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"Fall In!"

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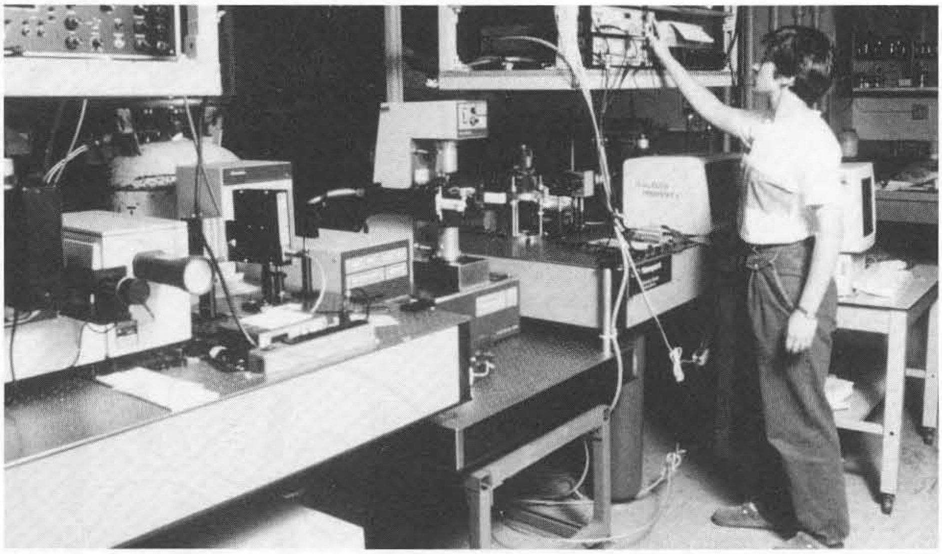
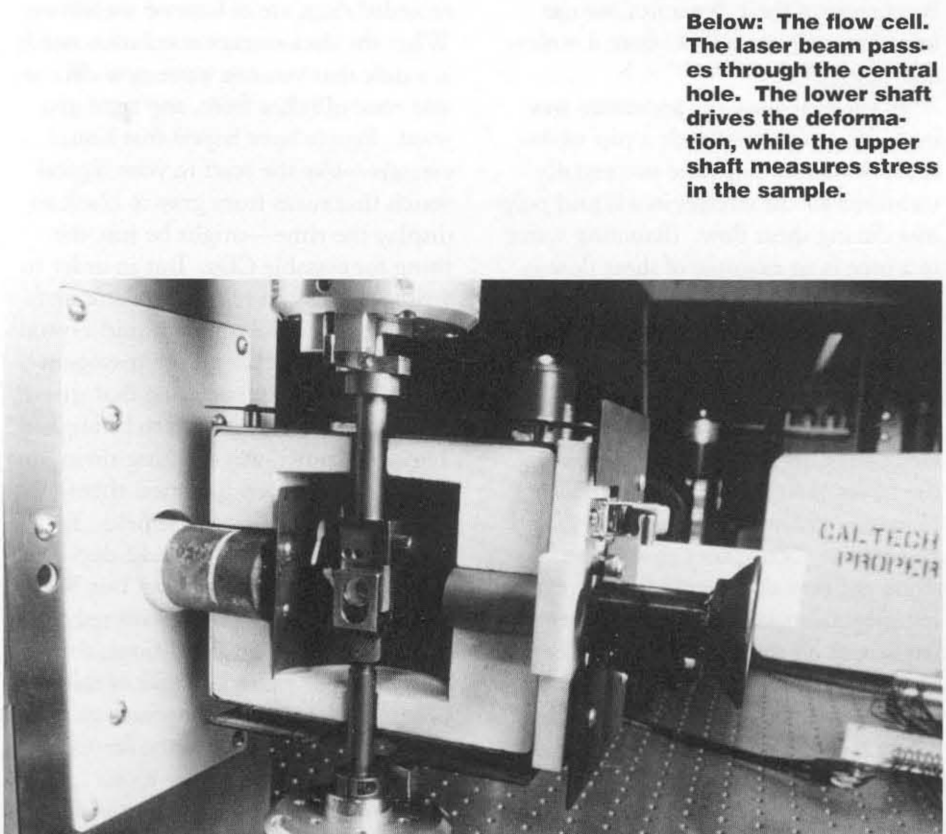
Polymers are long, usually highly flexible molecules. Left to their own devices, they like to lie like cooked spaghetti in a colander. When straightened out and aligned, like a fistful of uncooked spaghetti, polymers can take on new properties. For example, Kevlar, of flak-jacket fame, has the tensile strength of steel but only one-fifth its weight. Other aligned polymers conduct electricity (*Engineering & Science*, Summer 1988), have unusual optical properties, and may even be magnetic. But to make the most of these properties, the molecules must be aligned. One way to persuade the molecules to align is to make them go with the flow, as it were. Molecules in a stream of molten plastic naturally tend to line up along the direction of flow. And although virtually everything plastic, from milk jugs to nylon stockings, is born from a molten polymer mass, very little is known about how flow processing actually works on a molecular level beyond the observation that these highly entangled molecules, particularly in concentrated streams, don't flow like everyday liquids.

In fact, relatively little is known about how the motions of a single polymer molecule, repeated ad infinitum, translate into such basic properties as viscosity and elasticity. To further complicate matters, many commercially important polymeric materials—bulletproof glass, for example—are blends of two different polymers. Many other polymers contain only one kind of molecule, but one that includes regions of different composition, like a necklace made of ten red beads alternating with ten green beads. Synthetic rubbers, such as the Kraton used in gaskets and O-rings, are like this. Trying to predict the viscosity, say, of such polymers without knowing why their molecules behave the way they do or how they interact has, not surprisingly, been a matter of guesswork. Flowing polymers have been studied for decades, but the mechanical methods used can't see how the molecules move, which really determines why the material flows the way it does. The optical methods by which molecular information can be gleaned were ill-adapted for studies of polymers in motion—the action had to be frozen and the sample removed for analysis. But now Julia Kornfield (BS '83, MS '84), assistant professor of chemical engineering, has developed a system that for the first time records not only the polymer's dynamic mechanical properties, but also the molecular and microscopic changes that occur during flow.

At the center of the apparatus, built by graduate student Rangaramanujam Kannan, is a flow cell consisting of two parallel plates. One plate is stationary while the other oscillates, rubbing the





Above: Kornfield and the lab setup. The laser and associated optics are at the left. The flow cell is in the center, mounted in what looks rather like a Mixmaster but is really the mechanical part of the apparatus.

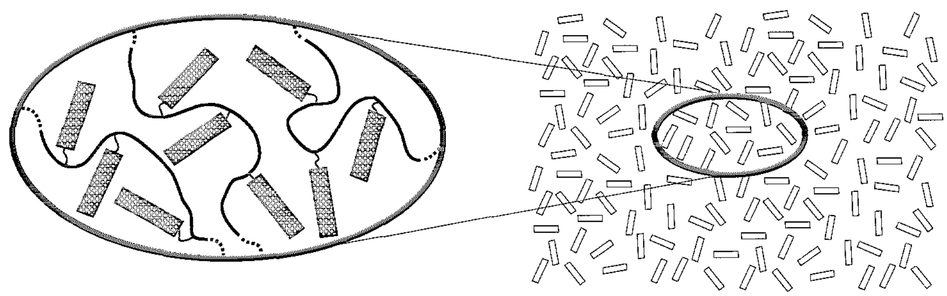
Below: The flow cell. The laser beam passes through the central hole. The lower shaft drives the deformation, while the upper shaft measures stress in the sample.

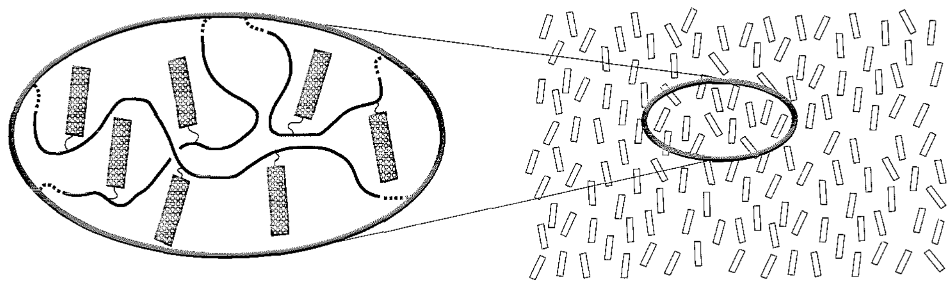
polymer sample between them like a wad of clay being rolled between the palms of your hands. (The apparatus can hold the sample at temperatures between –150° and 400° C, a range broad enough to ensure that practically any polymer will be malleable somewhere within the span.) Stuck to both plates, the sample flows like pulled taffy with each oscillation, stretching and contracting while sensors record the stress on it.

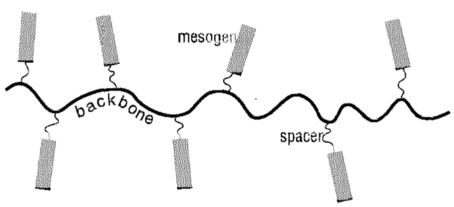
Windows in the flow cell allow optical instruments to collect data on the flowing sample. A laser beam, polarized so that all of its light waves vibrate in a single plane, is sent through the sample and to a set of detectors. One detector measures how much the phase of the polarized light has been rotated by its passage through the polymer, which provides information about how segments of the long, chainlike molecules are oriented by the flow. The other detector measures how the light is absorbed differently depending on the plane of its polarization, which provides information about the orientation of specific molecular structures in the polymer. This specificity is achieved by deuterium labeling: replacing a chosen hydrogen atom in the molecule with deuterium, its heavier cousin, lowers the frequency at which the bond connecting that atom to the molecule vibrates. An infrared laser tuned to that lower frequency will

Below: In side-chain liquid crystals, like the ones that may be the basis for erasable CDs, the mesogens dangle from the polymer backbone like charms from a bracelet.

Right: Normally, the mesogens are randomly oriented, as in the top diagram. But under the right conditions, they will form ranks.







"see" that bond and no others. Says Kornfield, "We can label one type of molecule in a mixture, or distinct parts of a polymer—a part of its backbone, or a bit that dangles off the backbone—and see how that piece behaves under flow. By observing their dynamics, we can learn how polymers flow, from a molecular point of view."

In the year since the apparatus was built, the group has made a pair of discoveries. First, they have successfully measured all the stresses in a liquid polymer during shear flow. (Running water in a pipe is an example of shear flow—the layer of molecules next to the pipe wall hardly moves at all, the next layer out moves a bit faster, and so on.) In fluids made up of small molecules, like air and water, the only stress is the one along the direction of the flow driving the layers of fluid over one another. However, polymer molecules are long and elastic. When they're stretched along the flow they tend to resist, exerting perpendicular forces, called normal stresses, in all three dimensions. "Everyone knows these stresses exist, but they are very difficult to measure precisely. There are theories about them but very few experimental results to test the theories against," explains Kannan. "We've been able to measure them for a variety of polymers."

Exciting as that is to the theorists, the group has just recently found something that may be useful to a new generation of data-storage media. Optical data storage on compact disks like those your CD player takes offer an efficient way to handle vast quantities of data. But today's disks, which only play back factory-recorded data, are of limited usefulness. What the data-storage revolution needs is a disk that you can write new data on, and erase old data from, any time you want. People have hoped that liquid crystals—like the stuff in your digital watch that turns from gray to black to display the time—might be just the thing for erasable CDs. But in order to write on a disk, it has to be blank first. In the case of a polymeric liquid-crystal disk that means that all the mesogens—the portions of the molecule that give it liquid crystallinity—have to be aligned. The only known way to bring them into alignment has been to anneal them in a strong electric or magnetic field. For a very long polymer, it can take days for the mesogens to form ranks. But Kannan and Kornfield have discovered that under the right flow conditions, the mesogens line up in a matter of minutes. "These discoveries have opened up a variety of opportunities for the future," says Kornfield. "There are a vast array of mysteries in the field of polymer dynamics that really demand molecular-level understanding. We're very excited that this new window on these fascinating materials is now open to us." ☐ —*DS*