Effects of Polymer Concentration and Molecular Weight on the Dynamics of Visco-Elasto-Capillary Breakup


aInstitut für Technische und Makromolekulare Chemie, Universität Hamburg, Germany
bDepartment of Mechanical Engineering, M.I.T., Cambridge, USA

ABSTRACT

Monitoring the coil-stretch transition of polymers in transient extensional flow fields provides a unique possibility to observe the stress distribution between polymer and solvent even for very dilute solutions (with sub-ppm concentrations). In this paper we will present recent investigations on the capillary break-up behavior of a series of polystyrene solutions with narrowly-distributed molecular weight that are progressively diluted in solvents with different viscosities. We show that there exists a critical dilution concentration below which the dominant stress resisting breakup is carried solely by the solvent. This observation is supported by numerical simulation of the stress evolution using a multimode FENE-P mode algorithm based on the one-dimensional analysis of Entov and Hinch for transient extensional flows. The influence of the molar mass as well as a molar mass distribution on the stress evolution and the critical dilution concentration is also discussed. Finally, we consider the influence of the chemical structure of more complex macromolecules on the transient extensional flow that arises in capillary break-up rheometers.

INTRODUCTION

The general definition of a dilute polymer solution refers to the critical overlap concentration $c^*$. It is generally accepted that for concentrations $c/c^* < O(1)$ the steric and frictional interactions of neighboring polymer coils are negligible and the rheological response of the fluid is solely governed by the hydrodynamical interactions of the isolated polymer coil and the solvent. However, this definition of diluteness is only applicable close to the equilibrium state of polymer coils. Especially in extensionally-dominated flow fields, the coil-stretch transition of a polymer coil leads to an increased interaction volume and therefore to polymer-polymer interactions even for concentrations of $c/c^* < O(1)$. The term “ultradilute” solution has been introduced recently to describe systems that remain truly dilute even when the polymer chains are in a highly stretched and deformed nonequilibrium state [1]. The Capillary Break-up Extensional Rheometer provides a convenient means for probing chain-chain interactions as a function of polymer concentration through measurements of the characteristic time-scale of the fluid in a strong extensional flow [2, 3].

However, in order to analyze the dynamics of the capillary break-up process it is necessary to answer the question of how much stress is carried by the polymer and how much by the solvent? In other words, under what physical conditions does a coil-stretch transition on the molecular scale occur and affect the resulting macroscopic fluid dynamics. This provides an effective distinction between a dilute ($c_e < c < c^*$) and an ultradilute ($c < c_e$) polymer solution?

Visco-elasto-capillary thinning and breakup of a fluid filament captures the naturally occurring transient extensional flow fields associated with jet break-up, drop formation and other free-surface deformations of complex fluids. Since the deformation rate is not constant in these surface-tension–driven flows, a satisfactory description of the occurrence of coil-stretch transition in this evolving flow field requires more than a simple definition of a critical concentration.

In this paper we present recent experimental investigations on a prototypical surface-tension-driven flow (visco-elasto-capillary thinning and breakup) of narrow distributed polystyrenes in dilute and ultradilute solutions. In addition, theoretical simulations of the stress evolution, using a FENE-PM chain algorithm, are utilized to determine the contribution of the polymer chains in different states of coil-stretch transition to the overall stress balance as a function of concentration and molecular weight.

RESULTS AND DISCUSSION

The transient uniaxial elongational flow resulting from capillary thinning of a viscoelastic liquid filament after the imposition of a rapid axial ‘step
strain’ is shown in Fig. 1 for an ideal elastic ‘Boger fluid’. After an initial period in which gravity and the solvent viscosity are important [4, 5], the dynamics are dominated by an exponential decay of the filament radius \( R_{\text{mid}} \) \[6\].

\[
R_{\text{mid}} = R_0 \left( \frac{\phi}{2} \right)^{1/3} \exp(-t/3\lambda)
\]  

(1)

with \( \phi \) being the elastocapillary number

\[
\phi = \lambda \sigma \left( \eta_p R_0 \right).
\]

(2)

Here \( \sigma \) is the surface tension, \( \eta_p = G/\lambda \) is the polymer contribution to the viscosity and \( \lambda \) is the characteristic relaxation time of the solution.

Numerous groups have used the prediction of eq.(1) to extract the characteristic relaxation time of viscoelastic polymer solutions from the slope of a semi-logarithmic plot of \( \ln(1/t) \). However, as we show in Figure 2, the initial ‘necking period’ in which the imposed capillary pressure \( \sigma/R \) is carried primarily by the solvent becomes progressively more important for increasingly dilute solutions. With progressive dilution of the initial viscoelastic fluid (\( c = 250 \text{ ppm; } c/c^* = 0.04 \)), the region of elastic thinning corresponding to eq.(2) – and therefore a linear decreasing radius in this semi-logarithmic plot of \( R_{\text{mid}}(t) \) – can no longer be observed at concentrations below 10 ppm. The filament dynamics show a necking failure that is increasingly like that observed in a viscous Newtonian fluid (as shown by the solid line in Figure 2). Upon first inspection this poses a quandary for CABER experiments, because Rouse-Zimm theory predicts that the relaxation time of a dilute solution is independent of polymer concentration.

\[
\frac{\sigma}{R} = 3\eta_p \dot{\varepsilon} + (\tau_{\text{ex}} - \tau_{\text{el}})
\]

(3)

in which the stretch rate is given by \( \dot{\varepsilon} = -2 \frac{d \ln R_{\text{mid}}(t)}{dt} \). The polymer contribution to the stress can be modeled using a multimode FENE-P model algorithm with the evolution equations (for \( i = 1, 2, \ldots, N_m \))

\[
\mathbf{A}_i = \frac{1}{\lambda} \left( \dot{f}_i \mathbf{A}_i - 1 \right), \quad f_i = \frac{1}{1 - n_i \tau A_i / L_i^2}
\]

(4)

here \( A_i \) is the ensemble average second moment tensor for the \( i \)th mode and the polymeric stress is given by

\[
(\tau_{\text{ex}} - \tau_{\text{el}}) = \sum_{i=1}^{N_m} n_k \tau f_i \left( A_{\text{ex},i} - A_{\text{el},i} \right).
\]

(5)

where \( n = c N_d / M_p \) is the number density of chains and \( k_B \) is Boltzmann’s constant. Results of the simulations for the experimental conditions in Fig. 2 are shown in Fig. 3 below and demonstrate good agreement with the experimental observations.

For dilute solutions, the simulations show that even for initially small contributions of elastic stresses, a fast crossover occurs from viscous to elastic stresses as the dominant contribution resisting the capillary stress driving the flow. This leads to constant extension rates \( \dot{\varepsilon} \approx 2/3\lambda \) in agreement with eq. (1).
However, for sufficiently low concentrations this crossover is not reached on the observable time frame prior to break up. Although the rate of chain unraveling (as measured by the time constant $\lambda$) may be independent of concentration, the polymeric contribution to the stress is not. Instead, it depends linearly on the concentration of chains and the magnitude of the polymeric stress is insufficient to modify the capillary breakup process.

The relative importance of elastic stresses in dilute polymer solutions undergoing elongational flows is determined by the elastocapillary number $\phi$ (Eq. (1)) and therefore by the ratio of the Deborah number $De$ to the Ohnesorge number $Oh$. As shown in Fig. 6, elastic effects in surface tension driven uniaxial flows are only dominant (and thus allow the relaxation time to be measured using the CaBER) when

$$De/Oh = \lambda \sigma/(\eta \tau_R) > 1$$

(6)

For each fluid, the minimum value of concentration or relaxation time that can be measured corresponds to $De/Oh \approx 1$. As expected, increasing the molecular weight results in a larger relaxation time and (at any fixed concentration) a slightly higher shear viscosity also. For all fluids, the relaxation time is found to be a power-law function of the concentration, even significantly below $c^*$. The physical origin of this phenomenon is not fully understood but must result from hydrodynamic interactions between the extended and overlapping macromolecules.

### REFERENCES