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Letter

Chain extension and degradation in convergent flow

Dear Sir

Recently, Nguyen and Kausch[1,2] reported some surprising experimental results concerning polymer degradation in a transient elongational flow through a converging channel. For example, even though the chain extensions were estimated to be much less than in a steady elongational flow, the macromolecules were found to rupture at smaller strain rates than those required for rupture in the latter. As Nguyen and Kausch remarked, such results cannot be reconciled with the conventional picture of polymer rupture. At the same time, their results were in full agreement with another, very specific, prediction of this picture, namely, that the macromolecules rupture in the middle.

A possible reason for such a paradoxical situation is a polymer-induced hydrodynamic instability of the converging flow. James and Saringer[3] observed such instabilities in similar channels; in some cases, the instability would appear almost as soon as the strain rates were high enough for the coil–stretch transition. The instability has its origin in the boundary-layer separation[4], which is soon followed by the appearance of a large-scale, unsteady vortex ring in the channel. If this happens, both the strain rate and the total strain can become much larger than their values in the undisturbed flow, used by Nguyen and Kausch[1,2].

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Reply

Dear Sir

We have read with great attention and interest the comments on our paper by Ryskin on 'Chain extension and degradation in convergent flow'[1]. It was reported that dilute polystyrene solutions are extensively degraded after a single passage through a narrow contraction whereas dozens of recirculations are required to achieve the same level of degradation in stagnant elongational flow[2,3]. Moreover, the frictional force at break in transient elongational flow, calculated from the slender body hydrodynamics, is orders of magnitude below the breaking strength of a covalent bond. Ryskin suggested that these paradoxical results could be explained if degradation stemmed from hydrodynamic instabilities induced by the presence of polymer in convergent sink flow. This type of turbulence has indeed been observed in our laboratory by means of flow visualization[4] and detected as random signal fluctuations during birefringence measurements[5]. Although degradation from turbulence is an interesting possibility and deserves due consideration in future investigations, recent experimental findings failed to corroborate the model. First, measurements by Hoagland and Price[6] revealed that chain scission in turbulent flow has a much weaker propensity for midchain scission than in transient elongational flow. Second, polymer-induced flow instabilities diminish with fluid strain rate, polymer molecular weight and polymer concentration. In the degradation experiments, highly dilute polystyrene solutions in the range of 5–10 ppm were always used. At these concentrations, no turbulence was detected, at least on the scale of a few tens of micrometres which has been investigated. Based on degradation and birefringence results, we would like to present an alternative explanation for the high degradation susceptibility reported in transient elongational flow. Birefringence measurements showed that in the birefringence zone in opposed jets flow is restricted to a narrow region along the symmetry axis and accounted for $<4\%$ of the total flow volume[3,4]. On the contrary, birefringence recorded in transient elongational flow filled out the immediate orifice surroundings completely. Since bond scission requires some straining of the molecular coils, it is plausible to assume that only the fraction of macromolecules which migrate through the birefringence zone could take part in the degradation process. Simple geometrical considerations showed that the degradation yield could reach $>95\%$ in transient elongational flow. The precision for midchain scission can be understood if the process of chain uncoiling can be described either by the 'yo-yo' model developed by Ryskin[7] or by the 'multiple blobs' model proposed by Brochard-Wyart for a tethered chain in 'strong' flow[8]. No satisfactory explanation could be offered for the low frictional force at break. It seems necessary at the present to rely on some rather vague hypotheses, i.e. that the kinetics of chain scission does not depend on the level of applied stress but on the total energy accumulated by the deforming polymer coil[3].

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