Specific Viscosity of Polymer Solutions with Large Thermal Blobs

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ABSTRACT: Literature viscosity data are reviewed in both entangled solutions and semidilute unentangled solutions, with several examples of using de Gennes' thermal blob to rationalize observations for flexible polymers dissolved in intermediate quality solvents. Some puzzling literature data in θ-solvents are also nicely understood with two parameter scaling upon reanalysis (where the correlation length and the tube diameter concentration dependences differ). However, some literature data seem to not be understood with this simple scheme, suggesting that our understanding of neutral polymer solution viscosity is incomplete. Lastly, combinations of experiments are suggested to better examine the concept of the thermal blob.

In scaling models for polymer solutions, solvent quality is incorporated by introducing a length scale, called the thermal blob size (de Gennes 1979, Rubinstein and Colby 2003). On scales smaller than the thermal blob, there is not enough cumulative excluded volume to alter the chain conformation from an ideal random walk. On scales larger than the thermal blob (up to the correlation length) the conformation of the chain is a self-avoiding walk of thermal blobs, see Figure 5.5 of (Rubinstein and Colby 2003). Most polymer solutions have excluded volume increase with temperature. In the high temperature (athermal) limit, excluded volume is strong and the thermal blob size is of order the Kuhn length of the polymer, where the chain adopts a self-avoiding walk on all scales between the Kuhn length and the correlation length. As temperature is lowered, the thermal blob grows, and close enough to the θ-temperature the thermal blob size is larger than the chain size, making the entire chain adopt a random walk conformation. In this note, we explore the consequences of solvent quality (thermal blob size) on polymer solution specific viscosity.

Specific viscosity of polymer solutions has long been correlated with the dimensionless product of concentration and intrinsic viscosity (Baker 1913, Weissberg, Simha et al. 1951, Brinkman 1952, Simha and Zakin 1962, Dreval, Malkin et al. 1973, Simha and Utracki 1973) c[η], in part because [η] can be measured with high precision (Kulicke and Kniewske 1984). Since the overlap concentration c* is inversely related to intrinsic viscosity (Graessley 1980, Graessley 2008), the overlap parameter is c[η] ≈ c/c*, and this simple scaling, based on either c[η] or c/c*, is found to work very well for both unentangled and entangled polymers in very good solvent (Jamieson and Telford 1982, Adam and Delsanti 1983). Plotting specific viscosity η_{sp} vs. c[η] or c/c* is known to reduce data for different chain lengths of polymer in good solvent to three common power laws (Rubinstein and Colby 2003, Colby 2010).

$$\eta_{sp} \equiv \frac{\eta - \eta_s}{\eta_s} \approx \begin{cases} c/c^* & \text{for} \quad c < c^* \\ (c/c^*)^{1.3} & \text{for} \quad c^* < c < c_e \\ (c/c^*)^{3.9} / \left[N_e(1)\right]^2 & \text{for} \quad c > c_e \end{cases} \tag{1}$$

The solution viscosity is η, the solvent viscosity is η_s and $N_e(1)$ is the number of Kuhn monomers in an entanglement strand in the melt. There are dilute ($c < c^*$), semidilute unentangled ($c^* < c < c_e$) (Graessley 1980, Graessley 2008) and entangled ($c > c_e$) (Berry and Fox 1968, Ferry 1980) concentration regimes. The entanglement concentration c_e is easy to determine, since the concentration exponent triples. For a given linear polymer type, simple scaling expects all molecular weights of that polymer in all very good solvents to have specific viscosity lie on the same curve, with three power law parts of that curve (Adam and Delsanti 1983, Kulicke and Kniewske 1984). Of course, such considerations ignore any changes in glass transition temperature with concentration, and hence really only work for semidilute solutions with small amounts of polymer present. Higher concentrations (all the way to the melt state) require correcting isothermal data to constant free volume or friction (Fujita 1961, Berry and Fox 1968, Masuda, Toda et al. 1972, Ferry 1980, Colby, Fetters et al. 1991, Yan, Zhang et al. 2014) to see the expected exponent of 3.9.

Figure 1 shows the data of (Kulicke and Kniewske 1984) for various linear polystyrenes (PS) with weight-average molecular weights noted in the Legend, plotted in the format of Eq. 1, in two solvents. Toluene is a good solvent for PS at 25 °C, while decalin at 25 °C is 10K above the θ-temperature. PS/toluene data nicely show the three expected power laws of Eq. 1, with superb data collapse for eleven PS molecular weights spanning a factor of 500 range.

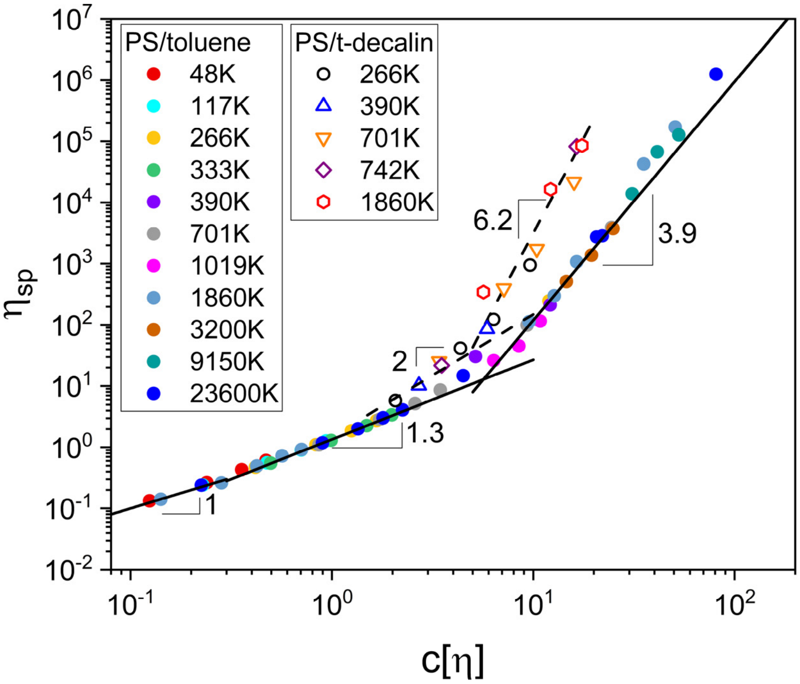

Figure 1. Colorized version of Figure 5 from (Kulicke and Kniewske 1984), showing specific viscosity data correlated with c[η] for eleven linear polystyrenes in toluene (filled symbols) and five of those polystyrenes in decalin (open symbols) at 25 °C. The power law slopes indicated are all expected by scaling theory except the apparent slope 6.2 for entangled solutions in decalin.

In a θ-solvent, the same three concentration regimes are again expected (Colby and Rubinstein 1990, Colby, Rubinstein et al. 1994, Rubinstein and Colby 2003).

$$\eta_{sp} \equiv \frac{\eta - \eta_s}{\eta_s} \approx \begin{cases} c/c^* & \text{for} \quad c < c^* \\ (c/c^*)^2 & \text{for} \quad c^* < c < c_e \\ (c/c^*)^{14/3} N_w^{2/3} / \left[N_e(1)\right]^2 & \text{for} \quad c > c_e \end{cases} \tag{2}$$

N_w is the weight-average number of Kuhn monomers in a chain. Below the entanglement concentration c_e, c/c* (or c[η]) should reduce all chain lengths of linear polymer to two common power laws with slopes of 1 in dilute solution and 2 in semidilute unentangled solution. The dilute slope of 1 is seen in the PS/toluene data for c[η] < 1 (no dilute data for PS/decalin in Figure 1). The semidilute unentangled data in PS/toluene are roughly consistent with the expected slope of 1.3 (Eq. 1) while the slope of 2 (Eq. 2) is clearly seen in the PS/decalin data of Figure 1. However, plotting specific viscosity vs. c[η] should not reduce entangled solution data for different chain lengths in a θ-solvent (Adam and Delsanti 1984, Roy-Chowdhury and Deuskar 1986), rationalized by so-called two-parameter scaling (Colby and Rubinstein 1990, Colby, Rubinstein et al. 1994, Rubinstein and Colby 2003), where the correlation length and tube diameter have different concentration dependences in θ-solvent. Close inspection of Figure 1 suggests there is more scatter than expected for entangled PS/decalin with $c > c_e$. The apparent exponent of 6.2 for PS/decalin in Figure 1 is considerably larger than the expected exponent of 14/3 = 4.7 for the entangled solution prediction of Eq. 2. Larger exponents, such as 6.2 for vinyl alcohol/vinyl acetate random copolymers in water (Parisi, Ditillo et al. 2022) and perhaps poly(methyl methacrylate) in *meta*-xylene (Gandhi and Williams 1971, Graessley 1974), are expected for associating polymer solutions (Rubinstein and Semenov 2001).

In Figure 2, the concentration dependence of specific viscosity is plotted for each of the five molecular weights of PS in decalin, clearly demonstrating that individual polymers each show a concentration exponent for specific viscosity of 4.9 or 5. So the apparent exponent of 6.2 noted in Figure 1 is in fact erroneous, the consequence of assuming simple c[η] scaling where it should not apply. Figure 3 tests the entangled prediction of Eq. 2 for PS/decalin, showing that $\eta_{sp} / N_w^{2/3}$ vs. c[η] nicely reduces the different chain lengths to a common power law (Colby and Rubinstein 1990, Colby, Rubinstein et al. 1994, Rubinstein and Colby 2003) close to the expected slope of 14/3 = 4.7. A slightly stronger concentration dependence was also noted with PS in cyclohexane data at the θ-temperature (Adam and Delsanti 1984, Rubinstein and Colby 2003). The entangled predictions of Eqs. 1 and 2 are based on the reptation model (Doi and Edwards 1986, Rubinstein and Colby 2003), with slightly larger apparent exponents for N and c dependences of specific viscosity expected by tube models that include thermal fluctuations in tube length (Doi 1981).

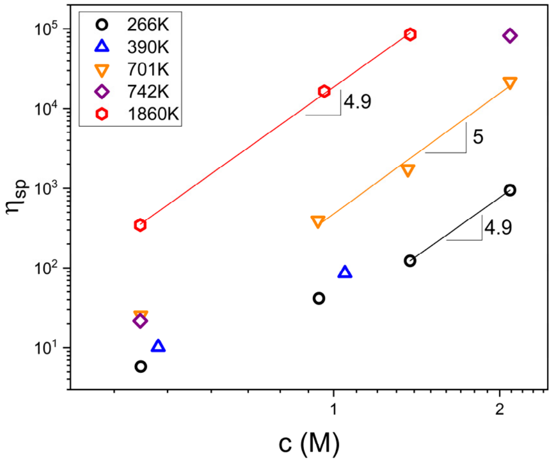

Figure 2. Concentration dependence of specific viscosity for five linear polystyrenes in decalin at 25 °C (Kulicke and Kniewske 1984).

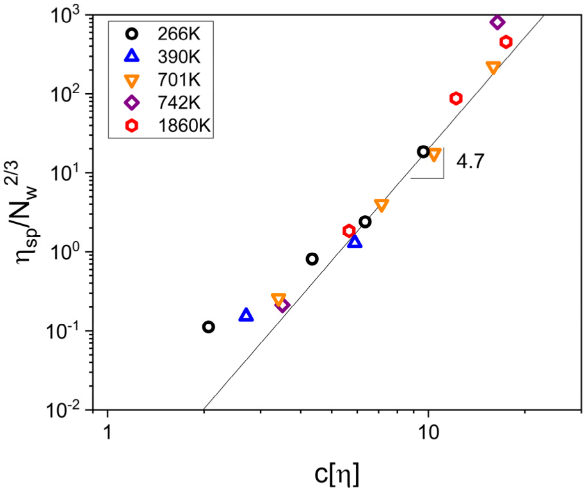

Figure 3. Concentration dependence of specific viscosity for five linear polystyrenes in decalin at 25 °C (Kulicke and Kniewske 1984), plotted in the format suggested by the entangled two-parameter scaling prediction of Eq. 2 for θ-solvent.

We conclude that PS/decalin with M ≤ 1860 kg/mol at 25 °C = θ + 10 K is in the θ regime, where θ-solvent scaling applies to the specific viscosity because the thermal blobs are larger than the correlation length, meaning that the entire chain is ideal (de Gennes 1979, Rubinstein and Colby 2003). That is precisely the expectation of Figure 5.1 of (Rubinstein and Colby 2003) and Figure 1 of (Colby, Rubinstein et al. 1994). As concentration is increased, the correlation length decreases and reaches the thermal blob size at c** (Dobrynin, Jacobs et al. 2021), beyond which the entire chain is ideal and is expected to obey the θ-solvent predictions. It is dangerous to apply simple c/c* scaling for solutions that are not far from the θ-temperature because two-parameter scaling may be needed. If one finds a peculiar apparent exponent (here 6.2 in Figure 1) it is best to analyze independently the concentration exponents for different chain lengths (Figure 2). If those plots show an exponent of 3.9 or 4, one concludes the solvent is a good solvent, where the simple scaling of Eq. 1 should apply (PS/toluene data in Figure 1). In contrast, exponents of 4.7-5 suggest the solvent may still be in the θ regime. To test that fully, one should construct the two-parameter scaling plot of Figure 3 (based on Eq. 2) to see whether all entangled data for different molecular weights are reduced to the same curve.

Roy-Chowdhury and Deuskar (1986) studied three fractions of *cis*-polybutadiene in benzene (good solvent) and two θ-solvents, dioxane (at θ = 20.2 °C) and isobutyl acrylate (IBA at θ = 20.5 °C). Just as was done in Figure 3, the *cis*-polybutadiene specific viscosity data in the two θ-solvents are reduced to a single curve by dividing specific viscosity by $N_w^{2/3}$ in Figure 4. The data in the two θ-solvents agree nicely with each other and with Eq. 2. Each chain length then has data roughly in agreement with Eq. 2 in the entangled regime, with slope perhaps slightly steeper than the predicted 14/3 = 4.7, quite analogous to the PS/decalin data in Figure 2. The data in their earlier study of various molecular weights of polychloroprene in two θ-solvents (Roy-Chowdhury and Deuskar 1984) exhibit a very similar data reduction. Taken together, the data in Figures 3 and 4 suggest an entangled concentration exponent for specific viscosity in θ-solvent that is slightly steeper than 14/3 = 4.7 (roughly 5), consistent with previous observations for polystyrene in cyclohexane (Adam and Delsanti 1984, Rubinstein and Colby 2003).

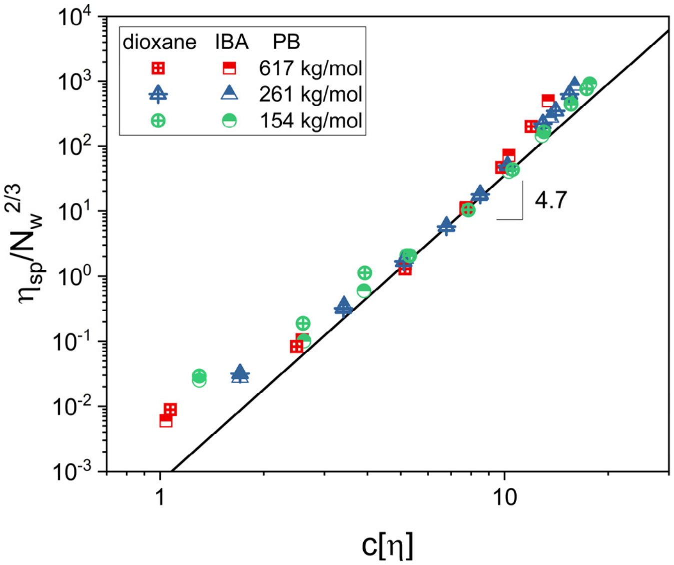

Figure 4. Concentration dependence of specific viscosity for three linear *cis*-polybutadienes in dioxane (at θ = 20.2 °C), isobutyl acrylate (IBA at θ = 20.5 °C) plotted in the format suggested by the entangled two-parameter scaling prediction of Eq. 2 for θ-solvent (Roy-Chowdhury and Deuskar 1986).

Figure 5 compares specific viscosity data of the three linear *cis*-polybutadienes in two θ-solvents with the same polymers in the good solvent benzene. The single entangled θ-solvent power law of slope 4.7 in Figure 4 is shown as three power laws in Figure 5, spaced relative to each other by the factor $N_w^{2/3}$. Figure 5 shows that in the semidilute unentangled regime, c[η] nicely reduces the different molecular weights to a common power law with the slope of 2, expected by Eq. 2. The entanglement concentration c_e is taken as the intersection of the slope of 2 with the slopes of 4.7, and it is clear that the semidilute unentangled regime is shrinking as chain length is increased, as it should (longer chains cross to entangled solutions at lower c[η], as expected by Eq. 2).(Colby and Rubinstein 1990, Rubinstein and Colby 2003)

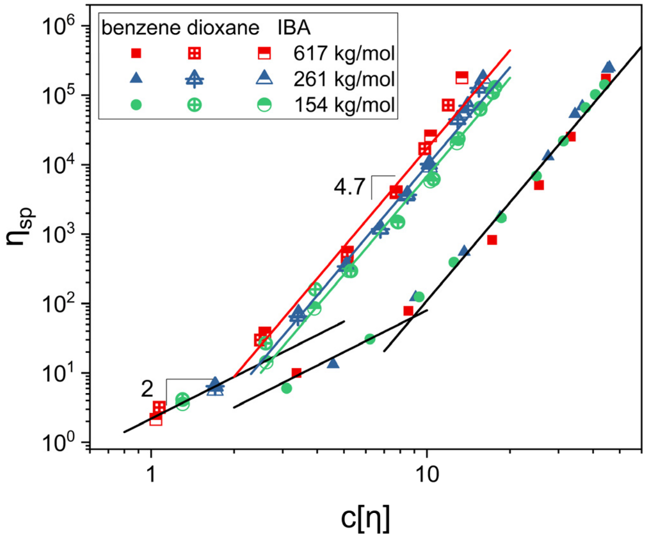

Figure 5. Specific viscosity of three *cis*-polybutadiene fractions in three solvents: Dioxane (at θ = 20.2 °C), isobutyl acrylate (IBA at θ = 20.5 °C) and the good solvent benzene at 20.5 °C. (Roy-Chowdhury and Deuskar 1986) The two θ-solvents show great agreement and are reasonably consistent with Eq. 2, with slope of 2 in the semidilute unentangled regime and slopes of 4.7 for entangled solutions. The three 4.7 slopes of the three molecular weights in the θ-solvents are spaced relative to each other by the $N^{2/3}$ factor of Eq. 2. However, instead of agreeing with Eq. 1 that expects an unentangled slope of 1.3, the data in benzene also show the unentangled θ-solvent slope of 2 and the entangled θ-solvent slope of 4.7, suggesting large thermal blobs with c** just below the range of the data in benzene. The overlap parameter c[η] collapses the data for the three molecular weights of *cis*-polybutadiene in benzene at 20.5 °C to a common power law, which is not expected. Also unexpected is the far wider semidilute unentangled regime in benzene; $c_e[\eta] \approx 9$ in benzene, while $2 < c_e[\eta] < 2.8$ in the two θ-solvents. This suggests the residual excluded volume in benzene affects how the chains entangle, which goes against the well-established result that the concentration dependence of plateau modulus is independent of solvent quality (Adam and Delsanti 1983, Adam and Delsanti 1984, Colby, Fetters et al. 1991, Rubinstein and Colby 2003, Milner 2005, Heo and Larson 2008, Colby 2010).

However, the good solvent data in Figure 5 (benzene) show a semidilute unentangled slope of 2 instead of the 1.3 expected by Eq. 1. Since each molecular weight has higher intrinsic viscosity in benzene than in the two θ-solvents, the line with slope 2 in benzene is seen at higher c[η]. This suggests a large thermal blob size in benzene and there should be a slope of 1.3 at lower concentration where the correlation length is larger than the thermal blob size, owing to excluded volume effects between these scales (Rubinstein and Colby 2003). Unfortunately, there are no data in the range $1 < c[\eta] < 3$ but *cis*-

polybutadiene in benzene does have good solvent Mark-Houwink exponent of 0.76 in dilute solution (Roy-Chowdhury and Deuskar 1986) (c[η] < 1), unfortunately measured only for M > 100 kg/mol. Measuring intrinsic viscosity at lower M in benzene should show a crossover to Mark-Houwink exponent ½ at lower M that would estimate the excluded volume and the size of the thermal blob. Fitting the intrinsic viscosity data of (Roy-Chowdhury and Deuskar 1986) for their three *cis*-polybutadienes in benzene at 32 °C, 25 °C and 20.5 °C to the good solvent Mark-Houwink power law $[\eta] \sim M^{0.76}$ and extrapolating to their θ-solvent Mark-Houwink power law $[\eta] \sim M^{1/2}$ in dioxane and IBA, estimates the molecular weight of chain inside a thermal blob as 4.0 kg/mol at 32 °C, 5.6 kg/mol at 25 °C and 6.3 kg/mol at 20.5 °C. The strong temperature dependence suggests that *cis*-polybutadiene in benzene should have a θ-temperature not far below this temperature range.

The ratio of semidilute unentangled specific viscosity in a θ-solvent and unentangled specific viscosity in a good solvent at the same c[η] ≈ c/c* (using the different c* or [η] values in good solvent and θ-solvent) allows estimation of the concentration c**, at which the correlation length reaches the thermal blob size in the good solvent (Dobrynin, Jacobs et al. 2021) and above c** the entire chain conformation is ideal.

$$\frac{\eta_{sp}^{\theta}}{\eta_{sp}^{good}} \approx \frac{\left(c/c_{\theta}^{*}\right)^{2}}{\left(c/c_{good}^{*}\right)^{2}}\left(\frac{c_{good}^{**}}{c_{good}^{*}}\right)^{0.70} \tag{3}$$

From Figure 5, this ratio is 2.7, making c_{good}^{**} roughly a factor of $2.7^{1/0.70} \approx 4$ above c_{good}^{*} for *cis*-polybutadiene in benzene at 20.5 °C. This suggests there might be a regime with the concentration dependence of specific viscosity showing the exponent of 1.3 expected by Eq. 1, over a factor of 4 range of concentration above the overlap concentration for *cis*-polybutadiene in benzene at 20.5 °C.

With $c_{good}^{**}[\eta]$ equal to 3 or 4, all the specific viscosity data for *cis*-polybutadiene in benzene at 20.5 °C in Figure 5 correspond to the θ-solvent scaling and Eq. 2 should apply to them. However, instead of three separate power laws seen in the two θ-solvents, all the data for the three molecular weights in benzene seem to be reduced to the same power laws with exponents 2 and 4.7; the latter is not expected by two-parameter scaling. Another related unexpected result is that the semidilute unentangled regime is much wider in benzene than in the two θ-solvents. Depending on molecular weight, $2 < c_e[\eta] < 2.8$ in the two θ-solvents, while $c_e[\eta] \approx 9$ in the good solvent benzene is actually typical for good solvents. Scaling expects the conformation of the chains in benzene to be identical to the ideal conformation in θ-solvent. Instead, it seems that some residual weak excluded volume affects how chains entangle.

We considered two experimental studies in the literature (Kulicke and Kniewske 1984, Roy-Chowdhury and Deuskar 1986), each with results that at first glance seem strange, and explain them by assuming the thermal blob is large. (de Gennes 1979, Rubinstein and Colby 2003) Polystyrene in decalin at 25 °C is 10K above θ and all specific viscosity literature data (with $c[\eta] > 2$) are shown to be consistent with the θ-solvent scaling of Eq. 2. The apparent steeper concentration exponent of 6.2 in Figure 1 is shown to be erroneous. *cis*-Polybutadiene in benzene is known to be a good solvent at 20.5 °C based on $[\eta] \sim M^{0.76}$ in dilute solution. However, all specific viscosity data on this system (with $c[\eta] > 3$) are consistent with the θ-solvent scaling of Eq. 2. Both polystyrene in decalin at 25 °C and *cis*-polybutadiene in benzene at 20.5 °C clearly show a semidilute unentangled regime where $\eta_{sp} \approx (c/c^*)^2$ and an entangled regime at higher concentrations with $\eta_{sp} \sim (c/c^*)^5$. That entangled concentration dependence is a bit steeper than the reptation prediction of Eq. 2, as seen previously for PS in the θ-solvent cyclohexane (Adam and Delsanti 1984, Rubinstein and Colby 2003).

Polymer solutions that are clearly good solvent in dilute solution but exhibit slopes of 2 and 4.7-5 for concentration dependence of specific viscosity in semidilute solutions are in no way unusual. For examples, polybutadiene in cyclohexane (Raspaud, Lairez et al. 1995), poly(ethylene oxide) in water (Rubinstein and Colby 2003, Ebagninin, Benchabane et al. 2009, Indei and Narita 2022A) for which the molecular weight of a thermal blob at 25 °C was estimated to be 3 kg/mol (Indei and Narita 2022B) and poly(methyl methacrylate) in ionic liquids (He, Kong et al. 2020) show this character. The polystyrene in toluene data of Figure 1 show the slopes of 1.3 and 3.9 expected for the very good (athermal) solvent limit (Eq. 1), suggesting that excluded volume is stronger for PS/toluene, making the thermal blobs smaller than the correlation length up to at least 0.14 g/mL. Polystyrene/THF solutions also show the slopes of 1.3 and 4 (Jamieson and Telford 1982). With apparent $c^* < c^{**} < c_e$, polystyrene in benzene and polyisoprene in cyclohexane perhaps show slopes of 1.3, 2.0 and 4.7 (Raspaud, Lairez et al. 1995) but since neutral polymer solutions never have more than a decade of concentration that is semidilute and unentangled, there are very few points showing clean slopes of either 1.3 or 2.0. There could even be solutions that would show slopes of 1.3, 3.9 and 4.7-5 at higher concentrations, with $c_e < c^{**}$ from an intermediate thermal blob size (Dobrynin, Jacobs et al. 2021) but we are not aware of any such data in the literature.

The scaling models can allow many literature observations on the concentration dependence of specific viscosity of polymer solutions to be understood if the thermal blob size is used as an adjustable parameter. Better understanding should arise from independent measures of the thermal blob size, which can be easily estimated in three ways, although the three ways may not agree perfectly. (1) Small-angle X-ray or neutron scattering (or osmotic pressure) in semidilute solution should find the concentration dependence of the correlation length change from $\xi \sim c^{-0.76}$ to $\xi \sim c^{-1}$, with the thermal blob size being the value of the correlation length at the crossover. Scattering and osmotic pressure are underutilized methods for rheologists and there are no such data showing this crossover in the literature so far. Scattering could also be used to detect the change in fractal dimension at the thermal blob scale. Scattered intensity $I(q) \sim q^{-2}$ inside the thermal blob and $I(q) \sim q^{-1.7}$ on larger scales (smaller wavevector q) but that crossover has very rarely been reported(Farnoux, Boue et al. 1978, Rawiso, Duplessix et al. 1987) and since the thermal blob is quite small there is a limited q range to study it. (2) Light scattering could be used to measure radius of gyration in dilute solution for a variety of short chain lengths as a function of temperature to determine the thermal blob size.(Tamai, Konishi et al. 1990, Abe, Horita et al. 1994, Hong, Lu et al. 2010).

(3) Using the zero-average contrast method in SANS (Kassapidou, Jesse et al. 1997) the concentration dependence of the radius of gyration could be measured to learn the concentration at which the ideal chain size is reached. That concentration has the thermal blob size equal to the correlation length.(Cheng, Graessley et al. 2009) The correlation length should also crossover from good solvent to θ-solvent scaling at the same concentration where radius of gryration reaches the ideal size. (4) Measure intrinsic viscosity (or second virial coefficient in dilute solution) over a wide range of molecular weight that includes short chains, to see the crossover from $[\eta] \sim M^{0.76}$ at high molecular weights and $[\eta] \sim M^{1/2}$ at low molecular weights, see Figure 8.3 of (Rubinstein and Colby 2003). This dilute solution crossover directly measures the molecular weight associated with the thermal blob but only if one assumes that the static and dynamic crossovers coincide. In practice, this intrinsic viscosity method seems to overestimate the static thermal blob size. (3) In some systems one could get lucky and detect changes in the specific viscosity -- concentration slope either from 1.3 to 2.0 in the semidilute unentangled regime or 3.9 to 4.7-5 in the entangled regime. Knowing the correlation length at the concentration of this crossover estimates the thermal blob size. However, the semidilute unentangled crossover is difficult since the entire semidilute unentangled regime is never more than a decade in concentration for neutral polymer solutions. A comparison of static measures of the thermal blob (osmotic pressure and scattering) with the viscosity measures could prove quite interesting, as it is not obvious that hydrodynamic interactions necessarily cross precisely where static conformation does.

The strangest observation from this study is the *cis*-polybutadiene data in benzene at 20.5 °C in Figure 5. It seems that our best estimate of the thermal blob molecular weight is 6.3 kg/mol, making benzene at 20.5 °C a not very good solvent, with slopes of 2 and 4.7, consistent with Eq. 2. However, plotting specific viscosity vs. c[η] seems to reduce the three molecular weights to a common power law in the entangled regime, expected for very good solvents but not for θ-solvents or not-so-good solvents with large thermal blobs, in the θ-regime. Also the semidilute unentangled regime for the *cis*-polybutadiene data in benzene at 20.5 °C in Figure 5 covers nearly a decade in concentration, suggesting that some small amount of excluded volume in this system strongly impacts how chains entangle. This suggests that a polymer/solvent system with a convenient θ-temperature in a nonvolatile solvent should prove very interesting to study in detail the specific viscosity $\eta_{sp}\left(c,N,T\right)$ over a wide range of temperature from θ to θ + 100 K (very good solvent), ideally with scattering measuring the thermal blob at each temperature.

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