Concentration-induced growth of polymerlike micelles

Yannick Rouault

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

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The present simulation shows the change of the static properties of wormlike micelles at high volume fraction ϕ. The analytically predicted nonalgebraic dependence of the mean contour length $\langle L \rangle$ of the wormlike micelles at high ϕ is observed. This confirms experimental results giving a higher apparent growth of $\langle L \rangle$ with ϕ when using a power-law dependence. Moreover, the molecular weight distribution is changed according to experimental observation and takes the form $C(L) \sim L^{-2\sigma} \exp(-L/\langle L \rangle)$. The value of $\sigma = 0.28$ found in the present work is in very good agreement with the experimental one, $\sigma = 0.25$. [S1063-651X(98)02111-4]

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The mean contour length of living polymer is a function, among other parameters, of the concentration [1]. Until now, this dependence has always been given in the form of a scaling law,

$$\langle L \rangle \sim \phi^{\alpha} e^{(E/2KT)}, \tag{1}$$

with E the energy gained for the creation of a bond.

The chain length distribution [or molecular weight distribution (MWD)], in the mean field theory, is given by

$$c(L,T) = \exp\left[-\left(\frac{E}{k_B T} \right) \right] \exp\left(-\frac{L}{\langle L \rangle} \right). \tag{2}$$

Experimentally, the exponent α takes values ranging from 0 to 1.3 [1]. Theoretically, an exponent of $\alpha = 0.5$ is predicted in the mean field theory. Some developments using scaling arguments slightly increase the value to $\alpha \sim 0.6$ [2]. Conformation space renormalization theory predicts that α should change from $\frac{7}{16}$ in dilute to $\frac{9}{16}$ in semidilute solution [3]. The predictions using renormalization-group techniques depend, however, theoretically on the chain length, the chains feeling excluded volume interactions differently as a function of their size [4], which is a real problem for the analytical study of this polydisperse system. The value of $\alpha > 0.6$ and $\alpha < \frac{7}{16}$ are explained by the presence of nonscreened electrostatic interactions [5,6]. Values of α above 0.6 have also been observed experimentally in the absence of electrostatic interactions [7] and are more difficult to explain.

It has been argued that the dependence of $\langle L \rangle$ on ϕ should not be a simple scaling law with a different value of α depending on the regime. In the presence of an excluded volume interaction, Eq. (1) may in fact take the form [8]

$$\langle L \rangle \sim \phi^{\alpha} e^{(E+\kappa\phi)/2KT} \tag{3}$$

in the concentrated regime, κ being a constant. Hence, the apparent greater value of α could come from a non-power-law distribution like the exponential one in Eq. (3).

Meanwhile, a molecular-dynamics simulation, made only at three different concentrations, shows also a non-power-law pronounced increase of the mean contour length [9] with concentration. The apparent stronger dependence of $\langle L \rangle$ on ϕ

appears at high density where the chains should feel a decreasing effect of the persistence length because of their increased mean contour length.

The MWD is not directly available experimentally. It has been shown by computer simulation that the distribution takes the Schultz-Zimm form $L^{\gamma-1} \exp(-L/\langle L \rangle)$ in the semidilute regime with γ the critical "enrichment" exponent relating the self-avoiding walk (SAW) to its configurational entropy [10]. Indirect experimental measurements have given a surprising result:

$$C(L,T) \sim L^{-2\sigma} \exp(-L/\langle L \rangle) \tag{4}$$

with $\sigma \sim 0.25$. This distribution can be understood in analogy with percolation clusters [11]. In the present work, we will show that the simulation at very high volume fraction of monomers lead to a result compatible with $\alpha > 0.6$ and the distribution Eq. (4).

Using a three-dimensional Monte Carlo simulation on a lattice, the mean contour lengths $\langle L \rangle$ and the mean square end to end distance $\langle R^2 \rangle$ were measured over a large range of concentration. The reptation algorithm was used with a breaking and binding algorithm [10,12] and is known to be in this case fully ergodic [13]. The details of the computational procedure can be found in [10]. The use of the simple lattice model [10,14] instead of the bond fluctuation model [12] (BFM) in the present case is particularly important. The BFM model is known to describe correctly the static and dynamic properties for a monodisperse melt. However, the binding process with different bond length seems at very high concentration to generate crossing chains configurations in a living polymer system [15]. This effect is strongly marginal and negligible in most of the simulation carried out [12,15]. In the present case, it will, however, be significant. It enlarges artificially the phase space leading to a possible decrease of the effective excluded volume interaction at high volume fraction of monomers.

Figures 1 and 2 present the variation of $\langle L \rangle$ with ϕ for two different domains of concentration and two values of the bond energy. In Fig. 1, for both values of E, the dependence of $\langle L \rangle$ on ϕ is presented on a log-log plot. For $0.08 < \phi < 0.7$ the slope of the curve leads to the expected exponent in the semidilute regime $\alpha = 0.6$. In Fig. 2, the plot is on a linear scale for both $\langle L \rangle$ and ϕ. The curves, when fitted by
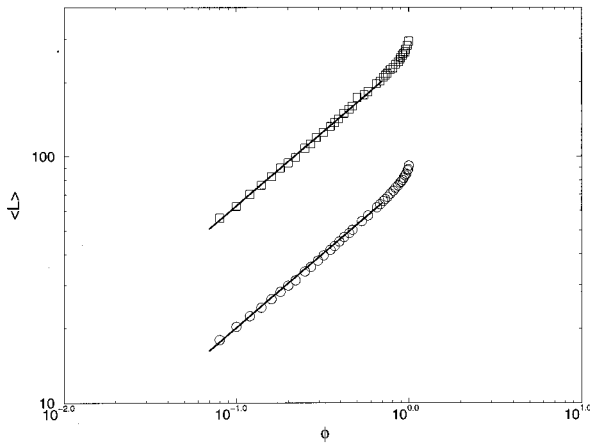
FIG. 1. Log-log plot of $\langle L \rangle$ vs ϕ. $E/k_BT = 7.5$ (circles), $E/k_BT = 10$ (diamonds).

Eq. (1), lead to a value of $\alpha = 1$ for the domain $0.7 \lesssim \phi \lesssim 1$. However, finite-size effects might be responsible for this behavior. In the present case, two kinds of finite-size effects are possible. The first one is the limited amount of monomers. This effect was mentioned in [12] where the empirical rule $P = \langle L \rangle / N < 0.1$ was chosen, N being the total amount of monomers in the system. A more accurate study of this size effect has been done in [15]. The relevant parameter is the evolution of the order parameter P as a function of the mean interchain distance $H = (\langle L \rangle / \phi)^{1/3}$. In Fig. 3, the curve P versus H is plotted for both values of E and shows that no finite-size effects are present in the system ($P \ll 1$) the lower values of P being obtained in each case for the densest system.

The second possible finite-size effect is due to the simulation box size. In this last case the very great chains may be cut off and the mean contour length $\langle L \rangle$ is reduced [16]. This finite-size effect acts against the growth of the chain with ϕ and can only limit the observed trend.

Once these important points have been checked, it seems that the observed enormous growth dependence on ϕ is not an artefact. To try to understand the origin of this unexpected behavior, the plot of $u = \langle R^2 \rangle / R_0^2$ versus $v = (\langle R_0 \rangle / H)^3$ is drawn in Fig. 4.
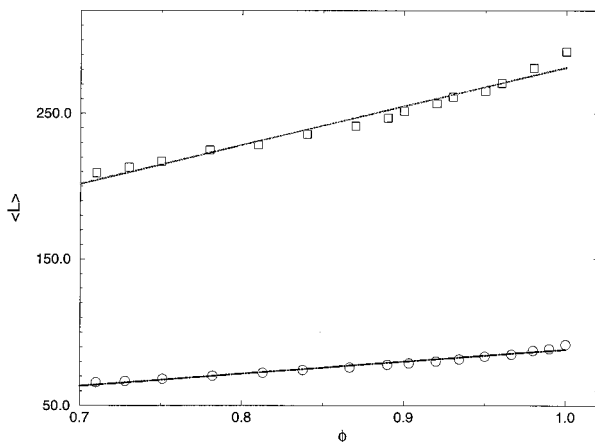

FIG. 2. Linear plot of $\langle L \rangle$ vs ϕ. $E/k_BT = 7.5$ (circles), $E/k_BT = 10$ (squares). The fits of the curves using Eq. (1) with $\alpha = 1$ or Eq. (3) are indistinguishable.

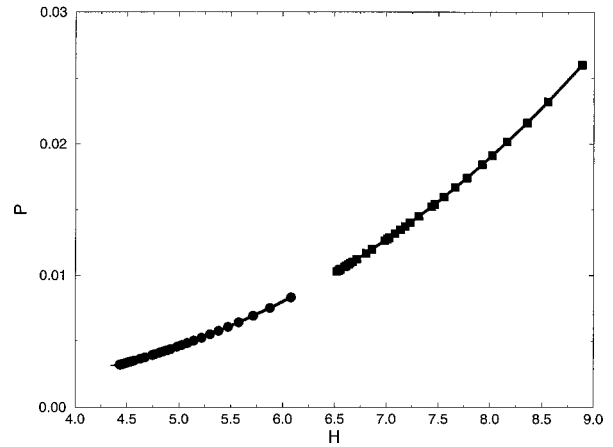FIG. 3. Plot of the order parameter P vs H. $E/k_BT = 7.5$ (circles), $E/k_BT = 10$ (squares).

Here, $R_0 = \langle L \rangle^v$ ($v = 0.588$) is the radius of the swollen dilute chain of length $\langle L \rangle$ and $v \sim (\phi/\phi^*)$ where ϕ^* is the overlap concentration. In the semidilute regime, $u \sim v^{-0.23}$ is expected both for living and dead polymers [15].

For a value of v above 10, the asymptotic regime is reached and u indeed scales with v at the power -0.23 as shown by the log plot of Fig. 4. It seems that also at very high concentration, for the simulation made at $\phi > 0.9$, the scaling still holds, although it is known that it is no more valid at very high concentration [17] for dead polymers. This can be understood as a swelling of the greater chains by the smaller chains. In the mean field approximation, it is shown that a chain of length N in a melt is swollen by chains of length $M < N^{1/2}$.

A fit of the data with Eq. (3) is only good for $\phi > 0.7$ (Fig. 2) although the semidilute regime (see Fig. 4) is reached at a much lower value of ϕ. The fact that Eq. (3) is only valid for a high value of ϕ well above the semidilute regime was clearly predicted in [8] and the present simulation clearly validates this assumption. The value of $\kappa = 0.39 \pm 0.02$ obtained for the two different values of the bond energy E is the same and of the order of the value estimated in [8]. The linear fit and the fit using Eq. (3) are indistinguishable in Fig. 2. It can be shown using a development of Eq. (3) in the limit $\phi \to 1$ that the quadratic term of the development is very
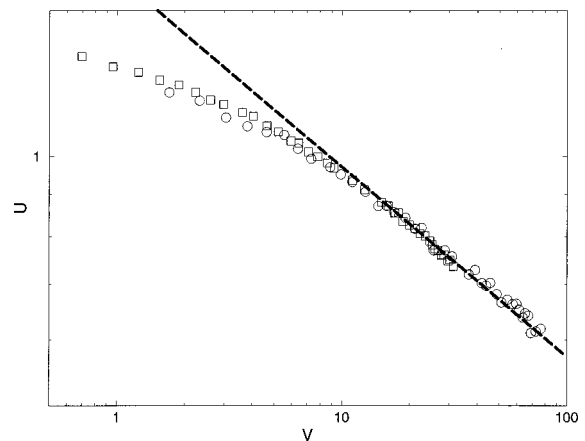

FIG. 4. Scaling of u vs v. $E/k_BT = 7.5$ (squares), $E/k_BT = 10$ (circles).

small with the numerical value of κ found, explaining that the linear growth of $\langle L \rangle$ with ϕ is a very good approximation.

Hence, it is not ruled out that the observation of an exponent $\alpha \gtrsim 0.6$ in absence of electrostatic interactions is due to the polydispersity and the swelling of the greater chains by the smaller. The important point is that in this highly polydisperse system, the chains are swollen, even at very high concentration and excluded volume interactions are always present. This situation is very different from that of the monodisperse system case where the screening of the excluded volume interaction takes place at high concentration. It is not ruled out that the increase in density could favor the excluded volume interaction in the system, since longer chains are built in this case which, according to [4], must even feel a stronger excluded volume interaction than smaller one. Hence, a nontrivial balance between the screening of the interaction due to the increase in density and the swelling of the longer chain by the smaller should take place, the latter effect depending on the chain contour length [4]. Strictly speaking, it is not clear to what extent Eq. (3) is or is not correct [18]. It is a crude approximation based on the DeGennes picture of a large chain in a monodisperse melt of smaller (Gaussian) chains. Nevertheless, it seems that the prediction given in [8] holds also for swollen chains.

Figure 5 shows the chain size distribution for $\phi = 0.99$. The curve fitted with Eq. (4) leads to an exponent of σ
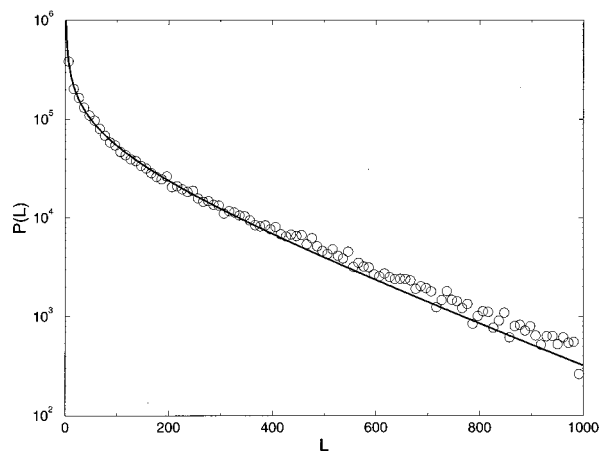

FIG. 5. MWD at $\phi = 0.99$ and $E/k_B T = 10$.

$= 0.28$ in excellent agreement with the experimental value of 0.25. Note that the value of σ is here derived through the MWD, a static property, independent of the dynamic of the chain [11]. It seems that an enormous growth with concentration is coupled with the apparition of a percolation-cluster-like distribution of the chain length.

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