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Submitted on 1 Jan 1997

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Dynamics in Blends of Long Polymers with Unentangled Short Chains

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(Received 20 January 1996, revised 5 April 1996, accepted 3 October 1996)

PACS.83.10.Nn – Polymer dynamics
PACS.83.20.Fk – Reptation theories
PACS.61.25.Hq – Macromolecular and polymer solutions; polymer melts; swelling

Abstract. — Scaling ideas for dynamics of polymer solutions are extended to the case of a solution of long chains (of \( N \) monomers) in unentangled short chains (of \( P \) monomers). The \( P \) chains can be sufficiently short to make the long chains partially swell (\( P < N^{1/2} \)). While the configurational statistics of the partially swollen long chains are perfectly analogous to the case of a long chain in marginal solvent, the dynamics are qualitatively different because of differences in the screening of hydrodynamic interactions. When the long chains are dilute and partially swollen (\( N > P^2 \)), hydrodynamic interactions control their terminal relaxation. When \( N < P^3 \), excluded volume is fully screened, and the dilute long chains relax by Rouse motion (with hydrodynamic interactions fully screened). The assumptions about hydrodynamic screening in dilute solution have consequences in the semidilute regimes of unentangled and entangled behavior, where we calculate the viscosity and the tracer diffusion coefficients. We end with a discussion of assumptions about hydrodynamic screening, and experiments are suggested to test those assumptions using binary blends with one unentangled component.

1. Introduction

Recently, a two-parameter scaling theory for dynamics in semidilute solutions of linear polymers has been proposed [1,2]. It is based on two important length scales. The screening length [3,4] \( \xi \), beyond which hydrodynamic and any excluded volume interactions are screened, obeys a power law in concentration [4],

\[
\xi \approx b \phi^{-\nu/(3\nu-1)} \approx R_0 (\phi/\phi^*)^{-\nu/(3\nu-1)}
\]  

(1)

Here \( b \) is the monomer size (Kuhn length), \( \phi \) is the polymer volume fraction, \( \nu \) is the exponent for the scaling of end-to-end distance in dilute solution \( R_0 \) with the number of monomers in the chain \( N \) (\( R_0 \approx bN^{\nu} \) with \( \nu = 1/2 \) in theta solvent [4] and \( \nu = 0.588 \approx 3/5 \) in good solvent limit [5]), and \( \phi^* \approx N^{1-3\nu} \) is the overlap concentration. The tube diameter of reptation theory [6,7] \( a \), has also been suggested to have a power law concentration dependence [1,2].

\[
a \approx a_1 \phi^{-x}
\]

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Here \( a_1 \) is the tube diameter in the melt. The exponent \( x \) is determined by assuming that binary contacts control entanglements. In good solvent, binary contacts are controlled by the screening length \([4]\), with \( a \sim \xi \) and \( x = \nu/(3\nu - 1) = 0.770 \equiv 3/4\). In theta solvent, the screening length counts ternary contacts because the effect of binary contacts on the free energy cancels at \( T = \theta \). Binary contacts still control the mechanical properties, and since the theta solvent corresponds to mean-field, \( \xi = (d - 1)/d = 2/3 \) in three dimensions [1].

Since \( a > \xi \) in semidilute solution [1], an important consequence of two-parameter scaling is that the concentration where chains start to show entanglement effects \( \phi_a \) is larger than the overlap concentration \( \phi^* \). This implies a concentration regime \( \phi^* < \phi < \phi_a \) which is semidilute but not entangled [2,8]. It should be noted at the outset that the scaling exponent of 2/3 for the tube diameter in theta solvent is somewhat controversial [9,10], but it appears to be consistent with experiment [11,12].

In this paper we combine the static scaling results for a mixture of long and short chains [4,13,14] with the dynamic scaling results for semidilute solutions [1,2] to derive dynamic scaling predictions for mixtures of long chains with unentangled short chains.

2. Chain Statistics

The static properties of a single long chain (degree of polymerization \( N \)) immersed in short chains (degree of polymerization \( P \)) are known [13]. The scaling approach to this problem has been discussed elsewhere [4,13,14], and will be briefly reviewed below. Recently, a more sophisticated analysis has shown the scaling is correct [15]. In the limit \( N > P^2 \), the long chain obeys Gaussian statistics on length scales smaller than the \( P \)-blob size \( \xi_P \), with \( P^2 \) monomers in a \( P \)-blob.

\[
\xi_P \cong b \left( P^2 \right)^{1/2} \cong bP \quad (3)
\]

The end-to-end distance \( R_0 \) of the dilute long chain surrounded by short chains is determined as a self-avoiding walk of \( P \)-blobs when \( N > P^2 \), while for \( N < P^2 \) the long chains are random walks.

\[
R_0 \cong \begin{cases} 
\xi_P \left( \frac{N}{P^2} \right)^{3/5} & N > P^2 \\
N^{1/2} & N < P^2
\end{cases} 
\]

\[
\phi^* \cong b^3 NR_0^{-3} \cong \begin{cases} 
P^{3/5}N^{-4/5} & N > P^2 \\
N^{-1/2} & N < P^2
\end{cases} \quad (5)
\]

When the long chains become semidilute (\( \phi > \phi^* \)) there are two length scales for statics. On length scales smaller than \( \xi_P \) the long chains are Gaussian, as in dilute solution, and thus equation (3) applies. In perfect analogy with semidilute solutions in a good solvent, a screening length (or blob size) \( \xi \) exists, above which excluded volume is screened. For sufficiently low semidilute concentrations, \( \xi_P < \xi \) and the configuration of the chain is a self-avoiding walk between these length scales. The blob (of \( g \) monomers) is thus a self-avoiding walk of \( P \)-blobs.

\[
\xi \cong \xi_P \left( \frac{g}{P^2} \right)^{3/5} \cong bP^{-1/5}g^{3/5} \quad g > P^2 \quad (6)
\]

The criterion for applicability of equation (6) arises from requiring \( \xi > \xi_P \). If this condition is not met, then the configuration of the entire long chain is a random walk, and the standard \( \theta \) solvent results apply (\( \xi = bg^{1/2} \)).
The concentration dependence of the screening length is obtained by the usual scaling argument [4]: the exponent for the concentration dependence is evaluated by requiring $\xi$ to be independent of long chain length at all concentrations, and at the overlap concentration $\xi = R_0$.

$$\xi \cong R_0 \begin{cases} (\frac{\phi}{\phi^*})^{-3/4} & g > P^2 \\ (\frac{\phi}{\phi^*})^{-1} & g < P^2 \end{cases} g \cong b \begin{cases} P^{1/4} \phi^{-3/4} & g > P^2 \\ \phi^{-1} & g < P^2 \end{cases}$$

Combining the $g > P^2$ results of equation (7) with equation (6) and the $g < P^2$ result of equation (7) with the standard $\theta$ solvent result ($\xi = bg^{1/2}$) gives the number of monomers per blob.

$$g \cong \begin{cases} P^{3/4} \phi^{-5/4} & g > P^2 \\ \phi^{-2} & g < P^2 \end{cases}$$

The configuration of the long chain is a random walk on all length scales when $g < P^2$, which occurs at volume fraction of long chains $\phi_\theta$.

$$\phi_\theta \cong P^{-1}$$

Notice that our criteria in equations (7) and (8) translate directly to criteria in concentration: $g > P^2$ means that $\phi < \phi_\theta$ and $g < P^2$ means that $\phi > \phi_\theta$. The coil is a random walk of blobs, with end-to-end distance $R$.

$$R \cong \xi \left(\frac{N}{g}\right)^{1/2} \cong b \begin{cases} P^{-1/8} N^{1/2} \phi^{-1/8} & \phi^* < \phi < \phi_\theta \\ N^{1/2} & \phi > \phi_\theta \end{cases}$$

In the limit $P \to 1$ equations (4–10) reduce to the standard good solvent scaling results [4], where the configuration of the chain is not a simple random walk until the solvent is all removed ($\phi_\theta = 1$) [4, 16]. The scaling of the size $r$ (the root-mean-square through-space end-to-end distance) of a subsection of chain of $n$ monomers is shown schematically in Figure 1, for mixtures of two chain lengths (with $N = 8000$ and $P = 5$, so that $N \gg P^2$) at various concentrations. On its smallest scales, the long chain is a random walk up to the $P$-blob size (Eq. (3)). When more than $P^2$ monomers are considered, the chain exhibits self-avoiding walk statistics in the range $P^2 < n < g$ (or $\xi P < r < \xi$). Beyond the screening length, the chain once again has random walk statistics. The coil size of the long chain (determined at $n = N$) varies continuously, between the largest (dilute) size $R_0$ (Eq. (4)) and the smallest ($\theta$ solvent) size $R_\theta = bN^{1/2}$, as the concentration of long chains increases. It is clear from Figure 1 that this is associated with a shrinking of the regime where self-avoiding chain statistics apply.

3. Entanglement

The existence of the fully screened concentration $\phi_\theta$ means that there are two criteria for the entanglement concentration, depending on whether the long chains are entangled at $\phi_\theta$ (throughout the paper we only treat the case of unentangled short chains, with $P < N_e$, the degree of polymerization of an entanglement strand for undiluted monodisperse chains). If $\phi_e > \phi_\theta$, the entanglement concentration $\phi_e$ is the same as in a low molar mass theta solvent [2], and is determined as the concentration where the tube diameter of equation (2), with $x = 2/3$, equals the coil size.

$$\phi_e \cong \left(\frac{a_1}{b}\right)^{3/2} N^{-3/4}$$
From equations (9) and (11), we conclude that the crossover between entanglement concentration criteria, occurring at $\phi_\theta = \phi_e$, corresponds to a particular degree of polymerization of the long chains.

$$N_\theta \approx \left( \frac{a_1}{b} \right)^2 \frac{P^{4/3}}{b^4}$$

(12)

For $N < N_\theta$, the long chains are unentangled at $\phi_\theta$ and equation (11) determines the entanglement concentration. For $N > N_\theta$, there is a concentration range $\phi_e < \phi < \phi_\theta$, where the tube diameter, controlled by binary contacts, adopts the concentration scaling of the screening length.

$$a \approx a_1 \frac{P^{-1/12}}{\phi^{-3/4}} \quad N > N_\theta \quad \phi_e < \phi < \phi_\theta$$

(13)

The $P$ dependence of equation (13) was determined by matching the theta result at $\phi_\theta = P^{-1}$. The entanglement concentration $\phi_e$ is determined as the concentration where $a = R$, from equations (10) and (13).

$$\phi_e \approx \left( \frac{a_1}{b} \right)^{8/5} P^{1/15} N^{-4/5} \quad \phi_\theta > \phi_e$$

(14)

Figure 2 plots the concentration dependence of the various length scales for $N = 8000$ and $P = 5$, so that $N > N_\theta$. Figure 2 shows that the static picture of a long chain in a solution of unentangled short chains is perfectly analogous to a long chain in a marginal solvent [2] ($T > \theta$, but not in the good solvent limit). The $P$-blob is analogous to the thermal blob [4]. Both impart random walk statistics on the smallest length scales of the long chain [2,4,17], making the crossover to $\theta$-solvent statistics occur at a long chain volume fraction well below unity. All static results presented in this paper translate to the static results of reference [2] by simply replacing $P$ with the quantity $T/(T - \theta)$, since the thermal blob is $\xi_T \approx bT/(T - \theta)$, where $\theta$ is the theta temperature.
Combining equations (5) and (11) \( N < N_\theta \), and equations (5) and (14) for \( N > N_\theta \), we get the width of the semidilute-unentangled concentration regime.

\[
\phi_e / \phi^* \approx \begin{cases} 
\left( \frac{a_1}{b} \right)^{8/5} P^{-8/15} & N > P^2 \text{ and } N > N_\theta \\
\left( \frac{a_1}{b} \right)^{3/2} P^{-3/5} N^{1/20} & P^2 < N < N_\theta \\
\left( \frac{a_1}{b} \right)^{3/2} N^{-1/4} & N < P^2
\end{cases}
\]

In the limit of \( P \rightarrow 1 \), we recover the standard good solvent scaling results for entanglement [2]. The crossover chain length in this limit becomes a simple entanglement criterion: \( N_\theta \approx (a_1/b)^2 \equiv N_e^o \), the degree of polymerization of an entanglement strand in a monodisperse melt. The width of the unentangled-semidilute range is simply determined by \( N_e \) [2]: \( \phi_e / \phi^* \approx (a_1/b)^{8/5} = N_e^{4/5} \). Undiluted polymers typically have \( 20 \leq N_e \leq 40 \), so a long chain in good solvent (\( P = 1 \)) has \( 10 \leq \phi_e / \phi^* \leq 20 \). As the \( P \)-chain length increases, the width of the semidilute-unentangled regime shrinks monotonically (see Eq. (15)) until \( P = N^{1/2} \), where we recover the standard theta solvent results [2] (the \( N < P^2 \) case of Eq. (15)). This is shown in the phase diagram (Fig. 3) by plotting the critical concentrations \( \phi^* \) and \( \phi_e \) as functions of the short chain length \( P \).

4. Dynamic Scaling with Dilute Long Chains (\( \phi < \phi^* \))

The viscosity of the melt of short chains is the effective solvent viscosity \( \eta_S \) of the blend. Since we only consider the case where the short chains are unentangled, their dynamics are described by the Rouse model [2, 7].

\[
\eta_S \approx \frac{\zeta}{b} P
\]

The friction coefficient of a monomer is \( \zeta \). The effective solvent viscosity is thus larger than the monomeric one by a factor \( P \).
Hydrodynamic interactions control the terminal relaxation of the long chains as long as they are swollen slightly \((N > P^2)\). Dynamics are thus determined by the Zimm model \([2, 7]\), and the diffusion coefficient \(D_{\text{Zimm}}\) of the long chains is that of a Stokes sphere.

\[
D_{\text{Zimm}} \approx \frac{kT}{\eta s R_0} \approx \frac{kT}{\zeta} P^{-4/5} N^{-3/5} \quad \phi < \phi^* \quad N > P^2
\]  

(17)

If \(N < P^2\), both excluded volume and hydrodynamics are fully screened, and the long chain dynamics are described by the Rouse model \([18]\).

\[
D_{\text{Rouse}} \approx \frac{kT}{\zeta} N^{-1} \quad \phi < \phi^* \quad N < P^2
\]  

(18)

The dilute diffusion coefficient is plotted as a function of the short chain length \(P\) in Figure 4. In principle, Rouse motion is always available to the long chain. However, when \(P < N^{1/2}\), the Zimm relaxation process is faster (see Fig. 4) and the long chains relax with strong hydrodynamics before they get a chance to relax by simple Rouse motions. Terminal relaxation in dilute solution is controlled by hydrodynamic interactions when the chains are swollen.

The relaxation time \(\tau\) of the long chain is determined as the time it takes to diffuse a distance equal to its size.

\[
\tau \approx \frac{R_0^2}{D} \approx \begin{cases} \frac{\eta s R_0^3}{kT} N > P^2 \\ \frac{\zeta N R_0^2}{kT} N < P^2 \end{cases} \approx \begin{cases} \frac{P^{2/5} N^{9/5}}{kT} \quad N > P^2 \\ N \quad N < P^2 \end{cases}
\]  

(19)

The long chain contribution to the solution viscosity is the product of the relaxation time and the effective modulus at the relaxation time \((G = \phi kT/Nb^3)\) which is \(kT\) per chain for both Rouse and Zimm \([7]\).

\[
\eta_c \approx G \tau \approx \begin{cases} \frac{\eta s}{\phi} \quad \phi < \phi^* \quad N > P^2 \\ \frac{\zeta}{b} N \phi \quad \phi < \phi^* \quad N < P^2 \end{cases}
\]  

(20)
Fig. 4. — Diffusion coefficient of dilute long chains (with $N = 2000$) as a function of short chain length $P$. For $P < N^{1/2}$, diffusion is dominated by hydrodynamic interaction (Eq. (17) Zimm model). For $P > N^{1/2}$, hydrodynamics are fully screened (Eq. (18) Rouse model).

The solution viscosity is the sum of contributions from the long and short chains ($\eta = \eta_S + \eta_L$). For the case with $N > P^2$ we have $\eta \cong \eta_S (1 + \phi/\phi^*)$, the standard Zimm result, with intrinsic viscosity as the reciprocal of the overlap concentration [19]. For $N < P^2$, the usual Rouse result [20] for a blend of two unentangled chains is recovered $\eta \cong (\zeta/b)[P(1 - \phi) + N\phi]$.

While the terminal relaxation is controlled by hydrodynamics when $N > P^2$, the mode structure of the relaxation of isolated long chains in short chains is distinct from that of the long chains in a monomeric solvent. On its shortest length scales, the long chain immersed in short chains has Rouse relaxation modes up to the $P$-blob size, with Zimm modes on larger length scales. The shear relaxation modulus $G(t)$ thus has two power law regions, as shown in Figure 5.

$$G(t) \cong \frac{\phi kT}{b^3} \begin{cases} \left(\frac{b^2\zeta}{tkT}\right)^{1/2} & t < \frac{b^2\zeta}{kT} P^4 \\ \left(\frac{b^2\zeta}{tkT}\right)^{5/9} P^{2/9} & t > \frac{b^2\zeta}{kT} P^4 \end{cases} \phi < \phi^*$$ (21)

The crossover time is simply the Rouse time of a $P$-blob (the relaxation time of a monomer, $b^2\zeta/kT$, times the square of the number of monomers in a $P$-blob, $P^4$). When discussing Figure 2, we mentioned an analogy between the statics of a long chain in short chains and a long chain in marginal solvent. The analogy does not hold for dynamics. The short chain solvent imparts Rouse modes in the short time mode spectrum, with $G(t) \sim t^{-1/2}$, whereas the long chain in a marginal solvent has $\theta$-solvent Zimm modes inside the thermal blob (with $G(t) \sim t^{-2/3}$). This qualitative difference should be evident in high frequency dynamic measurements, such as oscillatory flow birefringence. Experimental confirmation of this would be very helpful, because even though it does not affect terminal dynamics in dilute solution, semidilute terminal dynamics are affected by the form of the dilute relaxation function, as shown below.
Fig. 5. — Shear relaxation modulus $G(t)$ of dilute long chains (with $N = 3000$) in short chains ($P = 5$). Since $N > P^2$, terminal relaxation is dominated by hydrodynamic interaction (Zimm model), but the short modes of the chain (on times $t < b^2 \zeta P^3/kT$) have fully screened hydrodynamics (Rouse model).

5. Dynamic Scaling with Semidilute-Unentangled Long Chains ($\phi^* < \phi < \phi_e$)

When the long chains overlap, the screening blob relaxation time $\tau_\xi$ is controlled by hydrodynamic interaction, as long as the blob is slightly swollen (for $\phi < \phi_\theta$). Otherwise, for $\phi > \phi_\theta$, the screening blob relaxes by Rouse motion.

$$\tau_\xi \approx \begin{cases} \frac{\eta_0 \xi^3}{kT} & \phi < \phi_\theta \\ \frac{\zeta g \xi^2}{kT} & \phi > \phi_\theta \end{cases} \approx \begin{cases} \frac{P^{7/4} \phi^{-9/4}}{\phi_\theta} & \phi < \phi_\theta \\ \phi^{-4} & \phi > \phi_\theta \end{cases}$$

Notice that the crossover at $\phi_\theta = P^{-1}$ is smooth. Between the overlap concentration and the entanglement concentration, the terminal relaxation is controlled by Rouse dynamics of the chain of screening blobs [2, 7].

$$\tau \approx \tau_\xi \left( \frac{N}{g} \right)^2 \approx \frac{\zeta b^2}{kT} \begin{cases} \frac{P^{1/4} N^2 \phi^{1/4}}{\phi_\theta} & \phi^* < \phi < \phi_\theta \text{ and } \phi < \phi_e \\ \phi_\theta < \phi < \phi_e \end{cases}$$

The diffusion coefficient of the long chains is determined from their relaxation time and coil size.

$$D \approx \frac{R^2}{\tau} \approx \frac{kT}{\zeta} \begin{cases} \frac{P^{1/2} N^{-1} \phi^{-1/2}}{\phi_\theta} & \phi^* < \phi < \phi_\theta \text{ and } \phi < \phi_e \\ \phi_\theta < \phi < \phi_e \end{cases}$$

The viscosity is the product of the relaxation time and the terminal modulus ($G = \phi kT/Nb^3$).

$$\eta \approx G \tau \approx \frac{\zeta}{b} \begin{cases} \frac{P^{1/4} N \phi^{5/4}}{\phi_\theta} & \phi^* < \phi < \phi_\theta \text{ and } \phi < \phi_e \\ N \phi & \phi_\theta < \phi < \phi_e \end{cases}$$

In the limit where $P \to 1$, equation (25) reduces to the good solvent viscosity prediction in semidilute-unentangled solution ($\eta \sim N \phi^{5/4}$) [2].
6. Dynamic Scaling with Entangled Long Chains ($\phi > \phi_\theta$)

The plateau modulus in the entangled regime is determined by the usual scaling [1], as each entanglement strand stores $kT$ of elastic energy, and the volume of an entanglement strand is $a^2 \xi$, since it is the product of the screening blob volume $\xi^3$ and the number of screening blobs in an entanglement strand $(a/\xi)^2$.

$$G \approx \frac{kT}{a^2 \xi} \approx \frac{kT}{a^2 \xi} \left\{ \begin{array}{ll} P^{-1/12} \phi^{5/4} & \phi_e < \phi < \phi_\theta \\ \phi^{7/3} & \phi_e < \phi \text{ and } \phi_\theta < \phi \end{array} \right.$$  \hspace{1cm} (26)

For $N > N_\theta$ there is a regime akin to good solvent scaling between $\phi_e$ and $\phi_\theta$. In all other cases, the entangled modulus is identical to the standard theta solvent result [1]. There are $g_e$ monomers in an entanglement strand, which is a random walk of screening blobs.

$$g_e \approx g \left( \frac{a}{\xi} \right)^2 \approx \left( \frac{a_1}{b} \right)^2 \left\{ \begin{array}{ll} P^{1/12} \phi^{-5/4} & \phi_e < \phi < \phi_\theta \\ \phi^{-8/3} & \phi_e < \phi \text{ and } \phi_\theta < \phi \end{array} \right.$$  \hspace{1cm} (27)

Above the entanglement concentration, simple Rouse motions are restricted to length scales smaller than the tube diameter $a$. On larger length scales, the chains must reptate [6, 7] to relax. Entanglement strands of $g_e/g$ blobs relax by Rouse motion (with relaxation time $\tau_e$).

$$\tau_e \approx \left( \frac{g_e}{g} \right)^2 \approx \frac{\zeta a_1^4}{b^2 kT} \left\{ \begin{array}{ll} P^{5/12} \phi^{-9/4} & \phi_e < \phi < \phi_\theta \\ \phi^{-8/3} & \phi_e < \phi \text{ and } \phi_\theta < \phi \end{array} \right.$$  \hspace{1cm} (28)

The reptation time of the chain of $N/g_e$ entanglement strands is the longest relaxation time.

$$\tau \approx \left( \frac{N}{g_e} \right)^3 \approx \frac{\zeta b^4}{a_1^3 kT} \left\{ \begin{array}{ll} P^{1/6} N^3 \phi^{3/2} & \phi_e < \phi < \phi_\theta \\ N^3 \phi^{4/3} & \phi_e < \phi \text{ and } \phi_\theta < \phi \end{array} \right.$$  \hspace{1cm} (29)

The diffusion coefficient of the long chains is once again determined from their relaxation time and coil size.

$$D \approx \frac{R^2}{\tau} \approx \frac{kT}{\zeta} \left( \frac{a_1}{b} \right)^2 \left\{ \begin{array}{ll} P^{-5/12} N^2 \phi^{-7/4} & \phi_e < \phi < \phi_\theta \\ N^{-2} \phi^{-8/3} & \phi_e < \phi \text{ and } \phi_\theta < \phi \end{array} \right.$$  \hspace{1cm} (30)

The viscosity is the product of the plateau modulus $G$ (Eq. (26)) and the relaxation time $\tau$ (Eq. (29)).

$$\eta \approx \frac{\zeta b^3}{a_1^4} \left\{ \begin{array}{ll} P^{1/12} N^3 \phi^{15/4} & \phi_e < \phi < \phi_\theta \\ N^3 \phi^{11/3} & \phi_e < \phi \text{ and } \phi_\theta < \phi \end{array} \right.$$  \hspace{1cm} (31)

In the limit $P \rightarrow 1$, we recover de Gennes’ reptation prediction in good solvent [4, 21] ($\eta \sim N^3 \phi^{15/4}$). The $\phi > \phi_\theta$ result is a factor of $\phi$ smaller than the theta solvent scaling result $\eta \sim \phi^{14/3}$ [2]. When the solvent is a polymer that does not partially swell the long chain, hydrodynamic interactions are screened, even inside the screening blob ($\tau_\xi \sim g_e^2 \sim \phi^{-4}$, Eq. (22)) whereas in theta solvent hydrodynamic interactions dominate inside the screening blob, with $\tau_\xi \sim \xi^3 \sim \phi^{-3}$ [2].
7. Discussion

Watanabe, Sakamoto and Kotaka [22] have measured the longest relaxation time of dilute long chains in short chains (both polystyrene), with $N > P^2$. They report that the relaxation time is independent of concentration of the long chains when they are dilute, as expected (Eq. (19)). The molecular weight of a Kuhn segment for polystyrene is 500 (effective monomer). Six of the blends studied in [22] have $P < N_e$ (using $P = 10$ and 21, while $N_e = 36$) using long chain lengths of $N = 850$, 2400 and 5600. The relaxation times of the long chain are plotted in Figure 6, as a function of $P^{3/5}N^{9/5}$, the expected scaling form (see Eq. (19)). The line drawn in Figure 6 is the result of linear regression, with an experimental slope of 0.99, in excellent agreement with the expected value of unity.

Montfort, Marin and Monge [23] have measured viscosity in a number of polystyrene blends, where the short chains are unentangled and the long chains are entangled ($\phi > \phi_e$). They report viscosity as a function of concentration for two blend systems. One has $P = 4$ and $N = 220$, with $0.4 \leq \phi \leq 1$. The second system has $P = 17$ and $N = 1800$, with $0.05 \leq \phi \leq 1$. Both blends thus have $N > P^2$, but also are at high enough concentration that excluded volume is fully screened ($\phi > \phi_0$). The data of [23] are plotted in Figure 7. Linear regression applied to each data set resulted in the lines in Figure 7, with $\eta \sim \phi^{3.31}$ for the $P = 4$ system, and $\eta \sim \phi^{3.61}$ for the $P = 17$ system. Both are in excellent agreement with the prediction (Eq. (31), $\eta \sim \phi^{11/3}$). Note that the separation between the two lines in Figure 7 is better described by $N^{3.3}$ than by the $N^3$ reptation prediction of equation (31) for the usual reasons (additional modes of relaxation in the standard tube model [7]). The recoverable compliance $J_e^0$ measured in [23] should scale as the reciprocal of the terminal modulus $G$ ($J_e^0 \sim \phi^{-7/3}$, Eq. (26)). Experimentally the agreement is not so good for $J_e^0$ as [23] reports $J_e^0 \sim \phi^{-1.95}$, and thus their relaxation time $\eta J_e^0$ also has a slightly stronger concentration dependence than predicted (Eq. (29)). The reasons for these discrepancies are not clear, but we do note that viscosity is the easier quantity to measure.

One complication with blends containing a component so short that it is unentangled, is that the glass transition depends on short chain length. This enters into our predictions by

Fig. 6. — Relaxation time of dilute long polystyrene chains in unentangled short polystyrene chains (data of Watanabe, Sakamoto and Kotaka [22]) plotted in the scaling form of equation (19). The linear regression line has slope 0.99 (unity is predicted by Eq. (19)).
changing the friction coefficient of a monomer $\zeta$ (in Eqs. (16–25) and (28–31)). Both [22] and [23] corrected for changes in the friction coefficient in standard ways [20].

Unfortunately, we are not aware of any data to test the other predictions presented here for the dynamics of long chains in short unentangled chains. This system is of particular interest because it allows us to test current ideas about hydrodynamic screening. We have assumed the standard idea that hydrodynamics are screened at the same length scale as excluded volume. The assumption is not at all obvious even for simple solutions of polymers in a monomer-sized good solvent. In a semidilute solution in good solvent, hydrodynamics are assumed to control relaxation on all length scales smaller than the screening length because, as de Gennes asserts [4], inside the screening length the chain behaves as if it were in dilute solution.

In the blends considered here, when $N > P^2 > 1$, the long chain adopts a random walk on its smallest length scales (up to the $P$-blob size $\xi_P \approx bP$). When the long chains are dilute, the chain is predicted to relax by Rouse motion on length scales smaller than $\xi_P$, where both excluded volume and hydrodynamics are assumed to be completely screened. Thus the high frequency (or short time) viscoelastic response in dilute solution (see Fig. 5) should be qualitatively different from theresponse of the same long chain in a dilute solution in good solvent. These two cases should be compared with careful high frequency viscoelastic measurements, such as oscillatory flow birefringence. A dilute chain in a marginal solvent also has random walk statistics on its smallest length scales (inside the thermal blob [4,17]) but we assume hydrodynamic interaction controls the relaxation inside the thermal blob (with $G(t) \sim t^{-2/3}$). The difference between the two cases is strictly a solvent effect. Unentangled short chains are assumed to interfere with the hydrodynamic interaction of monomers on the long chains up to the size of the $P$-blobs (i.e., a section of $P^2$ monomers), whereas monomer-sized solvent does not interfere at any scale.

The predictions for dynamics when the long chains overlap and are partially swollen by the short chains ($\phi^* < \phi < \phi_0$) are even less intuitive. Hydrodynamic interactions are only important on intermediate length scales (for $\xi_P < r < \xi$). The screening of hydrodynamic interactions has consequences on the terminal dynamics of the long chains (whether they are
unentangled or entangled with each other). Thus measurements of terminal response in blends of short unentangled chains and long chains, where the long chains are semidilute, would be very valuable for testing our current notions about hydrodynamic screening.

8. Conclusions

We have extended dynamic scaling to the case of binary blends of long chains in short unentangled chains. Using the standard assumption for linear chains, that hydrodynamic screening occurs at the same length scale as the screening of excluded volume, we predict the dynamics of the long chains. Recent work by Rubinstein [24] indicates that the coincidence of dynamic and static crossovers is only true for fractals with Gaussian (screened) fractal dimension of 2 (such as linear polymers). For more general fractals, the crossovers are decoupled.

The particular class of blends studied here can be used to test our assumptions regarding hydrodynamic screening. One such test would come from comparing the relaxation mode spectra of a dilute long chain in unentangled short chains (with $N > P^2$) and in monomerized solvent. We expect qualitative differences in these mode spectra, as described above in the discussion section, with a change in slope at the time scale where hydrodynamics are no longer screened (see Fig. 5). There are also differences in the terminal response of the long chains when they are semidilute. For example, the diffusion coefficient in the unentangled semidilute case should decrease as the short chain length increases as $D \sim P^{-1/2}$ (see Eq. (24)). We hope that this work will provide motivation for such experiments.

Acknowledgments

I thank M. Daoud, M. Landry and particularly M. Rubinstein for helpful discussions.

References

[18] The fact that the hydrodynamic crossover occurs as $N = P^2$ can be seen by matching the Rouse friction of the chain ($\zeta N$) with the Zimm friction of the chain ($\eta_R \sim \zeta P^{4/5} N^{3/5}$), which are equal at $N = P^2$.