Notes

Molecular Weight Dependence of Network Length Scales in Polymer Solutions

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The physical understanding of nondilute polymer solutions rapidly improved after de Gennes introduced the blob concept[1] for a general description of semidilute solutions. Recently, the applicability of the concept was experimentally confirmed also for highly concentrated solutions using flexible linear polymers with high molecular weights.[2] However, the applicability to solutions of semirigid polymers[3] remains questioned since they have a relatively small number of Kuhn segments, typically <20. Polymers are fully flexible only when the contour length is at least 2 orders of magnitude[4a,b] longer than the Kuhn segment length,[4] l_k. When the molecular weight, M_w, is decreased so that the number of Kuhn segments becomes small, the physical properties change dramatically. For example, if linear polymers with sufficiently high M_w are dissolved in a good solvent below the overlap concentration, the chains are fully swollen; i.e., the fractal dimension,[5] Δ, of the chain is 5/3 (see Figure 1). However, when M_w is decreased such that the radius of gyration of the chain, R_g, becomes smaller than the thermal blob radius,[4] ξ_τ, the chains cannot be swollen even in a good solvent since the local segmental stiffness starts to suppress two-body excluded-volume interactions.[2a,4a,6] Consequently, the chains are ideal ($\Delta = 2$). Moreover, when R_g reaches $l_k/2$ with decreasing M_w, the chains become "flexible-rod-like"[2,7] ($\Delta = 1$). Therefore, when M_w is small, various static properties such as the mesh size and conformation of the polymer network and also dynamic properties such as collective diffusion and specific viscosity strongly depend on M_w above the overlap concentration. This is in sharp contrast to the behavior of flexible polymer solutions.[1,4b,6,8] Here, we have examined the generality of the blob concept using solutions of styrene chains with different molecular weights, as a model system for linear chains with different numbers of Kuhn segments. We show for the first time that the blob concept is applicable also to solutions of semirigid chains.

The blob concept[1,2c,6,8] describes the structure of nondilute polymer solutions. Each chain in a nondilute solution is highly overlapping with other chains. Therefore, only shorter segments, i.e., subchains, have no effective interactions with other chains.[9] According to the concept, each subchain will thereby occupy its own territory (the so-called blob) and thus retain a conformation identical to that in a dilute solution. Two independent parameters can describe the blobs: the radius of gyration of the subchain, ξ, and the number of monomers of the subchain,

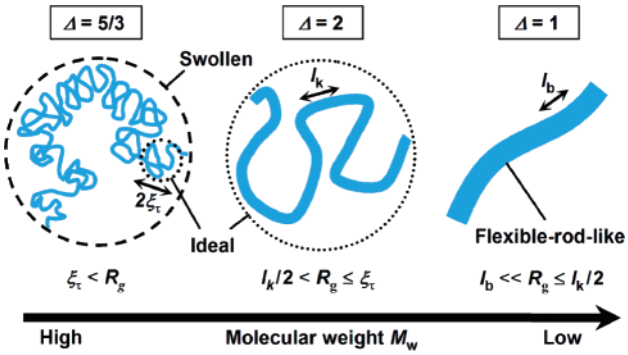

Figure 1. Relation between the molecular weight, M_w, of linear chains and the expected conformations in dilute solutions in a good solvent. Δ, ξ_τ, l_k, l_b, and R_g are the fractal dimension of the chain, thermal blob radius, Kuhn segment length, the bond length of the backbone, and the radius of gyration of the chain, respectively. The thickness of blue lines indicates an approximate length scale.

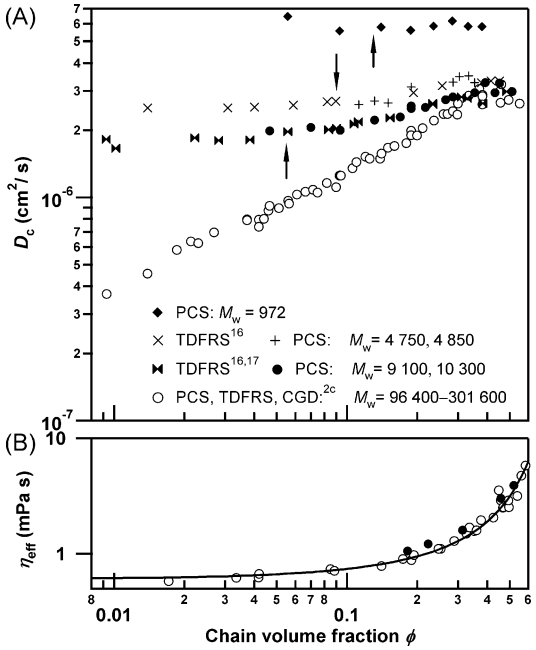

Figure 2. (A) Collective diffusion coefficient, D_c, as a function of chain volume fraction, ϕ, for solutions of atactic styrene chains with different molecular weights (M_w = 972−301 600) in toluene at 25 °C, obtained from different techniques (indicated in the figure). Our new data for M_w = 972, M_w = 4850, and M_w = 10 300 are displayed with filled diamonds, crosses, and filled circles, respectively. The vertical arrows indicate simple estimates of the overlap volume fractions, ϕ^*, for M_w = 972−10 300, using the relation $\phi^* = 1/(2A_2M_w)$ with literature data[22] for the second virial coefficient A_2. Note that $\phi^* < 0.01$ for M_w = 96 400−301 600. (B) Local effective viscosity, η_{eff}, vs ϕ for solutions of atactic styrene chains at 25 °C. Filled and open circles indicate the data for M_w = 18 000 and M_w = 100 000−280 000, respectively. The curve represents a free volume theory expression[23] fitted to the data for M_w = 100 000−280 000.

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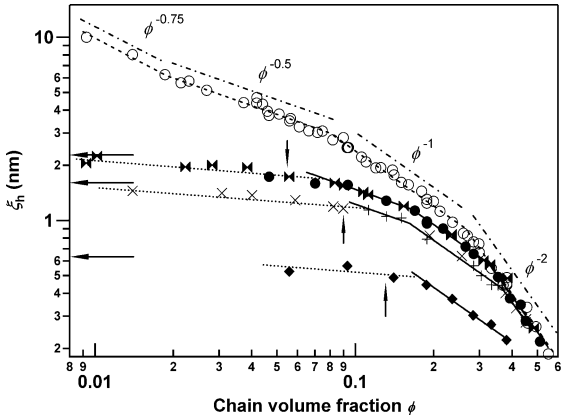

Figure 3. Dynamic correlation length, ξ_h, as a function of chain volume fraction, ϕ, for solutions of atactic styrene chains with different molecular weights (M_w = 972−301 600) in toluene at 25 °C, obtained from the D_c and the η_{eff} curve shown in Figure 2. The symbols for data and the vertical arrows are as in Figure 2A. The horizontal arrows indicate the hydrodynamic radius[8] of the intermediate and low-M_w (972−10 300) chains at infinite dilution, derived from D_c data at infinite dilution.[10] The dashed and dash−dotted lines are least-squares fits to the data for high M_w (96 400−301 600) using theoretical exponents for flexible polymer solutions in a good solvent and the theoretical power law dependence for flexible polymer solutions in a good solvent, respectively. The solid lines represent least-squares fits to the data for intermediate and low M_w (972−10 300) using the theoretical exponents discussed in the text. The dotted lines show a weak concentration dependence of ξ_h below $\phi \approx \phi^*$ also for the solutions.

g. The parameter g is inversely proportional to the number of interchain contacts per chain which will increase as $\phi^{(n-1)}$ with increasing chain concentration,[10] where ϕ is the chain volume fraction and n is the effective number of chains at interchain contacts.[11] Therefore, the radius of gyration of the subchain (ξ) will decrease with increasing concentration, following a simple relation: $\xi \sim g^{1/\delta} = \phi^{-(n-1)/\delta}$, where δ is the fractal dimension of the subchain. However, both δ and n have different values in different concentration regimes. Therefore, $\xi(\phi)$ will follow a series of power laws.[2,6,10] If flexible polymers, i.e., polymers with sufficiently high M_w, are dissolved in a good solvent just above the overlap concentration, δ is initially 5/3 since the subchain is swollen, and n is 9/4 since two-body excluded-volume interactions dominate.[1] However, when ξ becomes smaller than ξ_τ with increasing concentration, similarly as for dilute solutions (see Figure 1), δ becomes two (ideal). Simultaneously, n becomes two since two-body excluded-volume effects vanish on the length scale of ξ_τ.[10] When the concentration exceeds the volume fraction where three-body interactions start to dominate, n becomes three.[12] Finally, when ξ reaches $l_k/2$ with increasing concentration, δ becomes unity (flexible-rod-like).[2] Therefore, ξ in flexible polymer solutions will experience four power law regimes with increasing concentration: $\phi^{-0.75}$ (δ = 5/3, n = 9/4), $\phi^{-0.5}$ (δ = 2, n = 2), ϕ^{-1} (δ = 2, n = 3), and finally ϕ^{-2} (δ = 1, n = 3).[13]

The parameter ξ can experimentally be observed as the dynamic correlation length,[1,2,8,10] ξ_h, that reflects the screening length for hydrodynamic interactions. ξ_h can be derived from the Stokes−Einstein relation[14] using the collective diffusion coefficient, D_c, taking into account the solvent backflow[1,10,15] and the effective local viscosity,[2] η_{eff}. Recently, we demonstrated that the observed ξ_h for solutions of high-M_w atactic polystyrene in toluene, i.e., a good solvent, follows the theoretical predictions for flexible polymer solutions.[2c] Here, we have investigated ξ_h in solutions of atactic styrene chains with lower molecular weights in toluene, using both literature data (M_w = 4750−18 000)[16−18] and new results (M_w = 972, M_w/M_n = 1.12; M_w = 4850, M_w/M_n = 1.05; M_w = 10 300, M_w/M_n = 1.03).[19] A comparison is made with literature data[2c] for high-M_w atactic polystyrene solutions.

Experimentally, D_c can be obtained using various techniques [photon correlation spectroscopy (PCS),[2,8,10] thermal diffusion forced Rayleigh scattering (TDFRS),[16,17] and classical gradient diffusion, (CGD)[20]]. In the present study, the PCS technique has been used (see Supporting Information). Figure 2A shows D_c data as a function of ϕ for styrene chain solutions with

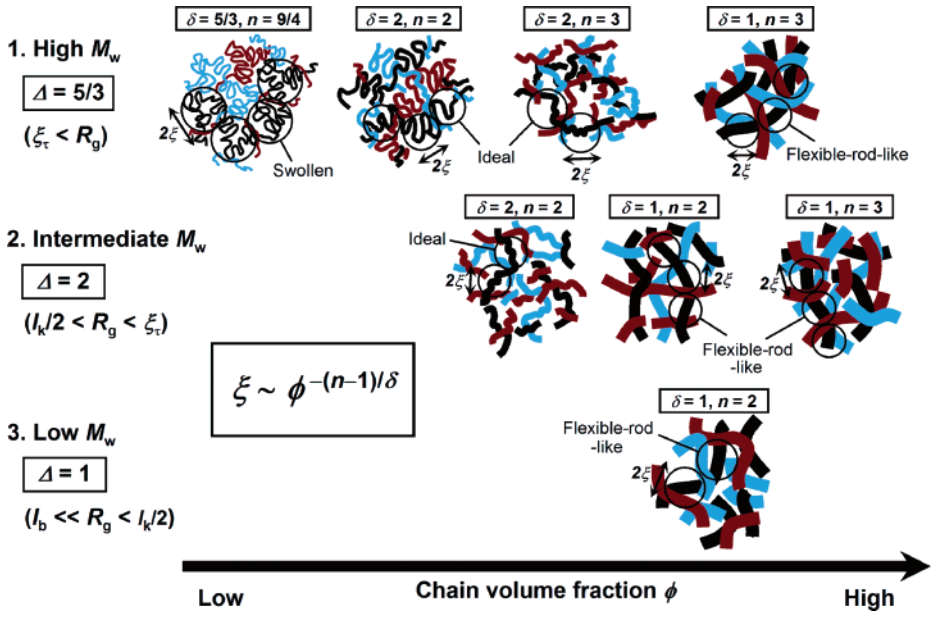

Figure 4. Relation between the molecular weight, M_w, of linear chains and the expected chain networks in nondilute solutions in a good solvent. Δ, ξ_τ, R_g, l_k, l_b, ξ, δ, n, and ϕ are the fractal dimension of the chain, thermal blob radius, the radius of gyration of the chain, Kuhn segment length, the bond length of the backbone, the radius of gyration of the subchain, the fractal dimension of the subchain, the effective number of chains at interchain contacts, and chain volume fraction, respectively. The color and thickness of solid lines represent the individual single chain and the approximate scale of each chain network, respectively. Note that ξ is directly related to the dynamic correlation length ξ_h according to the blob concept.[1,2c,8,10]

different molecular weights, i.e., high M_w (96 400−301 600), intermediate M_w (4750−10 300), and low M_w (972), roughly corresponding to 120−400, 6−13, and 1 Kuhn segments, respectively.[4a] An indication of the changes in Δ (see Figure 1) is seen for solutions with M_w smaller than the intermediate value,[21] where D_c strongly depends on M_w even above the estimated overlap volume fraction,[4b] ϕ^*. This is in contrast to the behavior of the high-M_w polystyrene solutions.

The local effective viscosity η_{eff} can be derived from the Stokes−Einstein relation using solvent self-diffusion data obtained from pulsed field gradient NMR.[2] This technique probes solvent dynamics on the same time scale as D_c is probed.[2c] Figure 2B shows η_{eff} data as a function of ϕ, derived from toluene self-diffusion data[2c,18] for styrene chain solutions with different molecular weights (M_w = 18 000−280 000). The η_{eff} data increase with ϕ but show no observable dependence on M_w. Therefore, the predicted curve[2c] of a free volume theory[23] for high-M_w polystyrene solutions can describe the data also for lower M_w (18 000) chain solutions. According to a recent study[24] on similar polystyrene solutions, the solvent self-diffusion coefficient does not vary even when M_w is reduced to ~1000. Therefore, we expect that the obtained η_{eff} data are applicable even to solutions of the lowest M_w (972) chains in the present study.[25] It is further noted for Figure 2 that η_{eff} has a stronger concentration dependence than D_c for the solutions of intermediate- and low-M_w chains and thus of great importance when determining ξ_h.

Figure 3 shows ξ_h as a function of ϕ. As previously demonstrated,[2c] the ξ_h data for the high-M_w polystyrene solutions (M_w = 96 400−301 600) follow the theoretical power laws for flexible polymer solutions. In contrast, a different concentration dependence of ξ_h is found for intermediate M_w (4750−10 300) and low-M_w (972) chains above $\phi \approx \phi^*$ before the ξ_h data collapse on those for the high-M_w chain solutions at high concentrations. As expected, ξ_h below $\phi \approx \phi^*$ remains roughly the hydrodynamic radius of the chain at infinite dilution, which is approximately equal to R_g.[8]

The observed change in the concentration dependence of ξ_h with decreasing M_w is due to changes in δ and/or n as M_w decreases (see Figure 4). At intermediate M_w (4750−10 300), the chain is ideal ($\Delta = 2$) even in a good solvent since R_g is smaller than ξ_τ (≈7 nm).[4a,b] Therefore, δ is two just above the overlap concentration, and n is also two since two-body excluded-volume effects vanish on the length scale of ξ_τ. When the concentration is increased such that ξ_h becomes smaller than $l_k/2$ (≈1 nm),[4a] δ becomes unity since the subchain will be flexible-rod-like. However, n remains two since two-body interactions still dominate due to the reduced M_w.[26] When the concentration reaches the volume fraction where ξ_h enters a regime with ϕ^{-2} ($\delta = 1$, $n = 3$) for high-M_w chains, finally n becomes three since the rodlike subchains start to experience three-body interactions. Therefore, for intermediate-M_w chains, two new regimes with $\xi_h \sim \phi^{-0.5}$ ($\delta = 2$, $n = 2$) and then $\xi_h \sim \phi^{-1}$ ($\delta = 1$, $n = 2$) are expected with increasing concentration. At the low M_w (972), the chain becomes flexible-rod-like ($\Delta = 1$) since R_g is smaller than $l_k/2$. Therefore, δ is unity just above the overlap concentration, and n is two since two-body excluded-volume effects have already vanished. Thus, for this chain, one new regime with $\xi_h \sim \phi^{-1}$ ($\delta = 1$, $n = 2$) is expected. To examine the predicted regimes for these chains with M_w = 972−10 300, we have performed least-squares fit to the data above $\phi \approx \phi^*$ using the theoretical exponents (see Supporting Information). We find that the exponents give an excellent description[27,28] of all the data (see Figure 3).

In summary, as M_w of chains decreases, the correlation lengths (ξ_h) and their concentration dependence dramatically change for nondilute solutions. The observed changes indicate new structures of the chain networks. However, the present findings can still be explained with the blob concept. The present study, for the first time, demonstrates structural changes of chain networks when the number of Kuhn segments is decreased. The findings therefore provide new insight into the physics of various semirigid polymeric systems including biopolymers like cellulose derivatives, DNA fragments, and filamentous actin.

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Supporting Information Available: Details concerning the present PCS studies and the least-squares fit procedure. This material is available free of charge at the Internet at http://pubs.acs.org.

References and Notes

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(2) (a) Uematsu, T.; Svanberg, C.; Nydén, M.; Jacobsson, P. *Phys. Rev. E* **2003**, *68*, 051803. (b) Uematsu, T.; Svanberg, C.; Nydén, M.; Jacobsson, *AIP Conf. Proc.* **2004**, *708*, 205−208. (c) Uematsu, T.; Svanberg, C.; Jacobsson, P. *Macromolecules* **2005**, *38*, 6227−6230.

(3) For example, biopolymers such as cellulose derivatives, DNA fragments and actin filaments, and synthetic semirigid polymers such as chains with a π-conjugated backbone, chains with bulky side chains and polyelectrolytes.

(4) (a) Norisuye, T.; Fujita, H. *Polym. J.* **1982**, *14*, 143−147. (b) Graessley, W. W. *Polymeric Liquids and Networks*: *Structure and Properties*; Garland Science: New York, 2004. (c) Ott, A.; Magnasco, M.; Simon, A.; Libchaber, A. *Phys. Rev. E* **1993**, *48*, R1642−R1645. (d) Kanematsu, T.; Sato, T.; Imai, Y.; Ute, K.; Kitayama, T. *J. Polym.* **2005**, *37*, 65−73. For typical synthetic polymers (e.g., atactic polystyrene and poly(methyl acrylate)) in a good solvent, $l_k \approx 1-2$ nm and $\xi_\tau \approx 5-12$ nm. For typical biopolymers (e.g., cellulose derivatives, DNA, and filamentous actin) in a good solvent, $l_k \approx 20$ nm−40 μm and $\xi_\tau \approx 60$ nm−100 μm. For synthetic semirigid polymers like poly(*n*-hexyl isocyanate) in a good solvent, $l_k \approx 80$ nm and $\xi_\tau \approx 250$ nm.

(5) The conformation of the chain can be expressed as $R_g \sim M_w^{(1/\Delta)}$, where R_g is the radius of gyration of the chain.

(6) Rubinstein, M.; Colby, R. *Polymer Physics*; Oxford University Press: New York, 2003.

(7) In this paper, we have used the terminology "flexible-rod-like" in order to stress the segmental flexibility; i.e., a flexible-rod-like chain can be easily deformed when interchain interactions occur. This behavior is expected only when R_g is considerably larger than the bond length of the backbone (l_b). Note: when R_g approaches l_b, we instead expect "rigid-rod-like" behavior, where the chain behave like a completely rigid rod.[2]

(8) Teraoka, I. *Polymer Solutions: An Introduction to Physical Properties*; Wiley-Interscience: New York, 2002.

(9) In this paper, the interchain interactions also include long-range interactions between segments belonging to the same chain, which are situated a long distance apart along the backbone.

(10) Schaefer, D. W.; Han, C. C. In *Dynamic Light Scattering: Applications of Photo Correlation Spectroscopy*; Pecora, R., Ed.; Plenum: New York, 1985; pp 181−243.

(11) This relation between g and ϕ will collapse at even higher chain concentrations when the radius of gyration of the subchain (ξ) approaches the bond length of the backbone (l_b). In the concentration regime, g is expected to be independent of concentration since the subchain is rigid-rod-like.[2]

(12) According to the blob concept,[10] the crossover from $n = 2$ to 3 will occur at $\phi \approx 1 - 2\chi$, where χ is the Flory−Huggins interaction parameter. For high-M_w atactic polystyrene in toluene,[2c] the crossover volume fraction is estimated as roughly 0.1.

(13) We also expect a fifth-power regime at even higher concentrations when ξ approaches the bond length of the backbone (l_b). In this regime, ξ is expected to be independent of concentration, i.e. $\xi \sim \phi^0$, since the subchain is rigid-rod-like.[2] In the present paper we will not discuss very high concentrations ($\phi > 0.6$) since the experimental

dynamic technique used in this study cannot probe ξ_h properly in the regime (see ref 24 in ref 2c).
(14) The Stokes−Einstein relation used for deriving the dynamic correlation length is $\xi_h = k_B T/(6\pi\eta_{eff}D_c)$, where k_B is Boltzmann's constant, T is the absolute temperature, η_{eff} is the effective local viscosity, and D_c is the collective diffusion coefficient.
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(19) The atactic styrene chains used for the present study have inert terminal groups, which are H-terminated at one end and *n*-butyl-terminated at the other end.
(20) Roots, J.; Nyström, B. *Macromolecules* **1980**, *13*, 1595−1598.
(21) Already when M_w is smaller than 78 000, the observed M_w dependence of D_c above the overlap concentration is also expected since R_g is smaller than ξ_τ (≈7 nm).[4a]
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(23) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 403−416. The applicability of the free volume theory discussed in the text is based on the assumption that the free volume parameters of the solutions are independent of M_w under the present experimental conditions. This assumption is supported since even the high-M_w chain solutions have a glass transition temperature similar to that of the solvent (≈130 K), not to the chain (≈350 K) (see e.g.: Floudas, G.; Steffen, W.; Fischer, E. W.; Brown, W. *J. Chem. Phys.* **1993**, *99*, 695−703). According to the free volume theory for glass transition (see e.g.: Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley-Interscience: New York, 2001), this is due to that there is much more free volume per unit volume for the solvent than the chain. Therefore, the applicability of the theory used in the present study can be valid as long as the contribution of the solvent still dominates that of the chains.
(24) Chekal, B. P.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 8126−8138.
(25) Note that when the $M_w \ll 972$, the obtained η_{eff} data are not applicable to the solutions since the free volume contribution of the chain becomes comparable to that of the solvent.[23,24]
(26) According to the second virial coefficient,[22] i.e. $\sim (1 - 2\chi)$,[8] when M_w is smaller than 10 000, the crossover from two-body to three-body interactions is expected to occur at much higher concentrations ($\phi \gg 0.1$) than that for the high-M_w chain.[12]
(27) We have also performed complementary curve fits with the exponents as free parameters. Such a curve-fit procedure yields exponents that are equal to the theoretical exponents within roughly 10% errors. A relatively large error was found in only one exponent for $M_w = 4780$ and 4850, at concentrations where a regime with $\xi_h \sim \phi^{-0.5}$ is expected. This can be ascribed to the limited number of data points for the solutions at the corresponding concentrations.
(28) We also find that the observed crossover from $\delta = 2$ (ideal subchain) to $\delta = 1$ (rodlike subchain) for intermediate M_w (4750−10 300) occurs at a slightly larger ξ_h value than that for high M_w (96 400−301 600) (see Figures 3 and 4). This can be a consequence of the intermediate M_w chains being more weakly deformed at the crossover concentration due to binary interchain interactions ($n = 2$) than the high-M_w chains that are experiencing ternary interchain interactions ($n = 3$) at the crossover concentration.

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