

quired, because neural crest cells have now been shown to be little different from earlier embryonic cells; they are able to differentiate into cell types of all three conventional germ layers, including endoderm, albeit just a little bit later in development.

The work by Buitrago-Delgado *et al.* sheds further light on the evolution of the neural crest and therefore of vertebrates. Retaining pluripotency may not have been the crucial evolutionary step that defines the neural crest. Closely related nonvertebrate animals share with vertebrates the expression of components of the neural crest gene regulatory network in cells at the neural plate boundary, including what we now understand are regulators of pluripotency (8). Instead, vertebrate neural plate border cells may have evolved the ability to undergo EMT, delaminate from the ectoderm, and migrate to different parts of the embryo (9, 10).

The Buitrago-Delgado *et al.* study raises questions about the identity of what we conventionally call the ectoderm. The most pressing issue is, however, how these cells at the neural plate border region selectively retain pluripotency while cells all around them become restricted in their developmental potential.

Buitrago-Delgado *et al.* follow in the footsteps of pioneering studies that have used the amphibian as a model system to uncover fundamental aspects of vertebrate development, from basic processes in embryonic induction (11–13) through uncovering the principle of somatic cell reprogramming (14). Like these earlier discoveries, now seen as pivotal in understanding human development and disease, this latest research has critically changed our perception of vertebrate evolution and development and demonstrates the importance of the neural crest. ■

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10.1126/science.aab2719

MEMBRANES

Outperforming nature's membranes

Ultrathin synthetic membranes that reach a record permeability can clean up organic solutions

By Viatcheslav Freger

Industrial chemical reactions or bio-synthetic processes rarely yield pure products, and the additional separation steps typically required often make up the largest part of the product cost. Membrane separations are considered among the most efficient methods, deriving inspiration from the membranes in living cells. Intriguingly, on page 1347 of this issue, Karan *et al.* (1) show that synthetic membranes may get close to and eventually outperform their soft biological counterparts in many aspects. They targeted the rapidly developing field of organic solvent nanofiltration (OSN) (2). Such membrane filtration of nonaqueous solutions may help make chemical synthesis (3) more efficient and environmentally friendly by separating and recycling solvents, reactants, products, and catalysts.

Synthetic membrane films work by selectively retaining or passing molecules. These processes require an energy input, e.g., pumping energy in the case of filtration. Development of an efficient membrane faces a twofold challenge: finding a highly selective material, and forming a large and defect-free film of a minimal thickness to maximize permeability and minimize pumping energy. Interfacial polymerization (IP) is a remarkably simple process that simultaneously achieves both goals. Two monomers dissolved in immiscible solvents, e.g., water and hexane, react at the interface to form a polymer film that eventually self-terminates its growth. With the right choice of monomers, typically, an aromatic triacid and a diamine, a thin polyamide membrane is obtained.

Usually, preparation is carried out on top of a thick porous supporting membrane, yielding a composite membrane with a polyamide top layer (see the figure, panel A). The advent of such polyamide composites some three decades ago revolutionized

membrane desalination, which today supplies drinking water to millions of people worldwide with unprecedented thermodynamic efficiency approaching 50% (4).

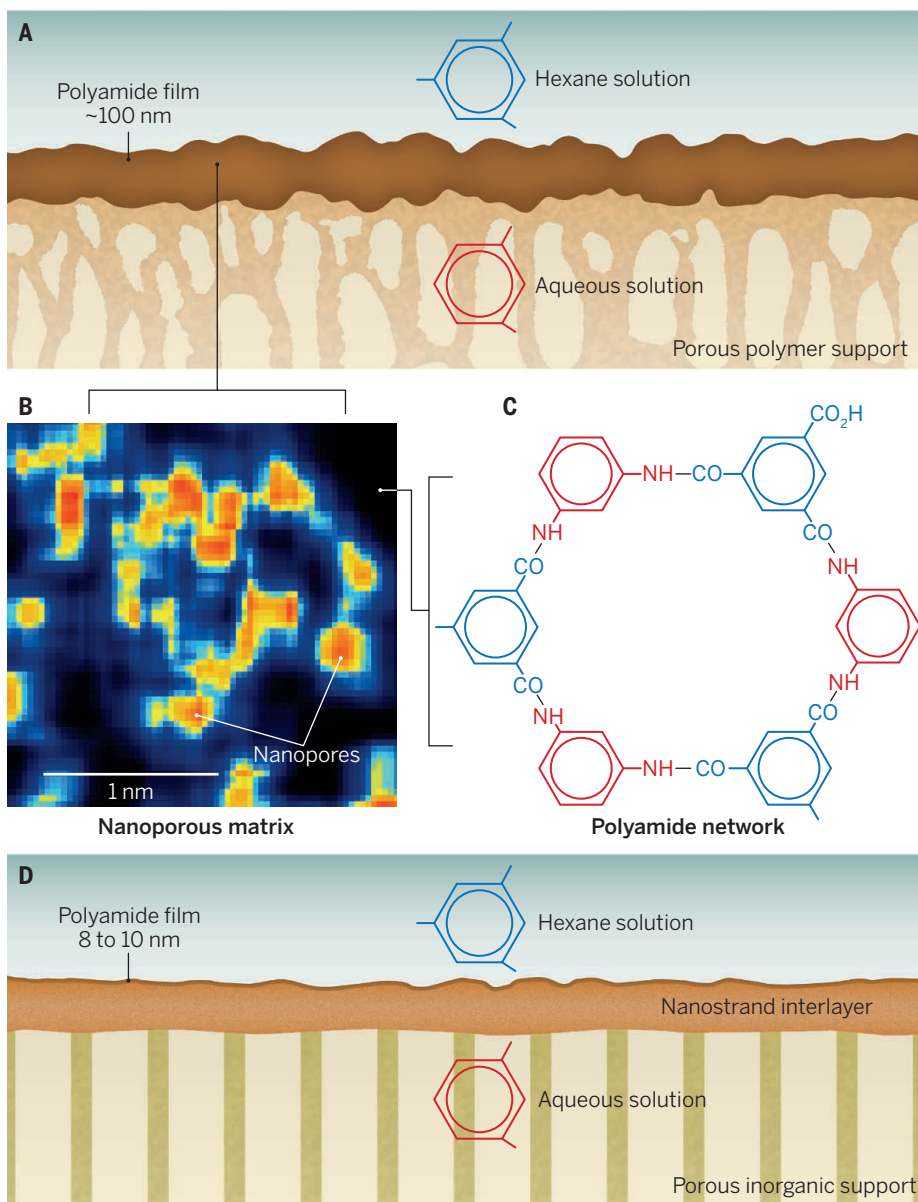
Although OSN membranes have not made a similar breakthrough, Karan *et al.* have taken a large step toward achieving this goal. The seemingly straightforward IP process turns out to be formidably complex as regards understanding the relation between the preparation conditions and the film's thickness, nanostructure, and permeability. Mean-field models (5) and molecular dynamic simulations (6, 7) reveal that IP proceeds as a complex aggregation process, resulting in a film of poorly defined thickness and structural irregularities at all spatial scales involved. The irregularities manifest themselves in intrinsic porosity that results from the high rigidity of the polyamide matrix (7) (see the figure, panels B and C). If not excessive, this porosity is beneficial, as it enhances membrane permeability (8). However, it is not at all straightforward to come up with rational recipes for controlling thickness and porosity and maximizing the permeability.

Karan *et al.* identified several new ways to manipulate the IP process and obtain a dramatic increase in permeability. One ingenious modification was to move film formation somewhat away from the solid

"To expand to new avenues and stay economically attractive, membrane development must constantly strive for higher permeabilities and seek new and better selectivities."

support by adding an intervening sacrificial interlayer made of needle-like cadmium hydroxide nanostrands (see the figure, panel D). Such a layer, easily formed by filtering nanostrand suspension through the supporting membrane and dissolved, once the IP reaction is complete, is far more porous and uniform than the support surface because of the very small size of nanostrands. Apparently, this structure facilitates a uniform access of monomers and enhances their flux into the growing film, which was shown to be inversely related to film thick-

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Making an ultrapermeable membrane. In a standard interfacial polymerization (A), an aqueous diamine solution impregnates the polymeric support and reacts with a hexane solution of trifunctional acid monomer to form a thin and highly selective polyamide film. The film is an aggregated structure with random subnanometer pores (B) in a rigid molecular network matrix (C). A critical difference is made by a sacrificial nanostrand layer that moves the reaction away from the solid support surface (D). This layer dramatically decreases polyamide thickness from about 100 nm to between 8 and 10 nm. When combined with film crumpling, “opening up” of polyamide with a swelling solvent, and the stabilizing effect of the rigid inorganic support, membrane permeability is increased by an unprecedented two orders of magnitude.

ness (5). As a result, uniform films could be prepared of a record-breaking 8-nm thickness, just shy of that of biological membranes (5 to 6 nm), yet strong enough to survive straining through a pipette tip.

Another performance-enhancing effect was crumpling of the film when the diamine concentration exceeded a certain threshold. Crumpling or folding increased the effective area and permeation rate for a given area. Suggestions that this effect could explain enhanced permeability of some commercial membranes were made in

the past (9). However, Karan *et al.* managed to explicitly show this by taking advantage of the easy transfer of the polyamide film from nanostrand layer to substrates more suitable for structural examination. They also pointed out that crumpling could be related to instabilities caused by excessive heat generation during IP reaction, in analogy with the Rayleigh-Bénard instability of a fluid layer heated from the bottom.

Although the prepared films already had outstanding characteristics, Karan *et al.* took the process a step further and treated

the film with a swelling solvent (dimethylformamide). This is known to “open up” polyamide, i.e., increase its porosity, but, unfortunately, when dimethylformamide is changed to another solvent, the permeability usually declines. Surprisingly, they found that the performance decline could be entirely prevented by using a rigid inorganic support instead of a regular polymeric one (see the figure, panels A and D). This change resulted in a staggering stable permeability of 112 liter m^{-2} hour $^{-1}$ bar $^{-1}$ for acetonitrile as the solvent, which surpasses that of biological membranes (10) by an order of magnitude and that of today’s desalination membranes by two orders of magnitude. This result suggests that the support might be as important as the selective layer itself for maximizing and stabilizing performance.

To expand to new avenues and stay economically attractive, membrane development must constantly strive for higher permeabilities and seek new and better selectivities. Karan *et al.* demonstrate great potential for improvements in relatively old approaches via smart manipulation of membrane preparation, use of novel nanomaterials, and attention to all components of the composite membrane. This effort must be assisted by in-depth understanding of the transport, rejection, and membrane formation mechanisms, as well as membrane nanostructure, which at present remains a challenge even for much older desalination membranes. The challenge increases many-fold for OSN, which must operate and remain stable in various media and rely on much weaker molecular interactions, compared to electrostatic forces dominating salt-water separations (11, 12). Nevertheless, the benefits of simpler, faster, and greener processing make it a worthy effort. ■

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10.1126/science.aab3727



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Viatcheslav Freger (June 18, 2015)

Science **348** (6241), 1317-1318. [doi: 10.1126/science.aab3727]

Editor's Summary

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