## POLYELECTROLYTE GELS

# Ionic partners split up

Polyelectrolyte gels are currently used as superabsorbers for polar solvents, such as water. Designing them so that the polyelectrolyte chains and their counterions don't get too close to each other makes them useful for absorbing less-polar solvents, too.

**Ralph H. Colby**
**is in the Materials Science and Engineering Department, Pennsylvania State University, University Park, Pennsylvania 16802, USA.**
**e-mail: rhc@plmsc.psu.edu**

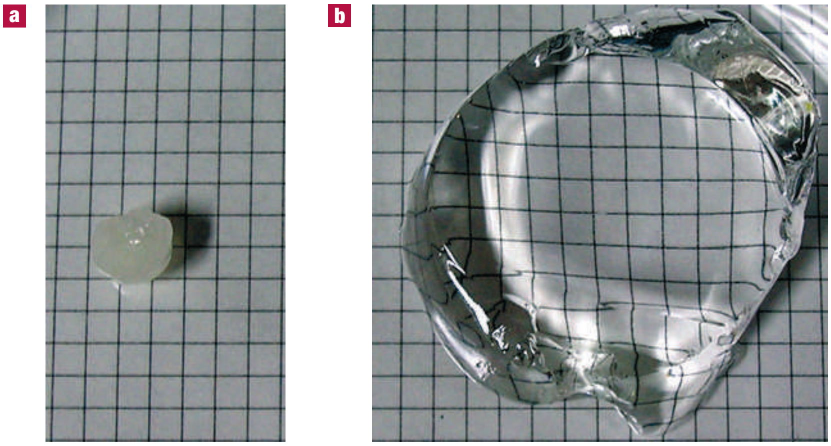

**Figure 1** Swelling of gel reported by Sada and colleagues[2]. **a**, Dried gel. **b**, Gel swollen in THF for 48 hours.

Polyelectrolytes — charged polymers with associated counterions — that form gels have long been used in babies' nappies and to clean up aqueous spills. These applications make use of the gels' remarkable ability to absorb large quantities of water that can be many hundreds of times the mass of the gel[1]. Charged gels are superior to neutral ones for these applications, because they swell to a greater extent, but they're only suitable for use in polar solvents such as water; in nonpolar solvents, they simply collapse. On page 429 of this issue, Sada and colleagues introduce a new class of polyelectrolyte gels[2] that swell in some common low-polarity organic solvents to sizes more than a hundred times their original volume (Fig. 1). The new gels enable a much wider range of solvents to be efficiently absorbed, greatly increasing their potential use for industrial spills. The authors hope that their design principles could be used to extend the range even further.

Neutral polymer gels are able to swell in low-polarity solvents because the increase in entropy associated with mixing polymer with solvent can stretch the polymer chains between crosslinks despite their restorative force. On the other hand, polyelectrolyte gels swell in polar solvents primarily because of the increase in entropy that comes from mixing counterions with solvent within the gel, which can be much greater than the entropy of mixing polymer with solvent[3].

Unlike in polar solvents, where the polymer ions and counterions can easily dissociate from each other and instead associate with solvent molecules — thereby becoming solvated — in less-polar solvents the oppositely charged ions in the gel tend to pair with each other. This ion pairing leads to dipolar attraction and aggregation that can cause the gels to collapse.

Sada and colleagues[2] have addressed this problem by creating polymer chains and counterions that both have four large covalently attached hydrocarbon or fluorocarbon groups. These prevent the ions from getting close enough to form strong ion pairs with each other in less-polar solvents[2,4,5]. As the counterions are kept apart by steric constraints, they can be effectively solvated, and can thus contribute to the entropy of mixing with solvent within the gel, causing the gel to swell.

To better understand the swelling mechanism, the authors also created neutral versions of their polyelectrolyte gels[2] — the same polymers but without attached ions or counterions. These swell most in chloroform, which has a dielectric constant, $\varepsilon$, of 4.8 (the dielectric constant is related to the polarity of a solvent — the lower the dielectric constant, the less polar the solvent). For solvents with a dielectric constant less than 5, the neutral and polyelectrolyte versions of the gels swell to similar extents[2], suggesting that the counterions do not dissociate in these solvents and that the polymer chains play the principal role in the gels' absorption properties. The swelling of both neutral and charged gels increases with solvent dielectric constant up to $\varepsilon = 4.8$. For dielectric constants between 5 and 10, the swelling capabilities of the neutral gels decrease as $\varepsilon$ increases, whereas the swelling of the polyelectrolyte gels increases[2] (Fig. 2), suggesting that counterions dissociate and their entropy contributes to the swelling of the gels. For $\varepsilon$ of 13 and greater, neither the neutral gel nor the polyelectrolyte gel swell much at all.

These experiments suggest that chloroform ($\varepsilon = 4.8$) is the best solvent for the polymer chains, presumably indicating that the neutral polymers themselves have dielectric constant near 4.8. The neutral gels show the usual poorer-solvent character, reflected in less swelling, as the solvent dielectric constant moves away from $\varepsilon = 4.8$. The polyelectrolyte gel has maximum swelling in a solvent of considerably higher dielectric constant (dichloromethane with $\varepsilon = 8.9$) than that of the neutral polymer, as shown schematically in Fig. 2. This suggests that, in contrast to the neutral gel, the paired ions in the polyelectrolyte gel raise the dielectric constant of the polymer, allowing swelling with more polar solvents. Once enough swelling occurs, some of the counterions dissociate, causing the increased swelling observed for polyelectrolyte gels compared with neutral ones[3].

A notable exception to the general picture described above is the solvent ethyl acetate, which does not swell either the neutral or polyelectrolyte gel at all, even though ethyl acetate has a dielectric constant of 6. Clearly, ethyl acetate has an unfavourable interaction with the polymer chain used to make these gels. Presumably another requirement for swelling polyelectrolyte gels is that the solvent must solvate the counterions, and ethyl acetate is known to not solvate ions and instead promotes the association of ions with each other[6].

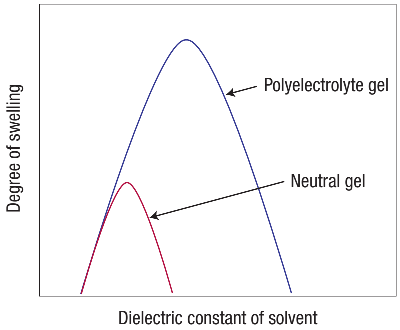

**Figure 2** Relative swelling degrees of neutral and polyelectrolyte gels.

A very interesting question is whether such gels could be used for separations. As tetrahydrofuran (THF; $\varepsilon = 7.5$) swells the gel greatly whereas dimethylformamide (DMF; $\varepsilon = 38$) does not, could these polyelectrolyte gels extract THF from a DMF/THF mixture? The entropy increase associated with mixing the counterions within the gel with solvent would have to work in opposition to the loss of entropy associated with the two solvents being separated.

In terms of applications, the most desirable possibility would be to find a gel that could absorb many times its mass of hydrocarbon oils to clean up oil spills that profoundly impact the environment[7]. Unfortunately, based on the fact that the maximum swelling of even these polyelectrolyte gels strongly decreases with decreasing dielectric constant of the solvent, the ability of a gel to absorb a solvent like a hydrocarbon oil, with $\varepsilon = 2$, is doubtful.

## References

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## MATERIAL WITNESS

# Feel the force

It was arguably high-temperature superconductivity that first made physicists realize how materials can be regarded as another 'variable' to be tweaked in the lab so that new aspects of physical phenomena can be probed. Of course, the history of using new materials to investigate new physics is older, perhaps beginning in earnest with the inception of semiconductor technology; but this was often characterized by a sense that one must take what one is given, or that at best a change of material offers minor variations on a theme.

The development of the new superconductors, though often hit-and-miss, showed that the nature of the material could be qualitatively bound up with the physics. With the advent of optical metamaterials, this notion has now been fully turned around: the physics, if you like, is put in by hand through materials design to enable things that elude nature.

The principle of using materials as a free parameter much like temperature or pressure is evident in recent proposals by Federico Capasso of Harvard University and his co-workers to engineer the Casimir force (F. Capasso *et al. IEEE J. Select. Topics Quant. Electr.* **13,** 400–414; 2007). This force between two objects separated by a very small gap arises from quantum zero-point fluctuations of the electromagnetic field between them: it is a kind of pressure due to the suppression of some fluctuation wavelengths in the intervening space.

Traditionally physicists have tended to regard the Casimir force as another 'given', a function merely of the geometry of the two interacting objects. The case of two metal plates first analysed by Hendrik Casimir in 1948 was later generalized by Evgeny Lifshitz to dielectrics, but that was about as far as it went in terms of recognizing a materials-dependent influence.

Although the Casimir force is basically the same phenomenon as the van der Waals attraction — crudely, it is what the latter becomes at larger separations — it is difficult to measure, because the interaction becomes strong only for rather large surfaces separated by small distances. Decisive high-precision measurements weren't made until 1997, and much recent work has focused simply on characterizing the force for real metals.

But the advent of engineering at the micro- and nanoscales has awakened interest in the consequences of the Casimir effect, both positive and negative, for devices such as microelectromechanical systems. Although this raises the notion of tuning the force to advantage, surprisingly little attention has been given to how the nature of the material might be exploited.

Capasso and colleagues show, for example, that a suitably chosen sandwich of layers should generate a repulsive rather than an attractive force, enabling 'Casimir levitation'. And materials with anisotropic optical properties (birefringence) would produce a force that varies with the angle between the optical axes, creating a torque. Capasso also suspects that an effect on the force should be felt when the materials undergo phase transitions, for example from metal to insulator or superconductor. All of this is largely unexplored territory, and promises rich pickings.

**Philip Ball**