and to be controlled by interactions between the adsorbed molecules. □

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Volume transition in a gel driven by hydrogen bonding

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INTERACTIONS between macromolecules fall into four categories: ionic, hydrophobic, van der Waals and hydrogen bonding. Phase transitions in polymer gels provide a means of studying these interactions. Many gels will undergo reversible, discontinuous volume changes in response to changes in, for example, temperature, gel composition or light irradiation[1–5]. These transitions result from the competition between repulsive intermolecular forces, usually electrostatic in nature, that act to expand the polymer network, and an attractive force that acts to shrink it. Volume transitions in gels have been observed that are driven by all of the above-mentioned forces except hydrogen bonding (ref 6–10; T.T. *et al.*, unpublished data; H. Inomata *et al.*, personal communication). Here we report on a phase transition in an interpenetrating polymer network of poly(acrylamide) and poly(acrylic acid) that completes this picture—it is controlled by cooperative 'zipping' interactions between the molecules which result from hydrogen bonding. Cooperativity is an essential feature of the interactions, in that independent hydrogen bonds would not provide a sufficient driving force for the transition. A further novel characteristic of this phase transition is that the swelling (in water) is induced by an increase rather than a decrease in temperature.

It is known[11–16] that poly(acrylamide) and poly(acrylic acid) form polycomplexes in solution through hydrogen bonding. The interpenetrating polymer network formed from these two polymers has been used for drug delivery systems, although volume transitions have not been observed[17]. To prepare such a network, we first prepared the acrylamide gel: 5 g of acrylamide and 0.133 g of N,N'-methylenebisacrylamide (BIS, crosslinker) were dissolved in 100 ml of water, to which 120 μl of tetramethylethylenediamine (accelerator) and 40 mg of ammonium persulfate (APS, initiator) were added[8]. The solution was inserted into capillaries of 0.34 mm inner diameter for gelation. The gels were extracted from the capillaries, washed with water, dried, and then inserted into capillaries of the same diameter. The dried gels were allowed to swell in a solution of 5 g distilled acrylic acid, 0.133 g BIS, 40 mg APS, and varying amounts of NaOH (which is necessary to ionize a fraction of the acrylic acid monomers; ionization was varied from 0 to 9 mol%) in 100 ml of water. Extensive polymerization took place at 60 °C.

Gel diameters as a function of temperature (±0.01 °C) were measured using a microscope. Figure 1*a* shows the swelling curves obtained as temperature was increased. The non-ionized gel undergoes a continuous transition at about 20 °C. The ionic gels undergo a discontinuous transition, often with the swollen and collapsed phases coexisting over a wide range of temperature. The horizontal lines in Fig. 1*a* denote the temperatures at which the collapsed phase disappears. The transition temperature decreases with increasing ionic content.

Figure 1*b* shows the swelling curves obtained as temperature was decreased. For the ionized gels, the transition temperature varies in different regions of the gel; the transition in Fig. 1*b* corresponds to the temperature at which a collapsed region first appears. The temperatures for collapse are lower than the temperatures for swelling (Fig. 1*c*). Hysteresis is more pronounced as the ionic content of the network is increased. The large hysteresis and relatively slow kinetics reflect the cooperative nature of the polycomplexation process.

To confirm the involvement of hydrogen bonding, we studied the effect on the phase transition of adding urea, which is known

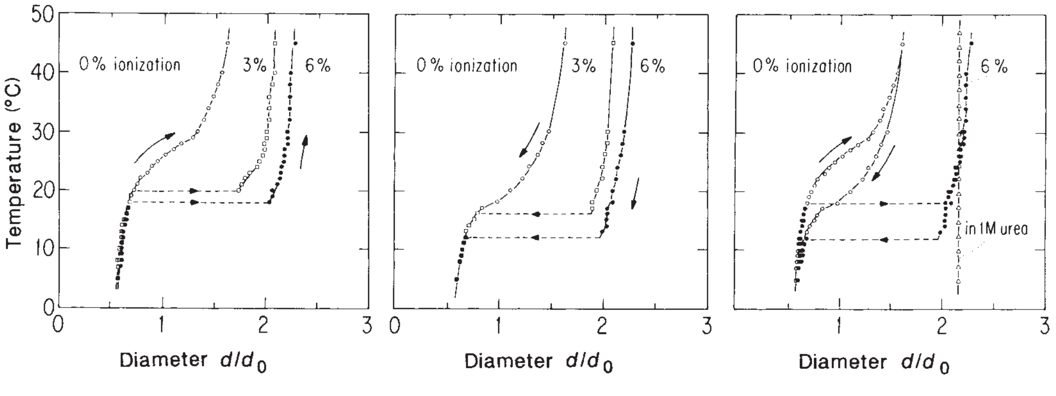


FIG. 1 Equilibrium diameter of the interpenetrating polymer networks of poly(acrylic acid) and poly(acrylamide) in water as a function of temperature. *a*, Increasing temperature. Original diameter $d_0 = 0.34$ mm. The percentage ionization refers to the acrylic acid groups. The transition is continuous for non-ionic gels but discontinuous in gels with ionization above 3%. *b*, Decreasing temperature. *c*, Superposition of two sets of data from *a* and *b*, and results for non-ionic polymer network in 1M urea solution (open triangles).

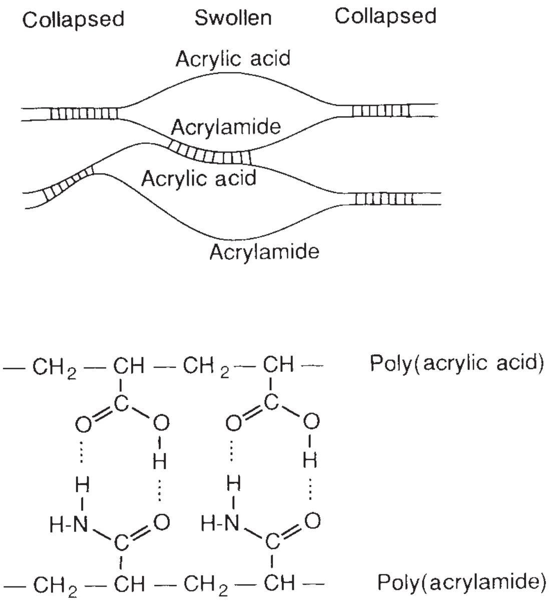
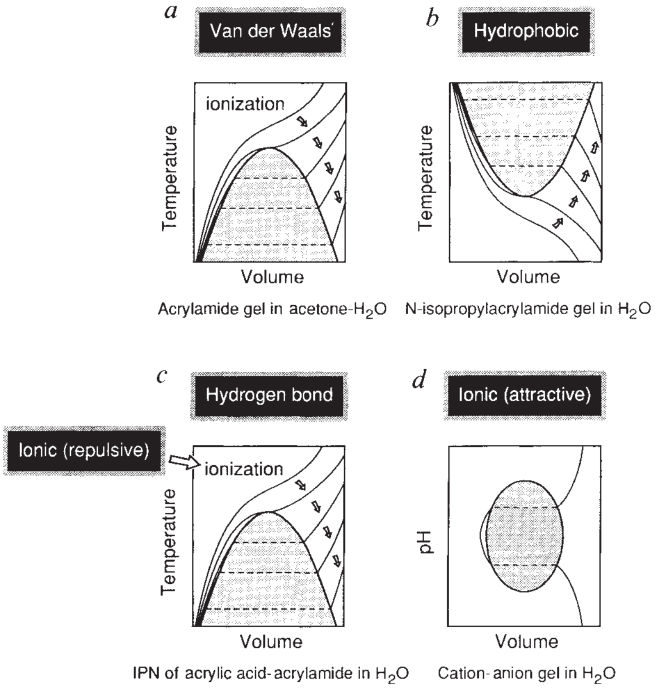


FIG. 2 Possible molecular configuration accompanying the phase transition of the interpenetrating polymer network of poly(acrylamide) and poly(acrylic acid).



Acrylamide gel in acetone-H_2O N-isopropylacrylamide gel in H_2O

IPN of acrylic acid-acrylamide in H_2O Cation-anion gel in H_2O

FIG. 3 Gel volume phase transitions induced by four types of intermolecular forces. *a*, The van der Waals interaction causes phase transitions in hydrophilic gels in a mixed solvent, such as an acrylamide gel in an acetone–water mixture. A non-polar solvent is needed to decrease the dielectric constant of the solvent. *b*, Hydrophobic gels, such as *N*-isopropylacrylamide gel, undergo phase transitions in pure water, from a swollen state at low temperatures to a collapsed state at high temperatures. *c*, Gels with cooperative hydrogen bonding, such as an interpenetrating polymer network (IPN) of acrylic acid/acrylamide gel, undergo phase transitions in pure water (the swollen state is the high-temperature state). The repulsive ionic interaction determines the transition temperture and the volume change at the transition[3]. *d*, The attractive ionic interaction is responsible for pH-driven phase transitions, such as that in acrylamide-sodium acrylate/methacrylamidopropyltrimethylammonium chloride gels[10].

to disrupt hydrogen bonds In the presence of 1M urea, a phase transition did not occur—the gels remained swollen over the entire temperature range (Fig. 1*c*). We checked that urea did not alter the phase behaviour of an acrylic acid/acrylamide copolymer gel, an acrylic acid/*N*-isopropylacrylamide copolymer gel, an acrylamide gel or an acrylic acid gel: it affected only the poly(acrylamide)/poly(acrylic acid) interpenetrating polymer network. Furthermore, in this system the only attractive force present to induce a transition is hydrogen bonding. These observations suggest that hydrogen bonding must indeed be responsible for the collapse of the gels. A possible molecular configuration that may accompany the gel phase transition is shown in Fig. 2.

It is now possible to classify all gel phase transitions in terms of the four biologically relevant intermolecular forces (Fig. 3), each of which may independently be responsible for a discontinuous volume transition in polymer gels. ☐

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Long-range transport of volcanic ash to the Greenland ice sheet

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BETZER *et al.*[1] reported the surprising discovery of 'giant' (>75 μm) mineral particles transported more than 10,000 km from their source. We have found volcanic ash containing glass shards as large as 300 μm in a section of Wisconsinian ice from the Dye 3 core in Greenland, which is similarly unexpected and raises interesting questions concerning the long-range aeolian transport of particulate matter. As the volcanic ash correlates well with similar ash in deep-sea sediment cores from the Atlantic, it also allows us to date the ice with some confidence.

The aggregates we found in the ice section range in size from a fraction of a millimetre to 3 mm and are scattered over a 78-cm-long section of ice core (Fig. 1). We examined two of the larger aggregates and found that they consisted mostly of highly silicic shards of clear glass, many of them >100 μm long. We also examined particles from one of the fine, parallel cloudy bands and found that they consist of similar volcanic ash particles. All the cloudy ash bands are parallel and inclined at an angle of 70° relative to the core axis, and several of them are very faint.

We retrieved one of the larger (3-mm) aggregates located 9 cm from the bottom of the section (Fig. 1) and examined it by scanning electron microscope (SEM). Figure 2*a* shows a representative group of particles from the aggregate. Most particles