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Steady-state Properties and Dynamic Behavior of Polymer Chains in Dilute Solution under Elongational Flow

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SUMMARY: The behavior of polymer chains in dilute solution under a steady, homogeneous elongational flow has been studied employing Brownian dynamics simulation. We first consider the dependence of polymer properties in steady state on the elongational rate, ε. When this rate exceeds some critical value, ε_c, the properties show a dramatic change from the values typical of the coil state to those of a stretched conformation. We describe the dependence of ε_c on chain length for different polymer/solvent conditions. Following the trajectories of individual molecules, we have characterized dynamic aspects of the coil-stretch transition. Each chain suffer the transition after some time, t_{trans}, has elapsed after the flow start-up. The values of t_{trans} vary remarkably from one molecule to another, and we have characterized the statistical distribution of this quantity. We also determine the kinetics of the coil-to-stretch process, which seems to follow a first-order kinetics after some induction time. The dependence of the statistical and kinetic parameters on chain length and elongational rate has been determined.

Introduction

When dilute solutions of flexible-chain polymers are subjected to flow of elongational type, whose strain rate, ε, exceeds a critical value, ε_c, the macromolecular coils stretch (*). This coil-stretch transition was theoretically predicted by DeGennes[1], and can be observed experimentally [2,3] using opposed-jets devices. The uniaxial, extensional flow so produced has the velocity field given by

$$v_x = \varepsilon x \quad , \quad v_y = -(\varepsilon/2)\, y \quad , \quad v_z = -(\varepsilon/2)\, z \qquad (1)$$

(*) The elongational rate is denoted as epsilon-dot. For typographical reasons, we simply write epsilon, ε.

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This flow has a stagnation point at the origin, and it can be assumed that the polymer chains experience a constant (in time and space) ε during a sufficiently long time.

In our work we simulate the behavior of polymer chains in dilute solution, representing the macromolecules as bead-and-spring models, including finite extensibility (FENE springs) and excluded volume, i.e., polymer-solvent interactions, by means of adequate intramolecular potentials. The behavior of the polymer chains is studied using the Brownian dynamics simulation algorithm developed in our laboratory [4)]. For computer calculations and for presentation of intermediate results, reduced, dimensionless quantities are useful. We employ dimensionless rates, $\varepsilon^*=\varepsilon\xi b^2/kT$, and dimensionless times, $t^*=t\, kT/\xi b^2$, where ξ and b are the friction coefficient and the root mean square end-to-end distance of the springs (subchains).

The characterization of this phenomenon can be done from two points of view. First, in a static view we consider the values of polymer properties in steady state. Here we will summarize the findings of a recent study of steady state properties [5)]. There is a second, dynamic view, which regards the response of individual polymer molecules, and we shall present here novel results from this alternative approach.

Steady-state Behavior

Macromolecular chains were subjected to elongational flow of constant rate of strain, during enough time in order to reach the steady-state. Then averages of the properties along the trajectory were calculated. This procedure was repeated for several values of ε. An example of the dependence of steady-state properties on the applied ε is given in Fig. 1., which illustrates the 'static' nature of the coil-stretch transition.

The critical value of the elongational rate, ε^*_c, is the same for FENE chains and for infinitely extensible Gaussian chains, which indicates that it is related to the properties of the macromolecule in its coiled state. Also, ε^*_c is the same for ideal chains as for chains with excluded-volume interactions that represent good solvent conditions. This critical rate is found to depend on chain length according to a power law, $\varepsilon^*_c \propto N^a$ (N is the number of beads in the model), or equivalently, $\varepsilon_c \propto M^a$ (M is molecular weight), with an exponent $a \approx -1.5$, and this value is the same for ideal chains (theta conditions) as for EV chains (good solvents). This conclusion adds a contribution to an existing controversy between authors (see for instance ref.[6]) who state that a is different in good solvents ($a \approx -1.8$) and others authors (see for instance ref.[7]) who find the same value ($a \approx -1.5$) in both theta and good solvents. Our results support the latter hypothesis.

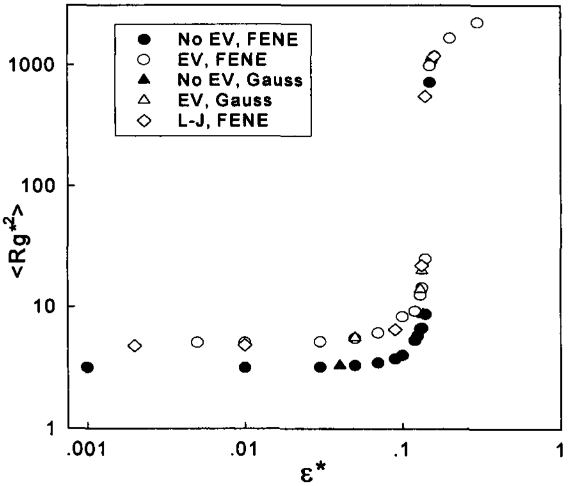

Fig. 1: Dimensionless mean square radius of gyration $<Rg^{*2}>$ vs dimensionless elongational rate ε^* for chains of N=20 with HI. The critical value is approx. ε^*_c=0.133.

The scaling law for the chain-length dependence of ε_c can be combined with those of other polymer properties in theta solvents, expressing compound quantities that are dimensionless and adopt universal values. A commonly expressed combination is that of ε_c with the longest relaxation time, τ_1, in the form of the product $\varepsilon_c\tau_1$. There are other possible combinations, involving the intrinsic viscosity, $[\eta]$, or the mean square radius of gyration, $<Rg^2>$, for which the definitions and our numerical value are:

$$\varepsilon_c \tau_1 = 0.50 \tag{2}$$

$$\nu_c = \varepsilon_c M [\eta]\eta_s / (N_A k T) = 1.01 \tag{3}$$

$$K_{\varepsilon R} = N_A k T / (\eta_s <Rg^2>^{3/2} \varepsilon_c) = 3.6 \times 10^{24} \tag{4}$$

The numerical values were obtained from our simulations, which considered the fluctuating, conformation-dependent nature of hydrodynamic interactions, so improving on previous treatments in which hydrodynamic interaction was considered in an approximate manner. Eqs. (2)-(4) can be used to predict ε_c from values of other, simple solution properties.

Dynamic Aspects

In another series of computer experiments, trajectories followed by individual molecules, were monitored after the start-up of an elongational flow. Chains suddenly change from the initial, coiled state to the stretched conformation, when some transition time, t_{trans}, has elapsed from the flow start-up. This is illustrated in Fig.2, where we note the essential aspect of this experiment: there is a great variability, from one molecule to another, in the t_{trans} values. This is the essential feature of the 'dynamic' view of the coil-stretch transition, and it has been indeed experimentally demonstrated$^{3)}$, and interpreted assuming that the kinetics of unravelling of the polymer chain depends on the intricacy of the initial coil conformation.

We have analysed the statistical distribution of t_{trans} values. A simple statistical parameter is $<t_{trans}>$, the average over a sample of chains. From results obtained for chains of different length, N, and with different ε, we have noticed that $<t_{trans}*>$ values plotted vs. $(\varepsilon^* - \varepsilon^*_c)$ follow the same universal curve with different N. In a log-log plot, the dependency is linear with slope -1. This suggest an universal law (valid for any chain length):

$$<t^*_{trans}> = Q (\varepsilon^* - \varepsilon^*_c)^{-1} \tag{5}$$

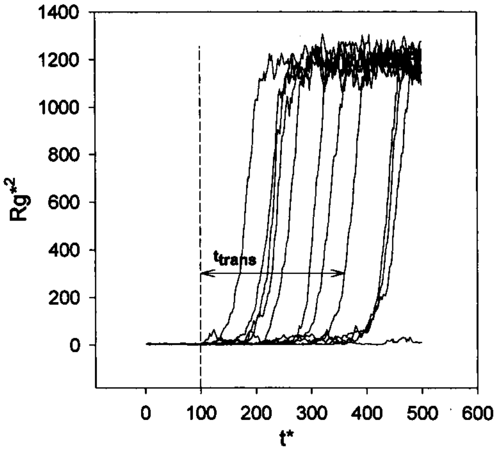

Fig. 2: Time evolution of the square radius of gyration of individual chains. Initial conformations are generated in the absence of flow (N=20, FENE (b_{max}*=10.), HI, noEV). The start-up of elongational flow occurs at t*=100. After some time, t_{trans}, has elapsed the individual chains suddenly experience the 'dynamic' coil-stretch transition. Note the variability of the t_{trans} values.

where the fitted value of the constant is $Q \approx 3.23 \pm 0.04$. The whole distribution function $p(t_{trans})$ can be obtained from the simulated values. The resulting histogram has the shape of an asymmetric bell, as illustrated in Fig. 3A.

From the simulations, we can quantify the kinetics of the coil-stretch transition in terms of the fraction of initial chains that remain in the coil state after a time t has elapsed, c(t). This is simply related to the distribution function $p(t_{trans})$ as

$$c(t) = \int_0^t p(t_{trans})\, dt_{trans} \qquad (6)$$

The aspect of the c(t) data, shown in Fig. 3B reveals two interesting features. First, during some, appreciably long time all the chains remain in the coil state and $c(t) \approx 1$. Then at longer times c(t) decays in an approximately exponential form, as revealed by a semilog plot of c(t) (Fig. 3B). This suggests that the coil-stretch transition can be regarded as a two-state process, C --> S, that has a kinetics similar to that of first-order chemical reaction, with the added peculiarity of an induction time, t_{ind}. Thus the kinetics could be described by the simple scheme:

$$c(t) = 1 \qquad \text{if } t < t_{ind}$$
$$c(t) = \exp[-k_{cs}(t - t_{ind})] \qquad \text{if } t > t_{ind} \qquad (7)$$

The previous finding that data for different values of N and ε are clustered when plotted vs. $t(\varepsilon\text{-}\varepsilon_c)$ is also found for the $p(t_{trans})$ and $c(t)$ functions, as seen in Fig. 3. Of the two parameters of the simplified kinetics, Eq. 7, one of them, namely t_{ind} seems to be universal when time is expressed in that way; we find $t_{ind}(\varepsilon\text{-}\varepsilon_c) = 2.22 \pm 0.15$.

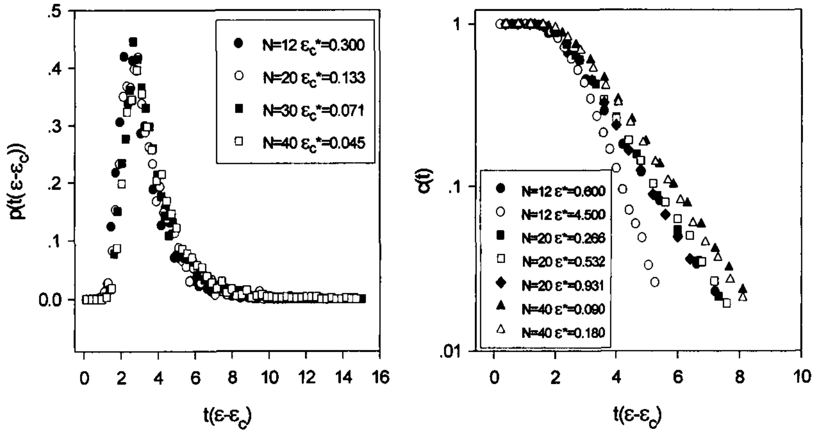

Fig. 3: (A) Histogram of the distribution function, $p(t_{trans})$, plotted vs. the compound quantity $t(\varepsilon\text{-}\varepsilon_c)$. Curves for various N and different ε_c appear to be nearly superimposed, although the small differences are statistically significant (B) Time dependence of the fraction of chains, c(t), that remain in the coil state, showing the apparent induction time and the first-order kinetics.

The first-order kinetic rate constant for the C-->S transition shows a more complex dependence on ε and N. For the analysis of the simulation results, we assumed an expression of the type $k^*_{cs}=C(\varepsilon^*\text{-}\varepsilon^*_c)^{a_\varepsilon} N^{a_N}$. A regression analysis of k^*_{cs} vs. $(\varepsilon^*\text{-}\varepsilon^*_c)$ gives $a_\varepsilon = 1.25 \pm 0.05$, and a further analysis in terms of N yields $a_N = 0.33 \pm 0.02$. The results from the dimensionless quantities can be put in terms of physical quantities if the exponents obey the relationship $a_\varepsilon = 1+2\,a_N/3$. This is satisfied by the pair of values $a_N \approx 0.33 \approx 1/3$ and $a_\varepsilon \approx 1.22 \approx 11/9$. Then, the empirical relationship for the dimensionless quantities can be transformed into a simple relationship obeyed by the physical quantities: $k_{cs} = \mathit{const}(\varepsilon\text{-}\varepsilon_c)^{a_\varepsilon}\,\varepsilon_c^{\,1-a_\varepsilon}$, where *const* = 0.60 ± 0.07. This gives predicted k_{cs} values whose deviation from the simulation results is of the order of 10%.

Sumarizing, the main results of our analysis are:

$$\langle t_{trans} \rangle = (3.23 \pm 0.04)\,(\varepsilon - \varepsilon_c)^{-1} \tag{8}$$

$$t_{ind} = (2.22 \pm 0.15)\,(\varepsilon - \varepsilon_c)^{-1} \tag{9}$$

$$k_{cs} = (0.60 \pm 0.07)\,(\varepsilon\text{-}\varepsilon_c)^{1.22}\,\varepsilon_c^{-0.22} \tag{10}$$

which are valid for a wide range of chain lengths and elongational rates.

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