of the actin protein filaments (which also are known to form ordered polyelectrolyte/lipid materials)[6]. Comparing their present results with the earlier work that used DNA and actin polyelectrolytes, Yang *et al.* show that the charge-matching principle can not only account for the stability and ordering of the complexes, but also for some finer structural differences between the various types of polyelectrolyte/lipid assemblies. Recent work, using α-helical polypeptides biologically synthesized through genetic engineering and tailored to have specifically chosen charge densities, illustrates this principle in a complementary way[7]. Complexes between charged membranes and α-helices are the structural cousins of the actin/membrane structure — forming double polyelectrolyte layers between the lipid bilayers (see Fig. 1b). In contrast, the virus/membrane materials of Yang *et al.* have a structure analogous to the DNA/membrane assemblies. Similar principles could be applicable to the design polyelectrolyte/lipid materials with non-lamellar architectures, using surfactants that promote the formation of hexagonal[8,9] or cubic[10] phases.

A surprising, and potentially useful, aspect of the virus/membrane assemblies is the high degree of structural order that they display despite the unusual size of the virus particles — they are ten times larger (thicker and longer) than the typical polymeric polyelectrolytes. The large lattice size of the resulting structure can be used to directly organize other macromolecules that might fit into the large empty channels in the polyelectrolyte/lipid complex (as shown in Fig. 1c). Yang *et al.* have used ruthenium dyes, but one can envision extending this strategy to other large organic and inorganic ions, or even nanoparticles. Further elaborations of the electrostatic self-assembly could involve synthesis of non-biological polymers with well-defined charge densities and conformations, as well as new lipids with charged groups of controlled size tailored to guide the ordering of organic or inorganic polyelectrolytes, such as nanoparticles or nanowires. Deeper understanding of new polyelectrolyte/lipid material architectures could also be gained from theoretical and computational studies that take into account the size and chemical structures of the interacting macromolecules and their respective counterions.

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POLYMERS

A multitude of macromolecules

The world of polymer science is running in 100 different directions. Some pursue the most basic chemistry and physics questions, others have immediate industrial concerns; remarkably, the end-points tend to converge.

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It is fascinating to observe the evolution of science in microcosm by observing what happens in one of its separate disciplines, as the famous polymer rheologist, John Ferry (1912–2003) once remarked. The 2004 IUPAC World Polymer Congress*, which took place in Paris, was an excellent place to observe the current state of evolution of polymer science. France is the home of two visionary spirits whose work is widely recognized to have transformed this discipline: Jean-Marie Lehn (Nobel Prize in Chemistry, 1987) and Pierre-Gilles de Gennes (Nobel Prize in Physics, 1991).

Good ideas spread quickly. If those prize-winning works were revolutionary at their time, they are so no longer. One of the most striking impressions from attending this congress was the absence of controversy. The discipline is varied, and it is vibrant, but no longer is it focused. It runs in 100 different directions at once! Still, there is the ageless distinction between those who make materials, and those who study them. In this personal account, we will highlight a few studies that bridge this gap using what is called by a fashionable name 'supramolecular architecture'.

Consider rubber. One ties one chain molecule to a second one, and this to a third, forming a cluster of molecules. If one continues tying the resulting clusters

*IUPAC (International Union of Pure and Applied Chemistry) MACRO 2004, Paris, France, 5–9 July, 2004.

of molecules together, the eventual result is rubber, a single macromolecule that spans its macroscopic container[1]. The formation of rubber is a continuous transition that contrasts starkly with the other liquid-to-solid transitions, such as water to ice. The crosslinking process, known as vulcanization of rubber, is one of the oldest discoveries of macromolecular science (made by Goodyear in 1839)[2]. What could possibly be added?

The novelty is that the paradigm of crosslinking can change. In all previous methods, crosslinked chains were tied together at specific sites: either by a chemical reaction or by some physical aggregation. It was only in theorists' dreams that chains would be tied together by 'slip-link' pulleys to model entanglements[3], and that elasticity of gels would be a consequence of their topology only[4,5]. This dream seemed dead from lack of implementation.

But advances in the field of rotaxanes showed that it is possible to thread some types of polymer chains through hollow ring-shaped molecules[6]. Kohzo Ito and co-workers (University of Tokyo), building on this earlier work, have discovered that these materials form unique solids when the rings are tied together[7]. Using clever chemistry, chains can be tied together entirely by topology, as theorists had dreamed. Fig. 1 shows this concept.

Kohzo Ito explained that although this new invention responds to forces elastically in the classic way of polymer rubbers, unprecedented new features are also present. The first surprise concerns the structure (probed by laser light scattering); the local 'butterfly' deformations are orthogonal to those in conventional rubbers. It implies that these gels are more liquid-like. In other words, disorder due to crosslinking is less important than the thermal disorder. Another surprise concerns the nonlinear elasticity of this new type of rubber; in contrast to all previous gels, which are either purely elastic or become softer as the deformation is increased, these slip-link gels become harder.

Hopefully other research groups will join their efforts and elaborate on these ideas to address the many questions that are only partially answered. In particular, still unclear is the extent to which the conceptual idea of having two chains tied together at well-defined slip-links (Fig. 1) has been strictly implemented. After chemists have sorted out the chemical details the challenge will return to the side of the theorists, who will need to explain the observed 'abnormalities' in the behaviour of slip-link gels.

Consider next the old question of polymer blending: coaxing two chemically distinct polymer chains to mix. The classical idea, built on seminal works of Paul Flory (Nobel Prize in Chemistry, 1974), was essentially that this cannot happen. The difficulty is simple to understand: enthalpic interactions are unfavourable in the absence of specific attractive forces such as hydrogen bonding or electrostatics; and entropy fails to come to the rescue unless chains are short. The now conventional solution is to combine two or more chemical moieties in a single copolymer made of two or multiple blocks[8]; this certainly helps, but doesn't solve all problems. Are there other options available?

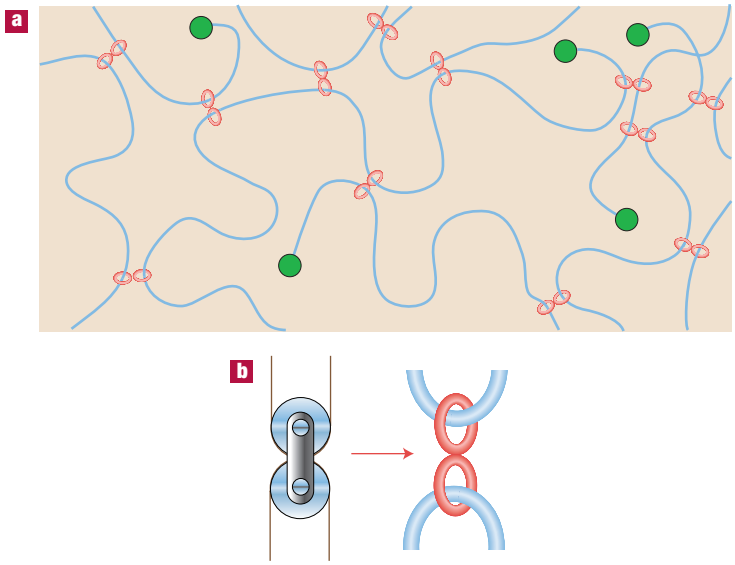

Figure 1 A theorist's dream come true. **a**, The slip-link gel prepared by crosslinking α-cyclodextrin in polyrotaxane has figure-of-eight crosslinks freely movable in polymer networks. **b**, Similarity between a figure-of-eight crosslink and a pulley. Figure adapted from material kindly supplied by K. Ito.

The field of polymer engineering knows many solutions that have received too little attention from polymer scientists. In a comprehensive review of the relevant techniques, Chris Macosko (University of Minnesota) surveyed the field of reaction engineering[9]. The main idea in this field is to mix small molecules, as is easy to do when they are small, and afterwards to crosslink them into long linear chains. Alternatively, it is possible to engineer intimate contact when the elementary building blocks are copolymers, and turn chemical polydispersity to advantage making use of principles justified by subtle ideas of statistical mechanics. Ludwik Leibler (ESPCI-Paris) showed both experimentally and theoretically that novel materials with interpenetrating chemistry, structured on submicrometre scales, can be thermodynamically stable[10]. In his talk, Leibler showed how these ideas developed from the work of a generation of polymer scientists around the globe, and concluded that these modern blends can be cost-effective on an industrial scale. This is cutting-edge macromolecular science — no need for a gap between fundamental understanding and technological relevance.

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