(\pm 7\%)$ Å. According to eq 8,

$$\xi_\phi = \{A\}\cdot\frac{\{C_{\max}\}}{C} = 3.21\cdot\frac{\{C_{\max}\}}{C}(\pm 7\%)\ \text{Å}$$

Equation 22 can be rewritten as

$$\xi_s = 5.24\cdot\frac{\{C_{\max}\}}{C}(\pm 5\%)\ \text{Å}$$

Equations 2 and 23 give rise to

$$\xi_D = 22.5\cdot\frac{\{C_{\max}\}}{C}(\pm 8\%)\ \text{Å}, \quad \text{for } C < 4.6 \times 10^{-4}\text{Å}^{-3}$$

Equations 1, 18, and 24 lead to

$$\xi_\Pi = 15.54\ \frac{\{C_{\max}\}}{C}\ \text{Å}$$

It is now straightforward to calculate the ξ ratios: We find $[[\xi_\phi/\xi_s]] = 0.61$ ($\pm$9%), $[[\xi_D/\xi_s]] = 4.29$ ($\pm$10%), and $[[\xi_\Pi/\xi_s]] = 2.97$ ($\pm$5%). To calculate $[[\beta_2]]$ and $[[\beta_4]]$, we combine eqs 18, 24, 32, and 35, which yield $[[\beta_2]] = 18$ ($\pm$22%). Hence $[[\xi_\Pi/\xi_\phi]] = 4.84$ ($\pm$8%) in view of eq 19. Furthermore, from eq 17, we obtain $[[\beta_4]] = 968$ ($\pm$28%).

Perdeuterated PS + CS$_2$ at 20 °C. Equations 15 and 25 with $[[P_\infty]] = 1.23$ ($\pm$4%) give rise to $\{C_{\max}A^{3-(1/\nu)}\} = 2.34$ ($\pm$8%) $\times 10^{-2}$Å$^{-1/\nu}$ and hence $\{A\} = 2.82$ ($\pm$6%) Å, whereas eq 26 yields $\{A\} = 2.75$ ($\pm$6%) Å. The average of these two $\{A\}$'s leads to

$$\xi_\phi = \{A\}\cdot\left(\frac{\{C_{\max}\}}{C}\right)^{\nu/(3\nu-1)} = 2.785\cdot\left(\frac{\{C_{\max}\}}{C}\right)^{\nu/(3\nu-1)} (\pm 7\%)\ \text{Å}$$

where $\nu = 0.588$. We also obtain $[[P_\infty]] = 1.20$ ($\pm$11%) using the same set of data (eqs 25 and 26), which agrees with the simulation results shown in section 4. Several ξ_s's for different concentrations are also given in section 4. From these data, we obtain $[[\xi_\phi/\xi_s]] = 1.23$ ($\pm$8%). In addition, by virtue of eqs 4 and 27, we determine $\xi_f/\xi_s = 1.27$ ($\pm$1%), which implies $[[\xi_f/\xi_\phi]] = 1.03$ ($\pm$8%). Equations 17 and 20 then determine the reduced moments $[[\beta_2]] = 4.8$ ($\pm$14%) and $[[\beta_4]] = 64$ ($\pm$21%).

PS + Toluene at 25 °C. Equations 15 and 28 give $\{C_{\max}A^{3-(1/\nu)}\} = 0.0273$ ($\pm$9%) Å$^{-1/\nu}$, where we set $\nu = 0.59$ and $[[P_\infty]] = 1.23$ ($\pm$4%). This in turn yields $\{A\} = 3.16$ ($\pm$7%) Å and

$$\xi_\phi = \{A\}\cdot\left(\frac{\{C_{\max}\}}{C}\right)^{\nu/(3\nu-1)} = 3.16\cdot\left(\frac{\{C_{\max}\}}{C}\right)^{0.77} (\pm 7\%)\ \text{Å}$$

Equation 29 can be written as

$$\xi_s = 2.57\cdot\left(\frac{\{C_{\max}\}}{C}\right)^{0.77} (\pm 5\%)\ \text{Å}$$

Equations 1, 18, and 30 give

$$\xi_\Pi = 9.80\cdot\left(\frac{\{C_{\max}\}}{C}\right)^{0.77} (\pm 3\%)\ \text{Å}$$

ξ_D is determined from eq 31:

$$\xi_D = 4.25\cdot\left(\frac{\{C_{\max}\}}{C}\right)^{0.75} (\pm 5\%)\ \text{Å}, \quad \text{for } 0.02 \leq C/\{C_{\max}\} \leq 0.08$$

The above results give $[[\xi_\phi/\xi_s]] = 1.23$ ($\pm$9%), $[[\xi_D/\xi_s]] =$

1.65 (±7%), and $[[\xi_\Pi/\xi_s]] = 3.81$ (±6%). By identifying eq 30 with eq 35, we obtain $[[\beta_2]] = 4.3$ (±23%), which yields $[[\xi_\Pi/\xi_\phi]] = 3.16$ (±8%) (eq 19). Equation 17 then gives $[[\beta_4]] = 61$ (±29%). These results are consistent with those of PS + CS_2 solution presented above.

6. Discussion

Solvent Quality. In good solvent cases such as PS + CS_2 at 20 °C, the relations between ξ_s, ξ_ϕ, ξ_f, and ξ_Π (eqs 17, 19, and 20) become strictly correct only for a sufficiently good solvents. Whether the solvent is good enough may be expressed using the notion of the thermal blob.[31] The size of the thermal blob $\{\xi_T\}$ marks the crossover between ideal chain and self-avoiding behavior. For chain sections of size much smaller than $\{\xi_T\}$, the polymer behaves as an ideal chain; for sections much larger than $\{\xi_T\}$, it exhibits excluded-volume expansion. In such solvents, the good solvent scaling properties disappear for high concentrations such that $\xi_\phi \leq \{\xi_T\}$. However, the good solvent behavior appears for lower concentrations such that $R_G \gg \xi_\phi \gg \{\xi_T\}$. Accordingly, the universal ratios reported in rows b and c of Table 2 should hold only in this same regime. To be more specific, when $R_G \gg \xi_\phi \gg \{\xi_T\}$, the first-order correction to those ξ ratios changes as some positive power of $\{\xi_T\}/\xi_\phi$. If ξ_ϕ(or R_G) is on the order of $\{\xi_T\}$; that is, the system is in the marginal solvent condition, and special care must be taken to interpret experimental data.[32] Here we note that $\{\xi_T\}$ is about 10−20 Å for PS + toluene at 25 °C[24,30,32] and less than 10 Å for PS + CS_2 at 20 °C.[10,28] It is straightforward to verify that the concentrations of these two systems used in this work are well in the good solvent regime; that is, $\xi_\phi > \{\xi_T\}$.

Consistency with Previously Reported Universal Ratios. In this work, we demonstrate the universal properties of semidilute polymer solutions by showing the constancy of those ξ ratios without referring to the dilute properties such as R_G. However, there exists an equivalent alternative, which relies on the scaling relations between dilute and semidilute properties.

In the appendix, we obtain a scaling formula for osmotic pressure Π (eq 36) and define a universal constant $[[k_\Pi]]$, which is related to the reduced moment $[[\beta_2]]$ (eq 37). Since $[[P_\infty]]$ and c_0 are known, and the reduced moment $[[\beta_2]]$ is given in Table 2, we determine $[[k_\Pi]] = 2.2$ (±22%) and 9.4 (±24%) for Θ and good solvents, respectively. For good solvent cases where $\nu = 0.588$, des Cloizeaux and Noda obtained $[[k_\Pi]] \approx 9.85$ using the renormalization group theory (to first order in ϵ).[33] Noda et al. reported $[[k_\Pi]] = 10.0$ and $\nu = 0.585$ for poly(α-methylstyrene) in toluene.[34] Adam et al. determined $[[k_\Pi]] = 9.7$ and $\nu = 0.586 \pm 0.006$ for semidilute polyisoprene in cyclohexane.[35] Their results together with ours confirm the universality of $[[k_\Pi]]$, and hence that of the ratio $[[\xi_\Pi/\xi_\phi]]$ for good solvent cases (eq 40).

Des Cloizeaux and Jannik defined the Kuhnian overlap length ξ_k as[9]

$$\xi_k = X(CX^3/N)^{\nu/(1-3\nu)}$$

where $X^2 = R_e{}^2/3 = 2R_G{}^2/[[\aleph]]$ in the dilute limit. R_e is the end-to-end distance of a dilute polymer. The numerical constant $[[\aleph]] \equiv 6R_G{}^2/R_e{}^2 \simeq 0.952$ for an isolated polymer in a good solvent.[9] ξ_k can be rewritten in a form similar to eq 38

$$\frac{\xi_k}{R_G} = ([[\aleph]]/2)^{1/2(3\nu-1)}\left(\frac{C^*}{C}\right)^{\nu/(3\nu-1)}$$

where $C^* \equiv N/R_G{}^3$ is the overlap concentration. Dividing eq 39 by the above formula gives rise to

$$[[\xi_\phi/\xi_k]] = ([[P_\infty]]/c_0)^{\nu/(3\nu-1)}([[\aleph]]/2)^{-1/2(3\nu-1)}$$

This implies $[[\xi_\phi/\xi_k]] = 0.318$ and 0.243 for Θ and good solvents, respectively. In addition, by use of $[[\xi_\phi/\xi_s]]$ given in Table 2, we determine $[[\xi_s/\xi_k]] = 0.522$ (±9%) for Θ cases, and 0.198 (±9%) for good solvent cases. The latter value agrees with that (0.18) reported in their book (Chapter 15 of ref 9).

Dynamic Length ξ_D. While the universality of the static ratios $[[\xi_\phi/\xi_s]]$, $[[\xi_\Pi/\xi_s]]$ and $[[\xi_f/\xi_s]]$ are robust, that of the dynamic ratio $[[\xi_D/\xi_s]]$ is less so. For semidilute polymer solutions, ξ_D goes as $C^{-\alpha}$, where the theoretical value of $\alpha = 0.77$ for good solvent conditions. Experiments, however, often report $\alpha = 0.5-0.75$.[27,36,37] The deviation of the exponent from the scaling theory prediction suggests the underlying dynamics of the cooperative diffusion of semidilute polymers might be more complex than the scaling theory can explain. Several attempts have been made to resolve this discrepancy by attributing it to the crossover behavior of the system under investigation.[32,37,38] Despite these controversies, we expect the scaling theory prediction should still hold in the semidilute limit, where $C^* \ll C \ll \{C_{\max}\}$ and $N \rightarrow \infty$, and this is confirmed by the experimental data collected in Schaefer and Han's review paper.[32] In this paper, we use their data to calculate $[[\xi_D/\xi_s]]$ for PS + toluene (eq 31).

7. Conclusions

Table 2 summarizes the ratios of those ξ's for semidilute polymers under Θ and good solvent conditions. These ratios are expected to be universal in the semidilute regime where $C^* \ll C \ll \{C_{\max}\}$ and the chain length $N \rightarrow \infty$. The static lengths ξ_s, ξ_ϕ, ξ_f, and ξ_Π are related to each other through the reduced moments $[[\beta_2]]$ and $[[\beta_4]]$ of the local concentration $\langle C(r)\rangle_0$. The universality of these length ratios is just the manifestation of the scaling property of $\langle C(r)\rangle_0$. The data in Table 2 provide a satisfying confirmation of this universality. Each of the reported ratios (except those involving ξ_D) was obtained from data over a substantial range of concentration—approaching an order of magnitude. The ratios were independent of concentration to a degree given by the quoted uncertainty. Furthermore, the reduced moments $[[\beta_2]]$ and $[[\beta_4]]$ were independently obtained for two solvents, CS_2 and toluene. The values obtained are not only similar for the two solvents but also consistent with the known results collected in section 6, which further supports the claim of universality. As mentioned in the Introduction, these ratios are valuable since they allow us to infer one quantity such as the cooperative diffusion coefficient D_c from another, such as the osmotic pressure Π. Moreover, $[[\beta_2]]$ and $[[\beta_4]]$ provide the information about the crossover behavior of $\langle C(r)\rangle_0$. It might be a challenge for polymer theorists who are interested in $\langle C(r)\rangle_0$ to work out $[[\beta_n]]$ and determine these ratios.

As noted in section 6, the concentration dependence of ξ_D may deviate from the scaling theory prediction. It seems to us that, so far there is no satisfactory explanation for this discrepancy. Thus, further theoretical and experimental investigations are needed.

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Appendix

Equation 10 can be rewritten as

$$S(q) = \int_V \mathrm{d}^3 r (\langle C(r)\rangle_0 - C) \exp(i\vec{q}\cdot\vec{r})$$

since the Fourier transform of any constant is zero as long as $q \neq 0$. $S(q)$ can then be Taylor-expanded with respect to q (cf. eq 3)

$$S(q) = S_0\left(1 - \frac{1}{2}\frac{\int \mathrm{d}^3 r\, (\vec{q}\cdot\vec{r})^2(\langle C(r)\rangle_0 - C)}{\int \mathrm{d}^3 r\, (\langle C(r)\rangle_0 - C)} \cdots\right)$$

where $S_0 = \int d^3 r\ (\langle C(r)\rangle_0 - C)$. A straightforward calculation leads to

$$\xi_s{}^2 = \frac{1}{6}\frac{\int_0^\infty \mathrm{d}r\, r^4(\langle C(r)\rangle_0 - C)}{\int_0^\infty \mathrm{d}r\, r^2(\langle C(r)\rangle_0 - C)} \tag{33}$$

By introducing $[[\beta_n]]$ (eq 16) and using eq 8

$$S_0 \rightarrow 4\pi[[\beta_2]] \int_{C_{\mathrm{A}>C}} \mathrm{d}r\, r^2(C_{\mathrm{A}}(r) - C)$$

$$= \frac{4\pi}{3}(3\nu - 1)[[\beta_2]]\{C_{\max}A^{3-(1/\nu)}\}\xi_\phi{}^{1/\nu} \tag{34}$$

$$= \frac{4\pi}{3}(3\nu - 1)[[\beta_2]]\{C_{\max}A^{3-(1/\nu)}\}^{3\nu/(3\nu-1)}C^{-1/(3\nu-1)} \tag{35}$$

Incorporating eqs 11, and 14 and the overlap concentration $C^* \equiv N/R_{\mathrm{G}}{}^3$ into eq 35 leads to

$$S_0 \rightarrow \frac{4\pi}{3}(3\nu - 1)([[P_\infty]]/c_0)^{3\nu/(3\nu-1)}[[\beta_2]](C/C^*)^{1/(1-3\nu)}\ N$$

where c_0 is defined in eq 12. Using this S_0 and eq 18, we obtain

$$\frac{N\ \Pi}{k_{\mathrm{B}}TC} \rightarrow [[k_\Pi]]\left(\frac{C}{C^*}\right)^{1/(3\nu-1)} \tag{36}$$

where

$$[[k_\Pi]] = (4\pi\nu[[\beta_2]])^{-1}\ ([[P_\infty]]/c_0)^{3\nu/(1-3\nu)} \tag{37}$$

Furthermore, eq 36 gives

$$\frac{\xi_\Pi}{R_{\mathrm{G}}} \rightarrow [[k_\Pi]]^{-1/3}\left(\frac{C^*}{C}\right)^{\nu/(3\nu-1)} \tag{38}$$

Similarly, eq 8 can be expressed as

$$\frac{\xi_\phi}{R_{\mathrm{G}}} \rightarrow ([[P_\infty]]/c_0)^{\nu/(3\nu-1)}\left(\frac{C^*}{C}\right)^{\nu/(3\nu-1)} \tag{39}$$

Combining eq 38 with eq 39 yields

$$[[\xi_\Pi/\xi_\phi]] \rightarrow [[k_\Pi]]^{-1/3}\ ([[P_\infty]]/c_0)^{\nu/(1-3\nu)} = (4\pi\nu[[\beta_2]])^{1/3} \tag{40}$$

By the same token, eq 33 is reduced to

$$\xi_s{}^2 \rightarrow \xi_\phi{}^2\left(\frac{1}{6}\frac{\left(\frac{\nu}{1+2\nu} - \frac{1}{5}\right)[[\beta_4]]}{\left(\nu - \frac{1}{3}\right)[[\beta_2]]}\right) \tag{41}$$

We may define another kind of dimensionless moment $[[r_n]]$ for $\langle C(r)\rangle_0$, which carries the same information as does $[[\beta_n]]$:

$$[[r_n]] \equiv \int_0^\infty dx\, x^n\left(\frac{\langle C(x\xi_\phi)\rangle_0}{C} - 1\right) \rightarrow \frac{(3 - 1/\nu)[[\beta_n]]}{(n + 1)(n - 2 + 1/\nu)}$$

where $x = r/\xi_\phi$.

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