Polymer Dimensions in Good Solvents: Crossover from Semidilute to Concentrated Solutions

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Using small-angle neutron scattering, we studied the variation of the polymer radius of gyration (R_g) as a function of polymer concentration (ϕ) for solutions of a flexible-chain poly(methyl methacrylate) in chloroform. We observed for the first time a distinct crossover between swollen coils in the semidilute regime, where $R_g^2 \propto \phi^{-0.26\pm0.03}$, and unperturbed coils in the concentrated regime, where R_g is independent on concentration. The crossover occurs at $\phi^{\ddagger} \approx 0.15$, a value that agrees reasonably well with $\phi^{\ddagger} \approx 0.21 \pm 0.035$, estimated with a scaling relationship between $\phi^{\ddagger}$ and the coil overlap concentration ϕ^*.

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In this Letter we consider how the pervaded volume of long, linear, flexible-chain polymer molecules dissolved in small-molecule solvents varies with concentration. At the phenomenological level, polymer solvents are commonly divided into three categories—poor, theta (θ), and good solvents—according to their ability to mediate the intrachain forces responsible for the collapse or swelling of polymer chains [1–3]. Pairwise attractions dominate in poor solvents, such that they can dissolve only short chains (low molecular weight M). They play no role in the work here. The sum of pairwise attractive and repulsive interactions between monomeric units cancels at the theta condition, typically at some temperature θ for suitably chosen solvents of the polymer species in question. At $T = \theta$ the radius of gyration $R_g(\theta)$ of long chains is not influenced by intrachain excluded-volume interactions. The chains are "unperturbed" and their dimensions are governed by random walk statistics, such that coil size for long chains is related to their molecular weight by

$$R_g(\theta) = K_\theta M^{1/2}, \tag{1}$$

in which the parameter K_θ depends on the polymer species. In the good solvent domain ($T > \theta$), excluded-volume repulsions dominate, the effect of which is to expand R_g beyond its unperturbed size. The expansion is largest in dilute solutions, i.e., solutions in which the volume fraction of polymer is much smaller than the coil overlap concentration, ϕ^*:

$$\phi^* \approx \frac{3M}{4\pi R_g^3 \rho N_a}, \tag{2}$$

with ρ the undiluted mass density of the polymer and N_a the Avogadro number. The size-molecular weight relationship for long chains is still a power law but with a different exponent:

$$R_g = KM^{\gamma}, \tag{3}$$

in which $\gamma = 3/5 = 0.6$ in the mean-field approximation [1] and 0.588, to within ±0.0015 according to self-avoiding walk simulations [4], renormalization group calculations [5], and experimental data for many polymer-solvent systems [3,6].

The overlap concentration defines a crossover from dilute solutions to the semidilute range. Chain dimensions decrease with increasing concentration beyond ϕ^* owing to a gradual screening out of the intrachain repulsive interactions by an increasing competition from the interchain interactions. At some concentration $\phi^{\ddagger} > \phi^*$, the excluded-volume repulsions should be effectively cancelled by screening. Accordingly, $\phi^{\ddagger}$ marks the crossover from semidilute solutions to the concentrated range. The chains take on their unperturbed size, in effect $R_g(\theta)$, and thus become independent of concentration for all $\phi > \phi^{\ddagger}$ to the melt state ($\phi = 1$). It is already well established for many species that $R_g(\theta)$ and R_g in the melt are the same within experimental uncertainties [3] and that R_g in theta solvents is insensitive to polymer concentration over the entire range [7]. The sequence of coil size from overlap to melt in good solvents is the focus of this Letter.

The behavior of both R_g and the correlation length of concentration fluctuations (ξ) in good solvents was considered by Daoud and Jannink [8]. They demonstrated that in the semidilute range, $\phi^* \lesssim \phi \lesssim \phi^{\ddagger}$, both R_g and ξ would decrease with concentration according to

$$R_g^2 \propto \phi^{-(2\nu-1)/(3\nu-1)}, \tag{4}$$

$$\xi \propto \phi^{-\nu/(3\nu-1)}. \tag{5}$$

The scaling exponents in Eqs. (4) and (5) may be calculated using mean-field exponent $\nu = 0.6$, in which case $R_g^2 \sim \phi^{-1/4}$ and $\xi \sim \phi^{-3/4}$ or the renormalization group exponent $\nu = 0.588$ which leads to $R_g^2 \propto \phi^{-0.23}$ and $\xi \propto \phi^{-0.77}$.

The effects of solvent quality (excluded-volume "strength") and concentration on chain dimensions are of fundamental importance for understanding the structure and dynamics of polymer solutions in good solvents. The proposed Eqs. (3)–(5) have also gained acceptance among the polymer science community. However, providing definitive experimental confirmation of the theoretical predictions of R_g vs ϕ has remained a challenge for the past three decades. Three notable attempts [9–11], all based on small-angle neutron scattering (SANS) methods, led to contradictory conclusions regarding both the values of scaling exponents in Eqs. (4) and (5) and the existence of a distinct crossover between semidilute and concentrated regimes [3], with the result that the relationship between R_g and ϕ over the full range of concentration is presently unresolved. The situation is not surprising, given the interrelated nature of the experimental design requirements for a SANS study based on the high concentration isotope labeling method [7]. The chains must be long and their dilute solution size very large to open a reasonable space between ϕ^* and $\phi^\ddagger$. Because $R_g(\phi)$ is the object of interest, narrow molecular weight distribution is highly desirable to avoid ambiguity in modeling; high neutron flux and resolution at small scattering angles is similarly essential as is the need to minimize proton content, and thus incoherent scattering by the component molecules; the largest possible ratio $R_g(\phi^*)/R_g(\theta)$ is desirable for accuracy through the semidilute range, meaning the "best possible" choice of good solvent character. Finally, a comparison body of high quality conventional characterization data for the polymer-solvent system to be used is highly desirable.

The system polymethylmethacrylate-chloroform (PMMA-CHL) was chosen for this study. Samples of the high molecular weight fully hydrogenous PMMA [(h-PMMA), $M_w = 592,000$, $M_w/M_n = 1.05$] and deuterated PMMA [(d-PMMA), $M_w = 580,000$, $M_w/M_n = 1.11$] were supplied by Polymer Standard Services. The solvent in all cases was 99.5% deuterated CHL (d-CHL) supplied by Sigma-Aldrich. Both polymer samples have moderately high syndiotactic content, similar to commercial PMMA [12,13], and dilute solution studies in CHL for samples of similar microstructure are available for comparison [14,15]. Those data also demonstrate the unusually strong excluded volume of this system [3,6,16].

The SANS-based high concentration isotope labeling procedure is the method of choice for determining polymer dimensions in solutions of strongly overlapping and interacting chains. The details of the method have been described in the literature (see, e.g., Ref. [7] and references therein). Briefly, the coherent neutron cross section, $I(Q)$ in units of cm^{-1} for solutions of identical protonated and deuterated polymers in a solvent, is given by

$$I(Q)/nN^2 = (b_H - b_D)^2\phi_H(1-\phi_H)P(Q) + [b_H\phi_H + b_D(1-\phi_H) - b_S(v_P/v_S)]S(Q). \tag{6}$$

In Eq. (6), $P(Q)$ is the single-chain (intramolecular) form factor which contains information on R_g; $S(Q)$ is the total scattering structure factor which embodies information on the total (both intra- and intermolecular) correlations between monomer units and is related to ξ. The scattering vector magnitude Q is $4\pi\lambda^{-1}\sin\theta$, in which 2θ is the scattering angle and λ is the neutron wavelength; n and N are the number density and degree of polymerization of the polymer molecules; b_H, b_D, and b_S are the scattering lengths of the protonated and deuterated monomeric units and (v_P/v_S) is the ratio of specific volumes for polymer and solvent; ϕ_H is the volume fraction of all chains that are protonated.

At $\phi_H = 0.63$, the solutions of h-PMMA and d-PMMA in d-CHL satisfy the zero average contrast condition: $b_S(v_P/v_S) = b_H\phi_H + b_D(1-\phi_H)$. Under this condition the second term on the right-hand side of Eq. (6) is zero, so the contribution of the total scattering structure is minimized, allowing R_g for the chains at the total polymer concentration ϕ to be determined from $P(Q)$. For unperturbed chains—at either the θ condition or in the melt—the intramolecular form factor $P(Q)$ is given by the Debye formula for Gaussian chains [17]:

$$P(Q) = (2/y^2)[(\exp(-y) - 1 + y] + B, \tag{7}$$

in which $y = Q^2R_g^2$ and B is a background term mostly due to the incoherent scattering from protons in h-PMMA. The exact analytical form of $P(Q)$ for polymers in good solvents is not known; however, the radius of gyration of the polymer may be determined by fitting the data to the model-independent Guinier formula [18]:

$$\frac{1}{I(Q)} = \frac{1}{I(0)}\left(1 - \frac{Q^2R_g^2}{3}\right). \tag{8}$$

If all chains are protonated ($\phi_H = 1$), the first term on the right-hand side of Eq. (6) is zero, and the correlation length ξ may be determined from $S(Q)$ using the Ornstein-Zernike (O-Z) formula [19]:

$$\frac{1}{I(Q)} = \frac{1}{I(0)}(1 + Q^2\xi^2) + B. \tag{9}$$

For $R_g(\phi)$ measurements, a set of solutions with (0.63 h-PMMA + 0.37 d-PMMA) was prepared in d-CHL for the range of the total polymer concentration $0.0044 \leq \phi \leq 0.399$. For $\xi(\phi)$ measurements, a set of h-PMMA + d-CHL solutions was prepared in the range of $0.0017 \leq \phi \leq 0.1158$. Each solution was contained in a 2 mm thick quartz cell, and the measurements were performed at $T = 25 \pm 0.05\,^\circ\mathrm{C}$.

SANS experiments were conducted at ORNL on the SANS-I instrument [20] with a neutron wavelength of $\lambda = 4.8$ Å$(\Delta\lambda/\lambda \sim 0.13)$ and at NIST (NG3 30 m instrument [21]) with a neutron wavelength of $\lambda = 6.0$ Å$(\Delta\lambda/\lambda \sim 0.15)$. Two sample-detector distances were chosen in each experiment to cover an overall Q range of $0.0038\ \text{Å}^{-1} < Q < 0.40\ \text{Å}^{-1}$. The data were corrected for instrumental background as well as detector efficiency and put on absolute scale [cross section $I(Q)$ in units of cm^{-1}] by means of precalibrated secondary standards [22] (ORNL) or the direct beam flux measurements (NIST). Scattering

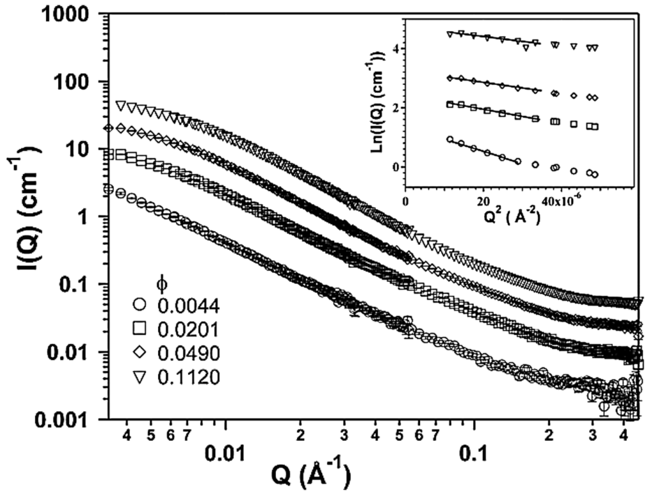

FIG. 1. Representative SANS intensity for PMMA-CHL solutions at zero average neutron contrast. The same data in Guinier coordinates are shown in the inset, where the straight lines are fits to Eq. (8).

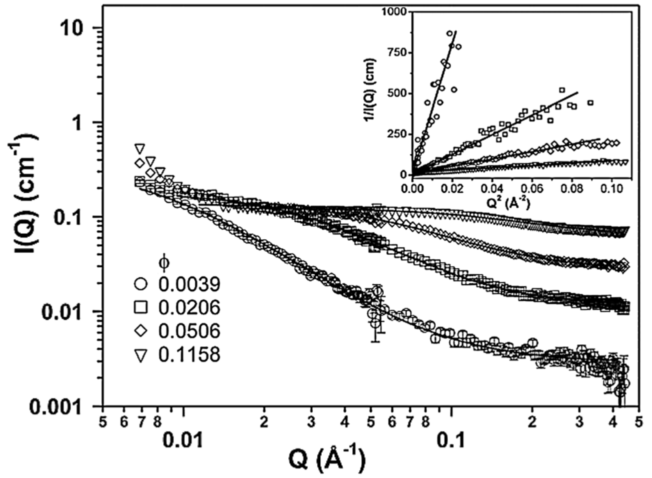

FIG. 2. Representative SANS intensity for PMMA-CHL solutions at full neutron contrast. The same data in the O-Z coordinates are shown in the inset where the straight lines are fits to Eq. (9) with subtracted background.

from the solvent was subsequently subtracted in proportion to its volume fraction. Representative sets of the scattering curves measured at zero average contrast ($\phi_H = 0.63$) and at full neutron contrast ($\phi_H = 1$) are shown in Figs. 1 and 2, respectively. The data measured at zero average contrast condition in semidilute regime $0.0044 \leq \phi \leq 0.112$ were fitted to the Guinier formula [Eq. (8) for $QR_g < 1$], and the data measured in concentrated regime $0.240 \leq \phi \leq 0.399$ were fitted to the Debye form factor for unperturbed Gaussian chains [Eq. (7)]. The data measured at full neutron contrast were fitted in the limit of small Q to O-Z formula [Eq. (9)] (see insets of Figs. 1 and 2). The values of R_g and ξ thus obtained are listed in Table I.

The variation of R_g as a function of the total polymer concentration is shown in Fig. 3, which represents the central result of this study. In the range $0.0044 \leq \phi \leq 0.112$, R_g decreases with concentration according to

$$\log R_g^2 = (4.43 \pm 0.06) + \log \phi^{-0.26 \pm 0.03}. \qquad (10)$$

The experimental scaling exponent thus lies within the experimental error of both the mean-field and renormalization group values, -0.25 and -0.23, respectively [note Eq. (4)]. The values of R_g for $\phi > 0.112$ remain constant within experimental error. The average of the three highest polymer concentrations, 210 ± 4 Å, is close to the size for predominately syndiotactic PMMA in the melt state [23]: $R_g = 0.27M^{1/2}$, leading to $R_g = 207$ Å for $M = 586,000$. Scaling behavior applies only up to $\phi^\ddagger$ in the semidilute regime. Using Eq. (10) to extrapolate, we calculate that the chain dimensions reach 210 Å at $\phi = 0.150$, which we thus take as $\phi^\ddagger$ for the PMMA-CHL system.

It is useful to compare this value of $\phi^\ddagger$ with calculations based on the relation between ϕ^* and $\phi^\ddagger$ suggested some time ago [24]:

$$\phi^\ddagger = \left[\frac{R_g(0)}{R_g(\theta)}\right]^{2(3\gamma-1/2\gamma-1)} \phi^*, \qquad (11)$$

where the exponent is 8.0 for the mean-field result ($\gamma = 0.6$) and 8.68 for the renormalization group result ($\gamma = 0.588$). Here, $R_g(0)$ is the radius of gyration of fully swollen individual coils in a good solvent, which may be estimated for the polymer studied in this work using the tabulated values of R_g vs M in dilute solution for the PMMA-CHL system [15]. A fit of those data gives $R_g(0) = 347$ Å for $M = 586,000$. Extrapolating with Eq. (10), we find that size is reached at $\phi = 0.00315$, which we take as the overlap concentration ϕ^*. Applying Eq. (11) with $\phi^* = 0.003\,15$, $R_g(0) = 347$ Å, and $R_g(\theta) = 210$ Å from the high concentration average, we obtain $\phi^\ddagger = 0.175$ with the mean-field exponent and $\phi^\ddagger = 0.245$ with the renormalization exponent, both somewhat larger than the extrapolation estimate, $\phi^\ddagger = 0.150$, but still in a reasonable range.

TABLE I. R_g and ξ of $(h + d)$ PMMA solutions in d-CHL.

ϕ	R_g (Å)	ϕ	ξ (Å)
0.0	(347)[a]	⋯	⋯
0.0044	348 ± 9	0.0017	178 ± 2
0.0101	278 ± 5	0.0026	157 ± 2
0.0201	272 ± 4	0.0039	111 ± 2
0.0307	263 ± 4	0.0064	74 ± 2
0.049	245 ± 2	0.0103	60 ± 2
0.112	220 ± 2	0.0206	33.5 ± 2
0.2396	208 ± 2	0.0314	23.4 ± 2
0.3333	207 ± 2	0.0506	15.5 ± 2
0.399	214 ± 2	0.0896	8.6 ± 2
1.0	(207)[b]	0.1158	6.4 ± 2

[a] From Ref. [15].

[b] From Ref. [23].

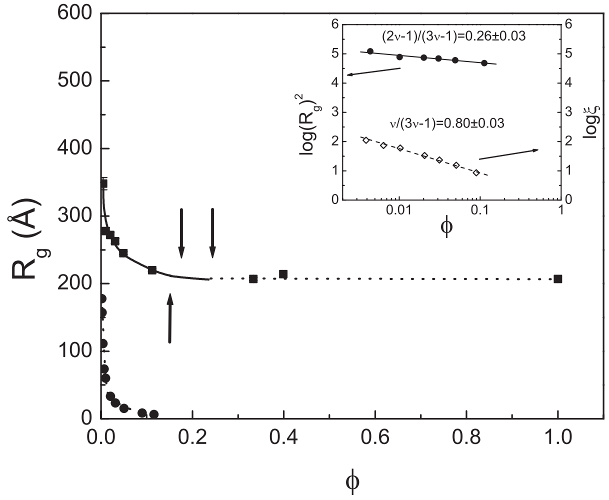

FIG. 3. Radius of gyration and the correlation length are shown as functions of polymer concentration for PMMA-CHL studied here. The solid and dotted lines are described by Eqs. (10) and (12), respectively. The dashed line shows $R_g = 210$ Å. The upward arrow indicates the crossover concentration between the semidilute and concentrated regimes, $\phi^\ddagger = 0.15$ determined using Eq. (11), as described in the text. Two downward arrows show $\phi^\ddagger = 0.175$ and $\phi^\ddagger = 0.245$ calculated using Eq. (11) using the mean-field and the renormalization group exponent γ, respectively. Radius of gyration of predominately syndiotactic PMMA in melt ($\phi = 1$, $R_g = 207$ Å) was obtained previously in Ref. [23]. Inset: solid lines are described by Eq. (10) and dashed line by Eq. (12).

In Fig. 3 we also show the concentration variation of the correlation length ξ that rapidly decreases from $\xi = 178$ Å in dilute solution of noninteracting coils ($\phi = 0.0017$) to $\xi = 6.4$ Å at $\phi = 0.116$. At higher concentration the scattering becomes very weak, which makes ξ indeterminable. Fit in the semidilute concentration range of $0.0039 \leq \phi \leq 0.0886$ gives

$$\log\xi = (0.143 \pm 0.06) + \log\phi^{-0.80\pm0.03}. \qquad (12)$$

Thus, the measured scaling exponent in Eq. (12) is somewhat higher than its mean-field value, −0.75, but agrees within experimental error with its renormalization group value, −0.77. Values in the same general range have been obtained by others, e.g., −0.72 [9], −0.70 [10], and −0.76 [25].

In summary, we have explored the variation over the full range of concentrations of polymeric chain dimensions for a good solvent system, demonstrating clearly and for the first time both the dilute-semidilute and semidilute-concentrated solution crossovers. Power-law exponents in the semidilute range were shown to be consistent with either mean-field or renormalization group predictions. Values for the crossover concentrations, ϕ^* and $\phi^\ddagger$, obtained by semidilute power-law extrapolations agreed well with those estimated by conventional but hitherto unproven methods.

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