Supporting Information

“A unified picture of static and dynamic length-scales in polymer solutions”,
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**Photon correlation spectroscopy (PCS):** We have measured the collective diffusion coefficient \(D_c\) for atactic polystyrene \(M_w = 301,600\ \text{g/mol,}\ \ M_w/M_n = 1.04\) in toluene at 25 °C, in order to derive \(\xi_h\) through the Stokes-Einstein relation. The PCS measurements were performed under homodyne conditions with a frequency doubled Nd-Vanadate laser (532 nm) and a correlator (ALV-5000/FAST) over the time range \(10^{-7}\ \text{to}\ 10^4\ \text{sec.}\) The obtained intermediate scattering functions exhibit bimodal relaxation behaviors composed of a fast diffusive process and a slow diffusive process, which can be described by two well-separated exponential decays. At lower polymer concentrations (roughly below 10 wt %), only the fast process is visible. The PCS results are in excellent agreement with literature\(^1,2\). We have derived \(D_c\) data using the observed fast relaxation time, \(\tau_{fast}\), following the standard procedure:

\[
D_c = 1/(\tau_{fast}q^2(1-\phi)),
\]

where \(q\) is the scattering vector, \(\phi\) is the polymer volume fraction, and \((1-\phi)\) corrects for the solvent backflow.\(^1\)
The least-squares fit procedure: In order to examine various power law regimes in the experimental data, the following functions were employed:

\[
\xi_s^{(i)} = \begin{cases} 
\phi^{-0.75} & \phi < \Phi_{I-II} \\
\phi^{-0.5} & \Phi_{I-II} \leq \phi < \Phi_{II-III} \\
\phi^{-1} & \Phi_{II-III} \leq \phi < \Phi_{III-IV} \\
\phi^{-2} & \Phi_{III-IV} \leq \phi < \Phi_{IV-V} \\
\phi^0 & \Phi_{IV-V} \leq \phi 
\end{cases}
\]

Figure 2A: The static correlation length, \( \xi_s^{(i)} \)

\[
\xi_h^{(i)} = \begin{cases} 
\phi^{-0.75} & \phi \leq \Phi_{I-II} \\
\phi^{-0.5} & \Phi_{I-II} < \phi \leq \Phi_{II-III} \\
\phi^{-1} & \Phi_{II-III} < \phi \leq \Phi_{III-IV} \\
\phi^{-2} & \Phi_{III-IV} < \phi \leq \Phi_{IV-V} \\
\phi^0 & \Phi_{IV-V} < \phi 
\end{cases}
\]

Figure 2A: The dynamic correlation length \( \xi_h^{(i)} \)

\[
\xi_s^{(i)} = \begin{cases} 
\phi^{-0.75} & \phi \leq \Phi_{I-II} \\
\phi^{-0.5} & \Phi_{I-II} < \phi \leq \Phi_{II-III} \\
\phi^{-1} & \Phi_{II-III} < \phi \leq \Phi_{III-IV} \\
\phi^{-2} & \Phi_{III-IV} < \phi \leq \Phi_{IV-V} \\
\phi^0 & \Phi_{IV-V} < \phi 
\end{cases}
\]

Figure 3B: The dynamical correlation length \( \xi_s^{(i)} \)

\[
g_s^{(i)} = \begin{cases} 
\phi^{-1} & \phi \leq \Phi_{I-II} \\
\phi^{-2} & \Phi_{I-II} < \phi \leq \Phi_{II-III} \\
\phi^{-3} & \Phi_{II-III} < \phi \leq \Phi_{III-IV} \\
\phi^{-4} & \Phi_{III-IV} < \phi \leq \Phi_{IV-V} \\
\phi^0 & \Phi_{IV-V} < \phi 
\end{cases}
\]

Figure 2B and 3C: The number of monomers, \( g_s^{(i)} \), per blob, \( g_h^{(i)} \), within \( 2\xi_h^{(i)} \).

Here, \( \xi_s, \xi_h, g_s \) and \( g_h \) are the static correlation length, the dynamic correlation length, the number of monomers per blob, and the monomer number within \( 2\xi_h \), respectively. \( \xi_{s0}, \xi_{h0}, g_{s0} \) and \( g_{h0} \) are the amplitudes, \( \phi \) is the polymer volume fraction, and \( \Phi_{i-j} \) denotes \( \phi \) at the crossover from regime \( i \) to regime \( j \). The above functions use the theoretical power law exponents of \( \phi \) for \( \xi \) and \( g \). In the fit procedure, the different \( \Phi_{i-j} \) parameters were used as fitting parameters. As a result, the following fitting parameters were obtained:

\[ \xi_s: \xi_{s0} = 0.19 \pm 0.02 \text{ nm}, \Phi_{I-II} = 0.017 \pm 0.006, \Phi_{II-III} = 0.106 \pm 0.008, \Phi_{III-IV} = 0.41 \pm 0.03, \Phi_{IV-V} = 0.65 \pm 0.03. \]

Note: In order to examine the influence of the large uncertainty in \( \Phi_{I-II} \) obtained using Equation 1 on the three parameters (\( \Phi_{II-III}, \Phi_{III-IV} \) and \( \Phi_{IV-V} \)), we also performed a least-squares fit with regime I excluded.
\[
\begin{align*}
\xi_h &= \begin{cases} 
\phi^{-0.5} & \phi \leq \Phi_{\text{II-III}} \\
\Phi_{\text{II-III}}^{-0.5} \phi^{-1} & \Phi_{\text{II-III}} < \phi \leq \Phi_{\text{III-IV}} \\
\Phi_{\text{II-III}}^{-0.5} \Phi_{\text{III-IV}}^{-2} \phi^{-2} & \Phi_{\text{III-IV}} < \phi \leq \Phi_{\text{IV-V}} \\
\Phi_{\text{II-III}}^{-0.5} \Phi_{\text{III-IV}}^{-2} \phi^{-2} \phi^0 & \Phi_{\text{IV-V}} < \phi
\end{cases} 
\end{align*}
\] (5)

The parameters (\(\Phi_{\text{II-III}}, \Phi_{\text{III-IV}}\) and \(\Phi_{\text{V-L-V}}\)) determined from both least-squares fit procedures are identical within errors.

The obtained uncertainty in \(\Phi_{\text{I-II}}\) might be ascribed to relatively low molecular weight polystyrene\(^3,4\) \((M_w \approx 110,000, M_w/M_n < 1.06)\) used for \(\xi_s\) at the concentrations where regime I is expected. The crossover from regime I to II can be expected only for high molecular weight polymer of which gyration radius, \(R_g\), is sufficiently larger than the thermal blob radius \((\approx 7 \text{ nm in the present system})\). However, the \(R_g\) \((\approx 9 \text{ nm})\) of the polystyrene used for \(\xi_s\) is barely above the thermal blob radius.

\[\xi_h \text{ (using the neat solvent viscosity): } \xi_{h0} = 0.33 \pm 0.02 \text{ nm, } \Phi_{\text{I-II}} = 0.017 \pm 0.003.\]

\[\xi_h \text{ (using the effective local viscosity): } \xi_{h0} = 0.31 \pm 0.02 \text{ nm, } \Phi_{\text{I-II}} = 0.019 \pm 0.002, \Phi_{\text{II-III}} = 0.080 \pm 0.003, \Phi_{\text{III-IV}} = 0.263 \pm 0.005.\]

Note: Complementary curve-fits with the power law exponents as free parameters yield: \(\xi_{h0} = 0.5 \pm 0.2 \text{ nm, } \Phi_{\text{I-II}} = 0.019 \pm 0.009, \Phi_{\text{II-III}} = 0.083 \pm 0.006, \Phi_{\text{III-IV}} = 0.26 \pm 0.01, \alpha_1 = -0.7 \pm 0.1, \alpha_\Pi = -0.53 \pm 0.03, \alpha_\Pi = -0.99 \pm 0.04, \alpha_\IV = -2.00 \pm 0.07.\) Here, \(\alpha_i\) denotes the observed power law exponent at the concentration range where regime \(i\) is expected.

\[g_s: g_{s0} = 9.3 \pm 0.4, \Phi_{\text{II-III}} = 0.107 \pm 0.007.\]

Note: The theoretical exponent change at the I/II-crossover for \(g\) is minor (i.e., -1.25 \(\to\) -1). Therefore, in order to increase the stability of the least-squares fit procedure, Equation 4 includes only two theoretical exponents (i.e., -1, -2) for \(g\) expected in the concentration regimes from regime II to IV. Thus, \(\Phi_{\text{I-II}}\) is not included in the results. \(\Phi_{\text{III-IV}}\) is also not included in the results since the theoretical exponent change at the III/IV-crossover for \(g\) is none.
\( g_{h0} = 4.5 \pm 0.1, \Phi_{\text{II-III}} = 0.076 \pm 0.003. \)

Note: We performed the same fit procedure as for \( g_s \). Thus, \( \Phi_{\text{I-II}} \) and \( \Phi_{\text{III-IV}} \) are not included in the results for the same reason as for \( g_s \).

References


