Section 13. Polymer viscoelasticity

Conformation and dynamics of star-branched flexible polymer chains in a flowing solution

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Abstract

When linear or star-branched polymer chains in dilute solution are subjected to extensional flow of adequate intensity, each chain in the sample experiences a coil-stretch transition. Using Brownian dynamics simulation, we have studied both static and dynamic aspects of this phenomenon. We have determined the power law that relates the critical extensional rate, \( \dot{\varepsilon}_c \), to the molecular weight of the chain. In the case of linear chains we have studied the distribution of transition times. If the accumulated strain is used to characterize the flow effect as seemingly universal behavior, independent of molecular weight is found. The molecular individualism is related to the excess of the applied extensional rate over its critical value, which will determine the transition time and other features of the coil-stretch transition.

1. Introduction

When dilute solutions of flexible polymers are subjected to extensional flow, the macromolecular chains remain in their coil state until the extensional flow rate, \( \dot{\varepsilon} \), reaches a certain critical value, \( \dot{\varepsilon}_c \), and chains are suddenly stretched. This phenomenon is known as coil-stretch transition [1]. From a steady-state point of view the transition is seen as an abrupt change in the dependence of steady-state values of the properties of a sample of molecules on \( \dot{\varepsilon} \). In a previous work [2], we used the Brownian dynamics (BD) simulation technique to study the coil-stretch transition of flexible linear polymers from this point of view. In this work we study the steady-state behavior of star-branched polymers subjected to extensional flow.

Another point of view of the coil-stretch transition is that in which one regards the time-evolution of the individual chains in the flow when \( \dot{\varepsilon} > \dot{\varepsilon}_c \). BD simulation of multi-bead chains has been an adequate tool to explore this aspect of the coil-stretch transition (see [3–7] as examples of very recent works). Recently and using new experimental techniques Perkins et al. [8,9] have been able to visualize the evolution of individual DNA molecules in extensional flow. The picture that emerges from experiments and simulations is that of a molecular individualism [10]: each chain of a homogeneous sample experiences the coil-stretch...
transition following a different dynamics and may reach a particular final conformation [9,11]. A primary aspect of the molecular individualism is that different chains in the solution undergo the transition at different times. After the inception of the flow, each individual chain remains in the coil state for some time, $t_{\text{trans}}$, after which the transition takes place in a practically instantaneous manner. In the present work we present an analysis of these $t_{\text{trans}}$ for linear chains and we show some preliminary results concerning the molecular individualism of star-branched polymers.

2. Methodology

We consider a dilute solution of linear or star-branched polymers in steady, homogeneous, uniaxial extensional flow with a velocity field given by

$$v_x = -\frac{1}{2} \dot{\varepsilon} x; \quad v_y = -\frac{1}{2} \dot{\varepsilon} y; \quad v_z = \dot{\varepsilon} z,$$

which is an adequate idealization of that produced by the opposed-jet device used in some experimental works [12].

Star-branched polymers were modeled as bead-and-spring chains with $N$ beads and $N - 1$ FENE (finitely extensible non-linear elastic) springs. We use the Warner approximation to the inverse Langevin function [13] for the spring force law.

Star-branched polymers are formed by $F$ arms, of $N_{\text{arm}}$ beads each, linked to a central bead. Thus, $N = FN_{\text{arm}} + 1$ for stars. The number of arms, $F$, is called the functionality of the chain. When excluded-volume (EV) effects are considered, interactions between non-neighboring beads are modeled using a Lennard-Jones (LJ) potential, with both attractive and repulsive terms. Details on the parameterization can be found in Refs. [2,14,15].

The macromolecular property evaluated to monitor the coil-stretch transition was the square radius of gyration, $s^2$. In case of star chains also the core-end distance for every arm (end-to-end arm distance) of the star was computed. As an operational criterion, we consider that the transition occurs when the square radius of gyration reaches the mean point, in a logarithmic scale between the coil and stretch limits:

$$\ln(s^2) = \frac{\ln(s_{\text{max}}^2) + \ln(s_0^2)}{2}.$$  \hspace{1cm} (2)

The brackets $\langle \rangle$ indicate average quantity. The value of $s_{\text{max}}^2$ for star chains is calculated as that of a linear chain with $N = 2N_{\text{arm}} + 1$ beads, because a fully stretched star will have its arms aligned along the flow direction at both sides of the core.

For the steady-state study, long molecular trajectories were generated at constant $\dot{\varepsilon}$. The first fifth of each trajectory was rejected to ensure that molecules reached the steady state. Steady-state properties were computed averaging over the remaining trajectory and over five of such trajectories. The critical extensional rate was taken as the minimum rate at which the criterion (2) holds.

In order to study the time evolution of individual linear chains, trajectories for a sufficiently large number of molecules (typically 2000) were generated at an extensional rate greater than the critical value. Fig. 1 displays the time-evolution of $s^2$ for a sample of linear chains with hydrodynamic interaction (HI) and no EV. When $s^2$ of the individual chain reaches the cross-over value in Eq. (2), the time $t_{\text{trans}}$ past the inception of the flow is registered. In this way we collected the $t_{\text{trans}}$ values.

![Fig. 1. Outcome of a typical computer experiment. Time-evolution of the square radius of gyration for 20 linear chains; $N = 20$, HI, No–EV (ideal chains). From $t' = 0$ to 100, $\dot{\varepsilon}' = 0.00$ and from $t' = 100$ to 500, $\dot{\varepsilon}' = 0.16 = 2\dot{\varepsilon}$.](image-url)
for all the molecules in the sample and carried out a statistical analysis of them. For the BD simulation, we employed the pseudo-second order, predictor-corrector algorithm of Iniesta and García de la Torre [16], including solvent flow. When fluctuating HI is taken into account, we used the Rotne–Prager–Yamakawa interaction tensor [17, 18] and a HI parameter $h^* = 0.25$. For the computational work and the presentation of results we use dimensionless quantities. Thus, time is written in reduced form as $t' = t/\zeta b^2/kT$, where $\zeta$ is the friction coefficient of the beads, and $b = (3kT/H)^{1/2}$ is the unit of length. In general, the simulation methodology is the same as in our previous paper [2], where more details about the algorithm and the parameters can be found. The time step in BD simulation was usually $\Delta t' = 10^{-3}$, except for LJ–EV chains, which require $\Delta t' = 10^{-4}$.

3. Results

3.1. Steady-state behavior

The steady-state behavior of linear chains was thoroughly studied in our previous work [2]. There we found that the power law that relates the critical extensional rate to the chain length, $N$, when HI is taken into account in a rigorous, fluctuating, manner is

$$\dot{\epsilon}_c = (14.1 \pm 1.1)N^{-1.55 \pm 0.03}. \quad (3)$$

Following the same methodology employed there we found an analogous power law for star-branched polymers. Fig. 2 shows the variation of $\langle s^2 \rangle$ with $\dot{\epsilon}$ for a star of $N = 49$ beads and $F = 6$ arms. An intramolecular potential of the LJ type was used to represent theta or good solvent conditions. As in the case of linear chains (Fig. 1 in [2]) it can be observed that there is a certain value of $\dot{\epsilon}$, the critical one, from which the steady-state value of the radius of gyration increases enormously respect to its value in a quiescent solution. Then, at high values of $\dot{\epsilon}$, the plot tend to reach a plateau, due to the finite extensibility of the springs used. In addition, only one coil-stretch transition is observed (the curve is unimodal). Also it is noted that at values of $\dot{\epsilon}$ greater than $\dot{\epsilon}_c$ the steady values of $\langle s^2 \rangle$ are the same for theta and good solvent conditions.

We determined and collected the values of $\dot{\epsilon}_c$ for star chains with different number of beads, $N$, and functionalities, $F$, taking into account fluctuating HI. We found, as appreciated in Fig. 3, that there is a clear dependence of the critical extensional rate on the number of beads per arm, $N_{arm}$ (i.e. on

![Fig. 2. Dimensionless mean square radius of gyration, $\langle s^2 \rangle^*$, vs. dimensionless extensional rate, $\dot{\epsilon}'$, for star chains of $N = 49$, $F = 6$ and HI. Intramolecular LJ potential is used to represent solvent conditions.](image)

![Fig. 3. Variation of the dimensionless critical extensional rate, $\dot{\epsilon}_c^*$, with the arm length, $N_{arm}$, for star chains of different type.](image)
the arm molecular weight), but not on the total molecular weight and the functionality,
\[ \dot{\varepsilon}_c = 4.7N_{\text{arm}}^{-1.5}. \]  

This power law is analogous to that found for linear polymers between \( \dot{\varepsilon}_c \) and the total polymer length, \( N \), (Eq. (3)).

In our previous work [2] we combined the value of \( \dot{\varepsilon}_c \) determined in our BD simulation with the longest relaxation time, \( \tau_1 \), obtained from BD simulations of electric birefringence decay [19], to get the dimensionless quantity
\[ \dot{\varepsilon}_c \tau_1 = 0.50. \]  

In an analogous way, we can combine the value of \( \dot{\varepsilon}_c \) with \( \tau_1 \) for star-branched polymers. According to Rey et al. [20], \( \tau'_1 = 0.26N_{\text{arm}}^{1.5} \). This \( \tau'_1 \) is the longest relaxation time related to dielectric relaxation. The longest relaxation time related to the birefringence and viscoelasticity will be \( \tau_1 = \tau'_1 / 2 = 0.13N_{\text{arm}}^{1.5} \). This leads to
\[ \dot{\varepsilon}_c \tau_1 = 0.6. \]  

It may be seen that this value is very close to 0.5. The discrepancy may be due to the short arm stars used in the work [20].

It is also interesting to note that, if expressed in terms of the longest linear sequence in the branched chain, i.e. \( 2N_{\text{arm}} \), the numerical factor in Eq. (4) becomes \( 4.7 \times 2^{1.55} \), very close to the constant 14.1 for linear chains.

3.2. Dynamic behavior

We will focus our analysis on flexible linear chains and take the mean transition time, \( \langle t_{\text{trans}} \rangle \), as a representative parameter of the sample evolution. Fig. 4 displays results for \( \langle t_{\text{trans}} \rangle \) of chains of various lengths, with and without HI. We find that, for extensional rates much larger than the critical values, \( \dot{\varepsilon} \gg \dot{\varepsilon}_c \), all the results merge and become independent of chain length and HI. When \( \dot{\varepsilon} \) tends to \( \dot{\varepsilon}_c \), each set of points approaches a vertical asymptote at \( \dot{\varepsilon}_c \): transition times become infinite at the critical extensional rate. If results are plotted versus the excess extensional rate, given by \( \dot{\varepsilon} - \dot{\varepsilon}_c \), all the points, with various \( N \)s, are described by a single function that can be deduced by least-squares fitting to a straight line in the log–log plot. Thus, we can write
\[ \langle t_{\text{trans}} \rangle = (3.23 \pm 0.04)(\dot{\varepsilon} - \dot{\varepsilon}_c)^{-1}. \]  

This result seems to be valid for any chain length, being in that sense universal.

When we study the time-evolution of individual star polymers in extensional flow, the situation is complex and rather interesting: molecular individualism appears not only for different chains of a sample, but also for the different arms of a same star chain. Fig. 5 shows how the core-end distance, along the flow direction, for every arm of a star of \( N = 49 \) and \( F = 6 \) evolves with time. It can be appreciated that every arm follows different stretching dynamics, experiencing the transition at a particular time. In the case displayed, three arms of the star (half of them) are stretched along one
side of the core and the other three along the opposite core side. A series of computer experiments revealed that the final arrangement of arms may vary from one chain to another, but the case of three arms on each side is the most frequent one. In such a case, it seems that the transition involves three pairs of arms, with the chain in each pair extending in opposite directions. This would be consistent with the possibility that the relevant moiety in the transition is the longest linear sequence in the star. This possibility will be investigated with detail in a further study.

4. Conclusions

Both linear and star-branched flexible polymers present a similar steady-state behavior when subjected to extensional flow. Both of them experience coil-stretch transition, i.e., there exists a critical value of the extensional rate, $\dot{e}_c$, from which the macromolecular properties increase enormously their values. Besides, in both cases there is a power law that relates the value of $\dot{e}_c$ with some characteristic molecular weight of the chain. They differ in that $\dot{e}_c$ of linear polymers scales with the total molecular weight, $N$, and $\dot{e}_c$ of star polymers scales with the molecular weight per arm, $N_{\text{arm}}$. Also the dimensionless quantity $\dot{\epsilon}_c \tau_1$ adopts a similar value for both topologies, around 0.5.

From a dynamic point of view, the time-evolution of a sample of linear flexible chains was studied using $\langle t_{\text{trans}} \rangle$ as representative of the distribution of transition times. If we denote $\dot{e}_c \equiv \dot{\epsilon}_t$ as the critical Hencky strain (as $\epsilon \equiv \dot{\epsilon}_t$ is the Hencky strain), then $(\dot{\epsilon} - \dot{\epsilon}_c) t \equiv \Delta \epsilon = \epsilon - \epsilon_c$ will be the excess (or overcritical) Hencky strain. Then, Eq. (7) suggests that the average value of the overcritical strain when the transition occurs adopts an universal value, independent of the chain length.

If we combine the result $\dot{\epsilon}_c \tau_1 = 0.50$ with Eq. (7), we get

$$\frac{\langle t_{\text{trans}} \rangle}{\tau_1} = (6.46 \pm 0.08) \left( \frac{\dot{\epsilon} - \dot{\epsilon}_c}{\dot{\epsilon}_c} \right)^{-1}$$

$$= (6.46 \pm 0.08) \frac{\epsilon_c}{\Delta \epsilon}.$$  \hspace{1cm} (8)

Some features of the coil-stretch transition will depend on the quantity $(\dot{\epsilon} - \dot{\epsilon}_c)/\dot{\epsilon}_c$. Thus, if $(\dot{\epsilon} - \dot{\epsilon}_c)/\dot{\epsilon}_c \ll 1$ (flow weakly overcritical), then $\langle t_{\text{trans}} \rangle \gg \tau_1$ and the time the molecules spend in their travel from the onset of the flow until they experience the the coil-stretch transition is much longer than their Brownian relaxation time. In this case fully stretched final conformations are expected. The opposite limit corresponds to strongly overcritical flows, i.e. $(\dot{\epsilon} - \dot{\epsilon}_c)/\dot{\epsilon}_c \gg 1$ and $\langle t_{\text{trans}} \rangle \ll \tau_1$. The transition occurs in a time much shorter than the Brownian relaxation time of the molecule, so that the final conformation will be determined essentially by the conformation of the chain when it begins to experience the flow, appearing metastable configurations: hairpins, kinks...

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References