POLYMER FILMS

Designing a slow leak

Richard B. Kaner

IF LARGE surface areas could be coated efficiently with pinhole-free polymer films of less than 50 nm in thickness, many important membrane-based technologies such as gas separators and sensors would be greatly improved. Langmuir–Blodgett and interfacial polymerization techniques have so far failed to produce nonporous ultrathin films on porous substrates, although ultrathin film coatings on smooth substrates are now possible[1]. C. Liu and C. R. Martin report on page 50 of this issue[2] an important advance in coating porous substrates by describing a method for growing ultrathin coherent films using photoinitiated polymerization. Capillary action is used to cover the surface of a porous material with a thin film of monomer solution. Irradiation with ultraviolet light then produces the high-quality films.

Scanning electron micrographs of the thinnest polymer films reported by Liu and Martin indicate uniform 40-nm thicknesses. The authors measured the gas permeabilities of oxygen and nitrogen to determine the film's porosity: pinholes would allow the gases to flow by Knudsen diffusion (at a rate inversely proportional to the square root of their masses) and the lighter element, nitrogen, would permeate 1.07 times faster than oxygen. But, oxygen actually permeated up to eight times faster than nitrogen, so that the films were defect-free, and can be used for gas separation.

Gas-separation techniques have evolved over the past 15 years into a large commercial enterprise, involving at least 20 major companies worldwide. The driving forces behind replacing conventional cryogenic gas separation by membrane-based methods are the potential reduction in energy consumption and capital costs and the greater ease of operation at remote plant sites. The largest current market is for nitrogen separated from air, for use in protecting perishable goods and blanketing inflammable materials. The oxygen-enriched byproduct can be used to accelerate combustion or for medical purposes. Other applications include recovering and recycling hydrogen during ammonia synthesis and petroleum refining. Carbon dioxide separated from natural gas can be reinjected into wells to assist petroleum recovery. Future applications could include pollution control.

For effective gas separation, membranes must both be highly selective and allow high flux rates. Flux is inversely proportional to the thickness of the membrane, so that the thinnest possible nonporous polymer is desirable. But the polymer must also withstand high pressures (up to 150 atmospheres), and separation is generally carried out with asymmetric membranes in which a thin skin of polymer is grown on a porous structural support. In 1979, workers at Monsanto Company introduced self-supporting hollow-fibre membranes[3]. These asymmetric tubules had a porous polymer support to withstand high pressures, a thin polymer skin to carry out separation and large surface areas to allow high gas throughput. The hollow fibres had walls 25–250 μm thick with a dense skin of 0.1–1 μm. Clearly if the separating layer could be reduced to 40 nm, as Liu and Martin have achieved, much higher flux rates could be possible. The real difficulty, yet to be tackled, will be producing ultrathin films over enormous areas without introducing pinholes. A typical gas-separation module (6 feet by 10 inches diameter) contains thousands of tubules with thousands of square feet of surface area.

Ultrathin films could also be used in sensors[4]. For example, surface-acoustic-wave devices can detect mass changes of less than one nanogram per square centimetre, by exploiting resonant-frequency changes in piezoelectric crystals. Sensitive detectors with rapid responses could be made by adding a coating film of selectively absorbing polymer. In this type of sensor, the thickness is the main limitation to response time. Other applications of ultrathin films may include bioreactors or drug-delivery systems[5].

Liu and Martin indicated that they can synthesize ultrathin films of polymers with the ability to exchange ions, or that have photoactive or electroactive properties. The latter types include conjugated, conducting polymers, which have been investigated over the past 15 years for use as active components in batteries, electrochromic displays and solar cells, or as antistatic coatings, electromagnetic shields and 'smart' windows[6]. Even gas sensors which operate at room temperature and can detect minute quantities of hydrogen sulphide or ammonia in air are possible[7]. Recently we reported[8] that the doping process that makes polymers conducting can be used to induce permanent morphological changes in free-standing, environmentally stable polyaniline films. This process results in even higher gas selectivities for oxygen/nitrogen, hydrogen/nitrogen and carbon dioxide/methane. If ultrathin film concepts can be combined with the superior gas selectivity of conducting polymers many novel devices should be forthcoming. □

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CYSTIC FIBROSIS

Acidification indication

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CYSTIC fibrosis is caused by mutations in a single gene encoding the cystic fibrosis transmembrane conductance regulator (CFTR)[1]. Although recent studies suggest that CFTR is a Cl^- channel[2,3], it is not yet clear how this accounts for the numerous abnormalities of the cystic fibrosis phenotype. On page 70 of this issue[4], Barasch *et al.* present a hypothesis to explain how some of the abnormalities might arise.

Ten years ago, the literature on cystic fibrosis was in confusion, with descriptions of a huge variety of clinical manifestations[5] and many bewildering research observations. It was difficult to develop a unifying hypothesis about the underlying defect, other than to note that the disease primarily afflicted epithelia. Interest began to focus on Cl^- channels when Quinton[6] discovered that the sweat-gland-duct epithelia of cystic fibrosis patients had decreased Cl^- permeability and Knowles *et al.*[7] made similar observations using airway epithelia. Subsequently, defective cAMP-dependent regulation of epithelial Cl^- channels drew increasing attention; after all, this defect was responsible for an all-or-none difference between normal and cystic fibrosis cells in several organs[8]. But more quantitative and tissue-specific observations remained enigmatic, such as increased Na^+ absorption in airway epithelia and increased sulphation and reduced sialylation of glycoproteins.

With the discovery of the gene responsible for cystic fibrosis[1], and the realization that it encodes CFTR, work centred around how mutations in it might eliminate the function of cAMP-regulated Cl^- channels. It seems that CFTR is itself a cAMP-regulated Cl^- channel[2,3]; if so, a loss of Cl^- channel function is tied to the defective gene. This link begins to explain the pathophysiology in the sweat gland duct (a loss of Cl^- channel function causes the reduced Cl^- permeability and hence the failure to reabsorb Cl^- from the sweat), the pathogenesis of meconium ileus (defective Cl^- channel function would impair intestinal fluid secretion, thereby generating a dehydrated meconium), and the pathogenesis of pancreatic disease