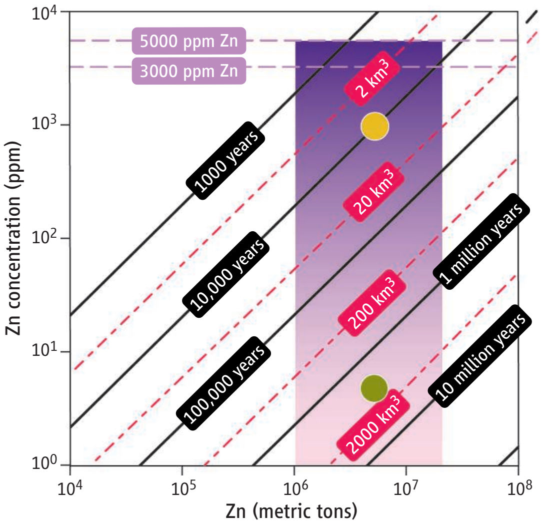

How to form an ore deposit. This modified "Roedder diagram" (*15*) shows the relationship between the amount of metal precipitated per unit mass of hydrothermal fluid (*y* axis) and the size of the ore deposit (*x* axis). The time (black diagonals) and volume of fluid (red dashed diagonals) required to form the deposit are contoured onto these coordinates. The width of the shaded box represents the range in ore tonnage for large to giant MVT Zn-Pb deposits (*10*). Wilkinson *et al.* report zinc concentrations of 5000 ppm and 3000 ppm (dashed lines near the top of the box). These concentrations are higher than previously reported and suggest that economic deposits can form faster than previously suggested (green and orange dots).

the Upper Mississippi Valley district of the United States (*13*).

Flow rates and duration of the ore-forming process reported by Garven (*11*) require total hydrothermal fluid volumes ranging from 2500 to 25,000 km^3 over the lifetime of the ore-forming system. Similar volumes of fluid would be required to form other large to giant MVT deposits if each kilogram of fluid only precipitates a few milligrams of metal. However, if the metal content of the ore-forming fluid is considerably higher, as suggested by Wilkinson *et al.*, then both the amount of fluid required and the duration of the ore-forming event would be reduced by orders of magnitude (see the figure). For example, if each kilogram of hydrothermal fluid deposited 10^3 mg of Zn (orange dot in the figure), then Pine Point and similar deposits could have formed in about 10^4 years from a few cubic kilometers of hydrothermal fluid, compared to the millions of years and hundreds of cubic kilometers of fluid required assuming that each kilogram of hydrothermal fluid deposited 5 mg of Zn (green dot in the figure).

The results presented by Wilkinson *et al.* further highlight the importance of depositional processes in the formation of economic occurrences of metals. Most ore geologists now agree that fluids with metal contents sufficient to produce economic mineralization are relatively common (*14*), and that it is the lack of a suitable depositional mechanism that often limits ore formation. Temperature decrease alone cannot be the dominant mechanism, because the solubility of most metals in most hydrothermal fluids decreases by only a small amount over the temperature range determined for most deposits. Thus, other processes—such as boiling or immiscibility, fluid mixing, or fluid-rock interactions—must operate to promote the precipitation of all (or most) of the dissolved metals transported by the hydrothermal fluids. The results presented by Wilkinson *et al.* provide important new insights into metal contents of ore-forming fluids and emphasize the need for continued research to constrain the amounts of hydrothermal fluids required to form world-class ore deposits and the duration of the ore-forming events.

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10.1126/science.1166394

MATERIALS SCIENCE

Confined Polymers Crystallize

Piet J. Lemstra

Squeezing very thin polymer layers can cause them to form polymer single crystals that could make plastic films less permeable to gases.

Plastics have been very successful in replacing glass, metals, and wood, in part because they are light and easy to process into complex shapes at high speed and at low cost. However, in applications such as packaging, molded plastics can be at a disadvantage compared with steel, aluminum, and glass because of their relatively high permeability to atmospheric gases such as O_2 and CO_2. This problem arises because the synthetic polymers that are the main component of plastics are rather randomly organized in the solid state with sufficient spaces between the molecules that allow for gas diffusion. Although the problem can be solved to some extent by adding less-permeable materials to plastics, ideally it would be desirable to find a way to arrange the long-chain polymer molecules in an orderly way, namely, into crystallites in which the molecules are closely packed. On page 757 of this issue, Wang *et al.* (*1*) report that very thin layers of a commonly used polymer crystallize through special processing conditions into so-called polymer single crystals, which is surprising given the known difficulties in getting polymers to form crystals.

The focus of most polymer research is on functional properties in emerging areas such as biomedical engineering (*2*), electronics (*3*), and energy [for example, plastic solar cells (*4*)], but the vast bulk of synthetic polymers are used in plastics. Packaging materials

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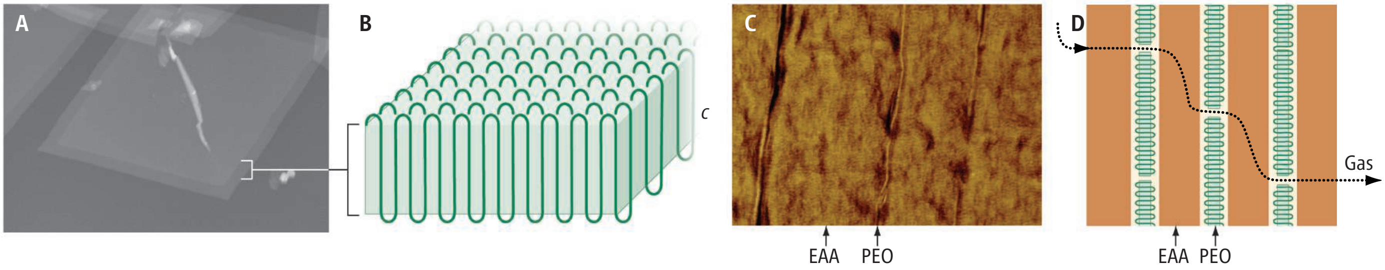
consume about 40% of the plastics produced. Plastics have surpassed steel in terms of production volume, with about 250 million tons of plastics produced annually worldwide.

Despite this widespread use, there are packaging applications where the gas permeablility of plastics, especially to oxygen, hampers their use, from beer bottles to coatings in advanced electronics. Plastics are quite permeable because their softening temperatures (the glass transition temperature, T_g) are low in comparison with those of silicate glass and much lower than the melt temperatures of metals. For commonly used plastics, T_g ranges from −100° to about 100°C, whereas for silicate glasses, T_g ranges from 500° to above 1000°C.

Gases or liquids permeate a plastic or glass by first dissolving in it and then diffusing through it. In the simplest theoretical description, the permeability is the product of the gas's solubility and its diffusivity. At room temperature, the diffusivity—the movement of the penetrating molecules—in silicate glass is almost zero because the silicate chains are "frozen" at ambient temperatures far below their T_g. The packing of these chains is not orderly but is still very tight and provides very little empty space and mobility for the penetrating molecules to pass through.



Packing polymer chains. Polymer single crystals can be obtained from very dilute solutions, e.g. polyethylene single crystals as visualized by AFM (**A**) in which the chains are folded (**B**) (*9*). Wang *et al.* have now succeeded in creating crystallized polymer layers (**C**) from the melt by extruding alternating thin layers of two different polymers. (**D**)These single-crystal layers inhibit gas diffusion by creating barriers that make the path that molecules take more tortuous.

In contrast, the segments making up the polymer chains are quite mobile at room temperature. This movement opens up pathways for low–molar mass molecules such as O_2 and CO_2 and, in the case of polar polymers such as nylon, for water. In general, the higher the T_g of a plastic, the better its barrier properties. For that reason, the polyester poly(ethylene terephthalate) (PET), with a T_g of ~ 80°C, can be used for carbonated sodas, but it is too permeable to oxygen for storing beer.

Various options exist to improve the barrier properties of plastic systems, such as applying a metal or ceramic coating or processing alternating layers of the plastic film with deposited ceramic film. More recently, nanoscale clay particles (made from exfoliated single layers of clay) have been dispersed in a plastic film (*5*). These thin clay layers are impermeable to gases and create a tortuous path for diffusing molecules; the path length for diffusion increases and slows gas exchange.

Another approach, but one that is much more challenging, is to enhance the barrier properties of polymers by getting them to crystallize because polymer crystals are impermeable to gases. However, the long chains of synthetic polymer molecules are entangled with each other, much like cooked spaghetti. How can these long-chain and highly entangled molecules form ordered crystallites?

The first efforts at polymer crystallization avoided highly entangled melts and started with dilute solutions. In the 1950s, Keller (*6*), Fischer (*7*), and Till (*8*) found independently that linear polyethylene (PE) can form platelet single crystals upon cooling dilute PE solutions (see the figure, panel A). The long-chain molecules are folded in these crystals (*9*). The fold length, which corresponds to the crystal thickness, is very small, on the order of 10 to 20 nm (see the figure, panel B). The concept of folded-chain crystallization continues to raise enormous interest among polymer physicists, because it is found that all polymer-chain molecules with a regular chemical structure form these folded-chain lamellar crystals.

However, well-defined folded-chain crystals, referred to as lamellae, can only be grown from dilute solutions, which is too slow and inefficient for manufacturing. In processed products such as films, containers, and fibers, the polymers that are cooled from the molten state are only partly crystalline. Although there is still a driving force for the long-chain molecules to form folded-chain crystals, this process is hampered because the chain molecules are highly entangled polymers.

Crystallization from the polymer melt starts from nuclei (catalyst residues or purposely added nucleation agents), and chain-folded crystallites emanate from such nuclei. However, the entangled polymer chains only partly incorporate into the crystallites, creating spherical crystal aggregates called spherulites. Thus, melt-crystallized polymers are semicrystalline because those chain segments that are not folded into crystallites remain amorphous. Partial crystallization improves the barrier properties to some extent, because the crystallites are not permeable and create a tortuous path for small molecules, just as in the case of the nanoclay platelets.

Wang *et al.* now show how poly(ethylene oxide) (PEO)—a crystallizable polymer—can be processed from the melt to form very thin layers consisting of polymer single crystals. The authors use a process in which alternating layers of PEO and EAA poly(ethylene-*co*-acrylic acid) are coextruded. The pressures applied in this process force the long-chain molecules of PEO into their most compact arrangement, that of large folded-chain lamellar crystals (see the figure, panels C and D), while the EAA layers remain amorphous. The permeability of PEO to oxygen decreased by about two orders of magnitude in this crystalline form.

Showing that large lamellar crystals can be grown from the melt is not only of high academic interest. The multilayer extrusion technique is used to create higher-value products through processing [for example, flexible mirrors (*10*)]. Crystalline polymers created in this way may in future function as barrier layers for semicrystalline polymers used in packaging.

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10.1126/science.1168242

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