asteroid. This interpretation is confirmed by characteristic shock effects in olivine and plagioclase within the unmelted host chondrites that indicate peak shock pressures in excess of 50 to 60 GPa (9). The findings of (*1*) and (*2*) have two key implications: (i) The observed high-pressure–phase assemblage is a quenched disequilibrium assemblage formed during shock pressure release at variably high shock-induced temperatures, and (ii) the high-pressure polymorphs crystallized in two different textural settings in the meteorite (see chondrite diagram) by two kinetically different processes (*1*, *2*): At the contact of the melt veins and in chondrite inclusions within the melt, primary grains transform in a "quasi–solid-state process" to ringwoodite, wadsleyite, (Mg,Fe)SiO$_3$ perovskite, (Mg,Fe)SiO$_3$ ilmenite, and clinoenstatite. Within the vein's matrix (Mg,Fe)SiO$_3$ perovskite, (Mg,Fe)SiO$_3$ ilmenite + ringwoodite, and majorite + magnesiowüstite (*2*, *10*) crystallize in this order from a melt above an estimated pressure of 23 to 26 GPa at temperatures well above some 900°C. These observations leave open questions. Why don't we see the predicted breakdown reactions of olivine (spinel) and orthopyroxene: perovskite + magnesiowüstite and spinel + stishovite, respectively? Is there any chance to find a (Mg,Fe)Al$_2$O$_4$ mineral with Ca-ferrite structure? Supporting theoretical studies and more elaborate shock-wave experiments are probably needed to solve the puzzle.

What is important about this discovery and what do we learn about the constitution of Earth's and planetary mantles and regarding the fundamentals of impact metamorphism of rocks? First, almost all of the high-pressure phases predicted to constitute the transition zone and lower mantle do exist in nature and can be formed by shock processes, ironically, in space, at the very surface of asteroids shattered by interplanetary collisions. Second, the shock-induced high-pressure phase assemblages in chondrites tell us about the kinetics of the crystallization of such phases, the partitioning of minor and trace elements, and the extent of solid solutions of the Mg and Fe silicate end members. In general, we learn from the observed disequilibrium assemblages something about the expected equilibrium conditions in the deep mantle, following an old principle of how to unravel the equilibrium conditions of rock metamorphism from metastable phases. Third, the high-pressure mineralogy of chondrites teaches a fundamental lesson about the pressure-temperature-time paths characteristic of impact metamorphism on planetary surfaces, leading to a better understanding of the collision history of asteroids.

Although the shocked meteorites carry a message that is not yet fully understood, the work by the Japanese and United States–German research groups will have a fundamental impact on the understanding of Earth's and planetary silicate mantles. In addition, this work represents another triumph of high-resolution analytical transmission electron microscopy. It will stimulate a more comprehensive study of all types of highly shocked meteorites, which very probably experienced quite different pressure-temperature-time histories and as a result may display variable high-pressure phase assemblages. More exciting information about Earth's deep interior may still be found in the asteroid belt.

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POLYMER SCIENCE

Fashioning Flow by Self-Assembly

Tom McLeish

The cytoskeleton, molten polyethylene, an egg white, knee-joint tissue, shampoo.... A strange juxtaposition of soft materials, but with a common thread: All require precisely tuned flow properties that are achieved by means of molecular engineering, whether human or natural. The strange properties of "viscoelastic" materials display solidlike and liquidlike behavior, depending on the time scale of the applied deformation. This balance is hard to achieve but is as important for polymer processing as it is for the structural stability and function of living cells.

Careful control of the macromolecular structures within these complex fluids is known to be the key. Moreover, in the biological sphere in particular, the polymers frequently self-assemble. Yet, this rapidly-growing area of study within the interdisciplinary science of soft condensed matter is hungry for simple model molecules that are sufficiently rich in their behavior. A report on page 1601 of this issue of *Science* from a group of polymer chemists at the Eindhoven University of Technology describes a promising new candidate (*1*).

When in concentrated solution or melt form, ordinary long-chain molecules of high molecular weight exhibit the twin characteristics of elasticity and long relaxation times, or "memory," for their internal stresses. Both properties have been the bane of the polymer-processing industry for many years. Since the 1970s and the work of de Gennes, Doi, and Edwards, the molecular basis for standard polymer viscoelasticity has been understood as arising from the topological interactions (or "entanglements") between the chains. The polymer solution acts as a fixed network under rapid deformation until the chains collectively escape from their mutual entanglements. For linear polymers, the dominant mechanism is random curvilinear diffusion along their own contours, around which they are trapped within a tube-like region. Termed "reptation," this snake-like motion gives rise to a dominant relaxation time that increases rapidly with molecular weight (*2*). Careful dynamical ("rheological") measurements on specially synthesized monodisperse polymer melts

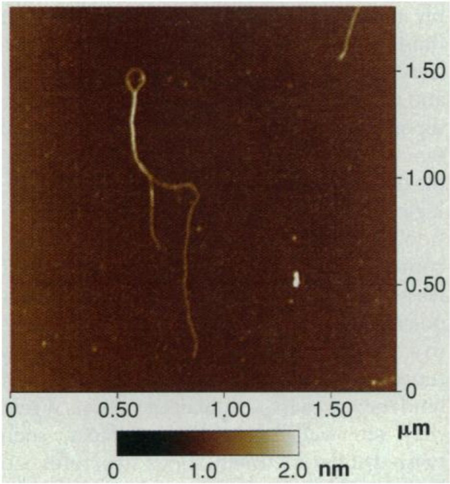

Image of self-assembled polymer with twisted ribbon structure taken with atomic force microscope. Color bar indicates height above substrate.

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confirm this prediction, along with the existence of faster relaxation processes originating from material near the ends of chains. Proximity to a chain end means a more rapid release from entanglements.

The flow and relaxation of entangled macromolecular fluids are extremely sensitive to molecular structure, as well as simply molecular weight. The inclusion of just one trifunctional branch point per polymer molecule (thus fashioning "star polymers") changes the entire shape of the spectrum of mechanical relaxation times. More complex architectures give whole families of different fluids, all exploring the same local field of entanglements but with different global consequences. Careful chemical synthesis of controlled molecular structures has gone hand-in-hand with physical experiment and theory (*3*).

But what if the molecular structures are not fixed on exit from the reaction vessel but are free to adapt to their surroundings? Such "living systems" abound with processes such as chain-scission, end recombination, branching, and end exchange, all of which may occur on time scales that affect the entanglement structure. The example most feverishly studied is the case of wormlike surfactant micelles. When aggregating surfactant molecules would rather form cylinders than spherical assemblies, the rodlike structures so formed may grow to huge lengths, at which they become flexible and entangle with each other, just like ordinary polymers (this is the mechanism behind the viscoelasticity of some shampoos). There is one important difference: the "polymers" undergo a perpetual partner-chase, breaking and recombining whole sections at rates that may greatly exceed the reptation time of the average chain. Theory and experiment (*4*) confirm that in this case, a remarkable "motional narrowing" occurs, and the viscoelasticity displays a single relaxation mode.

If the surfactants show us that self-assembly in polymer liquids can lead to simpler fluid behavior, then a more recent case illustrates that it can also increase its complexity and richness. A group of us at Leeds recently reported self-assembled polymers with a local tapelike structure based on highly anisotropic β sheets of model peptides (*5*). The rheological evidence points to a "reptation reaction" regime of behavior along the chain contours like the wormlike micelles, but at least one other order of self-assembly is now possible, as is reflected in some bizarre effects in strong flows. The tapes can be molecularly tuned to stack up to a degree limited by their tendency to twist, like plaited ribbon. When they are well-behaved at surfaces, such twisted and sometimes looped structures can be imaged by atomic force microscopy (see figure). The enormous scope for molecular design by means of peptide synthesis makes these materials interesting candidates for applications in biomimetics, drug-delivery, and rheological modification.

The peptide assembly works by means of hydrogen bonding, but with the complications of the stacking associations. One of the interesting implications of the Dutch work (*1*) is the potential synthesis of more controlled hydrogen-bonded self-assembled polymers that do not have any other interactions. Even branched structures may be included or excluded at will by the admixture of trifunctional moieties containing the same quadruple–hydrogen-bonded units. This work may help to confirm or deny some interesting recent speculations on the dynamics of branched self-assembled wormlike surfactant micelles (*6*), where even proving that the branch points exist is a challenge.

It is hard, of course, to be really pure or simple in this life, and the new self-assembling family will need to be subjected to a wider range of structural and rheological probes than has so far been possible. The authors' reference to the "history-dependent phase behavior" (*1*) of some of their materials indicates that more might be lurking beneath the benign appearance of the model fluids. It recalls another pressing question in the science of soft matter: the role of metastability. Observing no change in a complex fluid for a time scale of hours or even days is no guarantee that one has achieved equilibrium. Very long relaxations in fluid properties have been observed in ordinary polymer melts and in the self-assembled peptide tapes, as well as in more distantly related colloidal suspensions. We are very far from understanding these slow processes, but another system that can be made to exhibit them does not therefore necessarily count as a disadvantage.

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SIGNAL TRANSDUCTION

A New Player in Cell Death

Timothy Hoey

Cytokines, small proteins secreted by cells, trigger growth or differentiation in other cells. Along with hundreds of other signaling molecules, these compounds orchestrate the life of a multicellular organism by triggering varied signal transduction pathways inside cells. Most of these pathways are complex, multistep cascades of biochemical events, but cytokines trigger some of their responses with only a few intermediate steps. They accomplish this by enlisting a unique family of proteins called the STATs (*1*). What usually requires four or five proteins acting sequentially, these versatile proteins supply in one package. The STATs are able to do this because they embody features both of early steps in signaling by cell membrane-associated molecules and of the final steps, executed by nuclear transcription factors. Like many membrane molecules, STATs are regulated by phosphorylation on a tyrosine residue and have a domain specialized for interacting with other proteins containing phosphorylated tyrosines, the SRC homology 2 (SH2) domain. But like nuclear transcription factors, STATs also have DNA binding and transcriptional activation domains.

Now STATs have been shown to be required in an unexpected place—a multistep signaling pathway for the induction of cell death (apoptosis) by tumor necrosis factor–α (TNF-α). Apoptosis is initiated by activation of a cascade of proteases (the Ice family or caspases) that cleave cellular proteins, resulting in the efficient termination of the cell (*2*). On page 1630 of this issue, Kumar *et al.* report a surprising connection between STATs and TNF-induced cell death: TNF-α–induced apoptosis is defective in cells lacking STAT1 (*3*).

This lack of programmed cell death in the STAT1 mutant cells correlates with a lack of constitutive, apparently unregulated, expression of Ice family proteases. Strikingly, STAT1's participation in the apoptotic

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