incorporation into the subsurface region may become energetically favorable.

On many surfaces, an intermediate surface oxide phase precedes the formation of the passivating oxide film, which has a typical thickness of 2 to 3 nm. Examples include oxygen on the (111) surface of silver, copper, and palladium, and the oxygen-induced missing-row reconstructions of the (110) surface of copper, nickel, and silver (*5–7*). Other surfaces such as Ni(001) and Al(111) oxidize directly from the chemisorbed state (*8*, *9*).

King and co-workers (*5*) have argued that the critical coverage at which an oxide nucleates on an oxygen-covered surface is determined by thermodynamics: Below the critical coverage, the heat of formation of the chemisorbed phase is higher than that of the oxide. Recent ab initio calculations support this hypothesis (*10*). On Ru(0001), oxygen incorporation in the surface-near region sets in at a critical coverage of about one monolayer.

To investigate the oxidation process of ultrapure Pb clusters without facing kinetic limitations due to oxygen dissociation, future studies may use atomic instead of molecular oxygen. For instance, with NO_2 as a source for atomic oxygen, the Ru(0001) surface can accommodate large amounts (equivalent to 20 to 30 monolayers) of oxygen without surface oxide formation, even after the oxygen-rich surface is annealed to elevated temperatures (*11*). This observation implies that Ru can store substantial amounts of oxygen either as subsurface (dissolved) oxygen or as buried oxide (see the figure). The presence of large amounts of dissolved oxygen is, however, difficult to reconcile with the exceedingly low solubility of oxygen in bulk ruthenium and other late transition metals. A buried oxide thus appears more likely (*12*).

Thürmer *et al.* (*2*) show that once nucleation has been initiated, the lead oxide layer grows autocatalytically in two dimensions; that is, the progressing oxidation is self-accelerated. They attribute the autocatalytic oxidation of Pb to the facile dissociation of oxygen molecules by PbO. This mechanism supplies the surface with atomic oxygen that takes part in the formation of the oxide compound.

This process of self-accelerating oxidation is not restricted to Pb. Because the sticking coefficient of oxygen increases dramatically on the oxide patches (see the figure) (*4*), the RuO_2 film on Ru(0001) grows autocatalytically in two dimensions once nucleation has been initiated (*12*). The further growth of thicker oxide films is generally limited by mass transport of oxygen and metal ions across the oxide film.

The work of Thürmer *et al.* (*2*) represents a key step toward a deeper understanding of the initial oxidation of Pb clusters and related systems. Future theoretical and experimental work should concentrate on general trends of the oxidation of metals and on their relation to physical properties of the metal systems. A comprehensive understanding of the complex atomic and molecular processes that actuate the corrosion of metals may hold technological promise for designing tailor-made materials.

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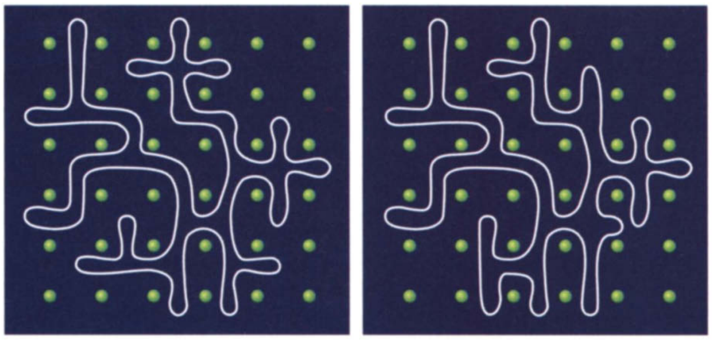
PERSPECTIVES: CHEMISTRY

Polymers Without Beginning or End

Tom McLeish



Basic dynamical move of a ring polymer entangled with a mesh of obstacles. The obstacles arise from the presence of other loops. The whole ring moves by retraction and reconfiguration of its constituent loops.

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"In my beginning is my end…In my end is my beginning," reflects T. S. Eliot in his wistful *Four Quartets* (*1*). Ends and beginnings concern science as much as poetry, and perhaps nowhere more so than in the polymeric state of matter.

Natural polymer molecules dominate biology, while artificial polymers are used as plastics or emulsifiers in countless modern products. Many characteristics of their crystalline, glassy, and fluid states can be traced back to the special properties generated by the ends of the molecules. But what would happen if there were no ends? What would be the properties of polymers composed entirely of closed loops? Answers may be within reach following the discovery reported by Bielawski *et al.* on page 2041 of this issue (*2*) of a polymerization catalyst that releases the polymer in the form of a closed ring.

These are not the first ring polymers to be studied. In the 1980s, Roovers synthesized small quantities of monodisperse polystyrene rings by anionic polymerization (*3*). His motivation was the growing interest in the dynamics of polymer melts, in which topological entanglements between chains dominate the pattern of their motion. Experiments with linear, star-shaped, and H-shaped molecules had shown that the architecture of the molecules had a stronger influence on the viscosity and viscoelasticity than their chemistry or molecular weight. For example, the time scales for stress-relaxation in flow can increase exponentially as a function of molecular weight if the molecules are branched, but only as a power law if they are not. The promising "tube model" (*4*) explained these effects: The key determinant of relaxation time is the time that the locally trapped region of

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the melt needs to wait for a chain end to diffuse to it through a maze of tubelike constraints around the polymer contour.

But what would happen if there were no ends to be found? Answering this question turns out to be delicate. Roovers found (correctly) that the relaxation times of the ring melts were much lower than those of linear melts of the same molecular weight. But other researchers disagreed. There are several reasons why ring molecules are difficult to study. First, it is essential to synthesize rings that are not interlinked (although such "olympic gels" are themselves interesting as rubbery solids with no molecular cross-links at all). Second, even small amounts of linear polymer contaminants in a melt of rings alter the dynamics, bringing relaxation times rapidly up to linear melt values. Finally, polystyrene, although relatively easy to work with, is composed of very bulky molecules that diminish the effects of entanglement.

These experimental challenges did not prevent theoretical speculation, however. Linear chains in dense melts display the statistical properties of ideal random walks, but a melt of rings should not behave in this way. The topological constraint that the rings are not linked is permanently set from their creation. This constraint in turn biases their conformations so that they grow in size more slowly with molecular weight than do linear chains (*5*). Instead of the snakelike reptation of linear chains, theory suggested that the dynamics of rings should resemble the motion of amoebae: Unentangled loops continually thrust out and retract in the complex hedge of constraints imposed by neighboring molecules (see the figure) (*6*).

Without ready supplies of material to test these intriguing ideas experimentally, the natural recourse has been simulation. Brown *et al.* recently provided strong hints that the earlier theoretical ideas may have been on the right track (*7*). Their simulated rings are indeed more compact in the melt, and diffuse much faster than their linear homologs.

The new catalysts of Bielawski *et al.* may help to test the theoretical models experimentally. The new synthetic route has many advantages: The rings are very unlikely to be linked, linear contamination is small, and the chemistry applies to the well-entangled polyolefin family. Synthesis from deuterated starting material should lead to ring polymers that can be studied with small angle neutron scattering, allowing direct measurements of their dynamics at the molecular level. Best of all, the method should allow synthesis of large amounts of ring polymer.

A minor drawback is that the spread of molecular weights is exponentially distributed and therefore not as narrow as that in principle obtainable from anionic methods. Nevertheless, rheological, diffusion, and scattering experiments on a range of molecular weights of these new materials should provide a test for the scaling-law predictions of the "amoeba dynamics" theories.

Their melt flow properties would, of course, affect the processing of any new plastics made from ring molecules. But the absence of chain ends promises to modify solid state properties as well. The mobility of the disordered glassy regions in solid polymers of low molecular weight has often been linked to the density of chain ends, conceptualized as sources of "free volume." A similar trend is expected from theories of glassy dynamics that invoke entanglement to explain the onset of the glass transition. Similarly, the degree of crystallinity (a strong determinant of strength and toughness) in polyethylene and its cousins must depend on the presence or absence of chain ends. Bielawski *et al.* observe a subtle change in the melting temperature of the new materials, but whether this is due to the lower entropy per chain in the melt, as the authors suggest, must wait for a study over a wider range of molecular weights.

The new polymers may not immediately result in new, competitive products, but they stand every chance of clarifying some unsolved puzzles of polymer science. They are also bound to pose new questions, giving us no cause to cease from our explorations.

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PERSPECTIVES: IMMUNOLOGY

Autoreactive B Cells Migrate into T Cell Territory

Yang-Xin Fu and Ursula Storb

B cells are prevented from producing antibodies against self antigens by the induction of tolerance, which results in deletion of autoreactive B cells. Sometimes autoreactive B cells escape this fate, and produce large amounts of antibodies against self antigens, which they generate through somatic hypermutation of their immunoglobulin (Ig) genes. High levels of autoantibodies generated through somatic hypermutation are found in certain autoimmune diseases, such as systemic lupus erythematosus (*1*, *2*). It has been presumed that autoreactive B cells, like normal B cells, accumulate in the follicles of lymphoid tissues after encountering antigen and begin to proliferate, producing high-affinity autoantibodies and forming germinal centers (*3*). But recent studies using various strains of mice lacking germinal centers suggest that autoreactive B cells can accumulate at other sites in lymphoid tissues (*4*). On page 2066 of this issue, William *et al.* (*5*) working with a mouse prone to developing autoimmune disease report the surprising finding that autoreactive B cells accumulate not in germinal centers of lymphoid tissues but at the T cell zone–red pulp border.

For their study, William *et al.* selected the MRL.Fas^{lpr} mouse strain, which develops systemic lupus erythematosus. They introduced into these mice a transgene encoding the heavy chain of an antibody raised against IgG2a antibodies of the "a" allotype (*5*). The transgenic heavy chain binds to endogenous light chains to create antibodies against "a" allotype IgG2a. The transgenic antibodies behave like the rheumatoid factor found in patients with rheumatoid arthritis, an autoimmune disease. Thus, in "a" mice the antibody is anti-self with the potential to cause autoimmunity. In contrast, in mice with the "b" allotype, no self antigen is present and the transgenic heavy chain is not involved in an autoimmune process.

In the MRL.Fas^{lpr} mouse, B cells encountering an antigen that binds to their surface antibody can alter the specificity

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