POLYMER PHYSICS

Molecular Individualism

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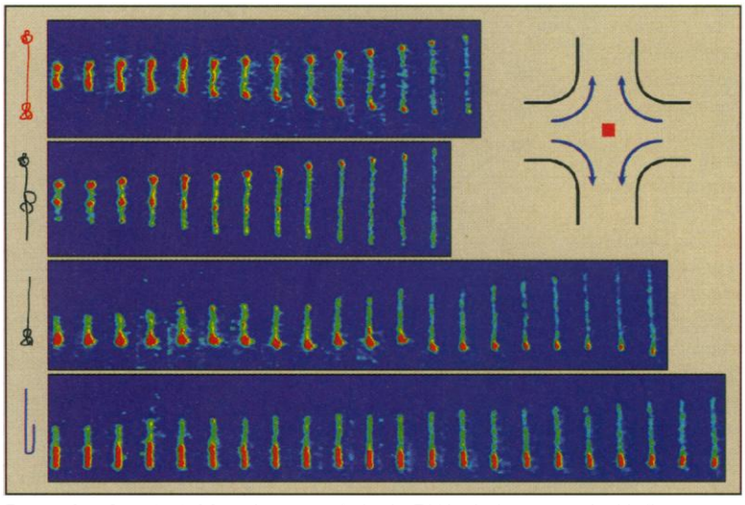
In 1922, Staudinger proved the existence of long chain molecules, but he saw them as rigid rods. It took another 20 years for Kuhn to show that most linear polymers are in fact flexible, and that the elasticity of rubber is a consequence of this flexibility. To check that an object is flexible, we pull on it and watch it deform. This is what Perkins *et al.* do on individual DNA molecules (*1*), as they report on page 2016 with their measurements of the elongation of single polymer chains.

Diffraction methods (neutrons, x-rays, and so forth) tell us about the size of a polymer coil, but not much about the shape. Another approach is to purposely deform the chain by imposing a nonuniform flow of solvent. The simplest setup is based on simple shear (between two parallel plates, one of which slides in its own plane). Here, at some moments, the chain is elongated, but it also rotates and contracts later. The overall effects of deformation are sizable (by mechanical measurements) but not huge. These effects were analyzed by Zimm and others (*2*) and confirmed by the experiments of Ferry (*3*) and others.

Another form of molecular torture is obtained in longitudinal shears [see the inset to figure 2B in (*1*)]. Here the chain is extended along one direction and squeezed along another axis. The effect is more dramatic. If we start from a coil, it elongates, offering more grip to the flow: This effect led some of us to expect a "coil stretch transition" above a certain threshold in shear rate.

In Bristol, Keller and co-workers did find a transition (*4*): They observed locally the birefringence of the solution, which is an optical measure of uniaxial alignment in the stretching direction. Beyond threshold, a birefringent streak shows up along the exit direction. The molecules that travel near this line have passed near the stagnation point and thus spend a long time in the cell; only the chains that have suffered long enough become very elongated.

The Bristol group also discovered that some of the chains break. The local stresses, due to the flow, on one chain unit are always weak, but they add up to large values along a stretched polymer. A good picture for this is a group of children divided in two teams: Each team pulls at one end of a thin rope. Although each child is relatively weak, the total tension at the midpoint may break the rope. Indeed, in the Bristol experiments, chain rupture occurs predominantly at the midpoint.



Scenarios for stretching. Images of single DNA chains tagged with fluorescent markers. The chains were observed at 0.13-s intervals as they were stretched in a flow gradient. Four different conformations are seen (from top to bottom): dumbbell, linked, half dumbbell, and folded. [From figure 2B of (*1*)]

These days, we can decorate a chain with fluorescent labels, and if it is long enough, it is then directly visible under a microscope. The group led by Chu at Stanford has used this technique to observe one distorted coil in longitudinal shear flows (*1*). They used a phage DNA molecule, which is long (21 μm in full extension), flexible at large scales, and precisely defined in length. They inserted these very dilute chains into a longitudinal shear cell, followed one of them, watched it distort, and counted the duration of the torture (t_{res}).

Here comes the surprise: Two chains that suffered the same length of time t_{res} may display completely different behaviors. Some chains elongate simply like a dumbbell (similar to the rope and the children): These chains extend quickly. Some others are folded like a hairpin along the stretching direction and elongate more slowly. There are many types, the most resilient being a globular coil (which may possibly be knotted on itself).

On the whole, we see here an unusual form of molecular individualism. A flexible chain at rest in its solvent changes its shape constantly because of Brownian motions of its various units; normally, the average coil shape is enough to describe many features. But not here.

The various "types" seen in the Stanford work give us a (distorted) image of what the chain looked like in its initial state. The image is probably a caricature; that is, a coil with a slightly protruding tail may become what Perkins *et al.* call a "half dumbbell" (see figure). But what exactly is the initial state? Is it a state at rest, or (possibly) a predeformed state under simple shear inside the inlet?

Longitudinal shear is not the only way to induce a strong deformation. In earlier papers, the Stanford group (and some others) observed a chain that was pulled at one end: A bead attached to the end was driven by optical tweezers. One feature may be common to many of these situations: the occurrence of "stems" and "flowers" (*5*). The chain portion near the pulling end is very extended (stem), whereas the other end is more open (flower); there can be a rather sharp boundary between the two. This concept may possibly apply also to longitudinal shear.

It must be stressed also that the distortion of long chains is not just a game. Many practical systems depend on polymers in strong flows: For example, polymer melts are extruded to produce plastics. Observing the deformations of one (decorated) synthetic chain in a sea of undecorated chains, under shear, may bring in other, important surprises.

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