



# The Gelation of Polyvinyl Alcohol with Borax

A Novel Class Participation Experiment Involving the Preparation and Properties of a "Slime"

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Classroom demonstrations are, in most instances, performed by the instructor or an assistant, with occasional involvement of a few student volunteers to enliven the presentation. Experiments that are done by every student in the class are rare, mostly because of cost, safety, and time considerations. In this report, we describe an interesting, safe, and inexpensive class participation experiment, easily and quickly done by all the students in small to moderately large lecture classes. It involves the preparation and observation of a borate cross-linked poly(vinyl alcohol) (PVA) gel which has such interesting properties that the popularity of this experiment among our students rivals that of the classic polymer demonstration, the Nylon Rope Trick (1).

Management of this participatory exercise is not difficult, even for moderately large classes. Students may form a line and each receive an expanded polystyrene cup containing about 50 mL of a 4% (by weight) solution of poly(vinyl alcohol). The instructor or an assistant then adds about 5–10 mL of a 4% (by weight) sodium borate (borax) solution to each cup. In practice, one does not need to measure these amounts very accurately. The student then stirs the mixture with a plastic spoon or wooden stirrer such as an ice cream bar stick or tongue depressor. Gelation begins almost immediately, and soon the material acquires the approximate consistency of a product known to most students as "slime". (The Slime sold as a novelty item in stores is a product of the

Mattel Toy Corporation, Hawthorne, California and is made by cross-linking guar gum with borax). After preparing the gel, students can grasp the material and knead it into an elastic, semi-rigid mass which has highly physical properties. For example, if the gel is simply suspended from the hand, it will flow and stretch. It can also be stretched by slow pulling although it will break if pulled abruptly. Chunks of the mechanically broken gel can be reworked into a single mass. When placed in a container, the gel assumes the shape of the container. When placed on a table or other flat, unbounded surface, it flows to form a film. A number of other intriguing experiments with commercial slime and other non-Newtonian fluids have been described. (2, 3).

The gelation experiment has been performed enthusiastically by audiences of various levels of sophistication. It has been done with elementary through high school and college level classes and has been included for discussion in a post-college professional education course offered to technical managers each year at Carnegie-Mellon University. It is also well-suited for use in special school or departmental events such as freshman science seminars or presentations for visiting prospective students and their parents. Quite aside from the undeniable entertainment value, the use of the experiment for science education is justified by the extremely interesting concepts of chemistry involved. These can be simply explained but are by no means simple-minded. Thus,

the exercise is of interest even at the level of advanced chemistry or polymer science instruction, depending on how deeply the student and teacher wish to explore the concepts related to the phenomenon.

### Relevant Concepts

While there are many concepts that can be illuminated by demonstrating the gelation of PVA with borate, the selection of these and the level of the explanation furnished must depend on the background, experience, and interests of the class or audience. The topics to which the gel experiment are pertinent include, but are not limited to, the following.

### General and Inorganic Chemistry

- 1) Borate chemistry, including structure and reactions.
- 2) Titration analysis of boric acid as aided by diol-borate complexation.
- 3) Dynamic equilibrium and restoration following displacement.
- 4) Water as a solvent and hydrogen-bonding agent; important in biology as well as chemistry.
- 5) Three-dimensional structure formation by multifunctional bonding agents.

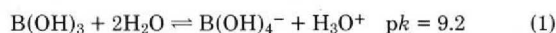
### Polymer Chemistry

- 1) Properties of poly(vinyl alcohol) and polyols in general.
- 2) Swollen polymer networks.
- 3) Viscoelastic and mechanical behavior of polymer networks.
- 4) Cross-linking of polymer chains.
- 5) Hydrogen bonding and water-soluble polymers.

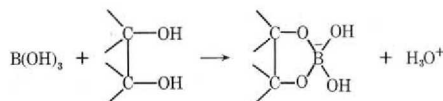
### The Chemistry of the System

The chemistry by which a cross-linked polymer gel is produced from linear polymer molecules has a straightforward explanation. Borax [ $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ], the salt of a strong base and a weak acid, hydrolyzes in water solution to form a boric acid-borate buffer having a pH of around 9 (4).

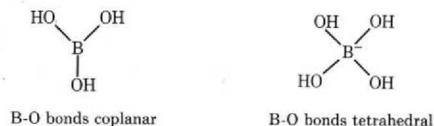
The buffer equilibrium is written as



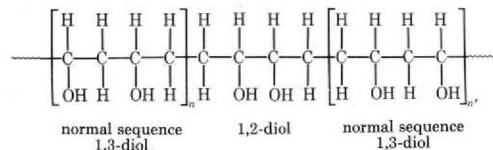
Note that boric acid is such a weak acid that it actually does not give up  $\text{H}^+$  but rather accepts an  $\text{OH}^-$  from the water. At low concentrations ( $\leq 0.025M$ ) both boric acid and borate ion are present as the monomeric species having, respectively, the structures



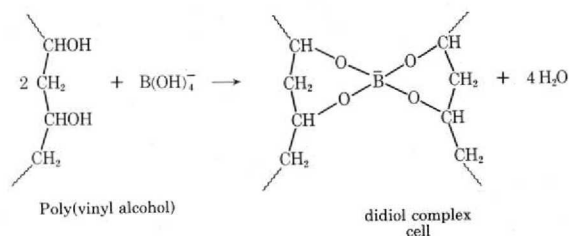
At higher concentrations borate can form cyclic tetramers and other polymers, but in the concentration employed in the gelation experiments these are not present. It has been helpful to analytical chemists who wish to titrate boric acid to exploit the fact that adding polyhydroxy compounds such as glycerol and mannitol to boric acid solutions increased the acid strength and makes boric acid titratable with strong bases (5). The diol complex must have the cis configuration, and a possible formulation for the increase in acidity on complexation is



Note that boric acid treated in this way is titrated as a monobasic acid. Many water-soluble natural products such as guar and other gums also contain long-chain polyalcohols which provide 1,2-diol groupings capable of complexation with boric acid (6). The same capability is inherent in the synthetic water-soluble polymer, poly(vinyl alcohol), which has occasional 1–2%, 1,2-diol structures amid a more predominant pattern of alcohol-OH groups on alternating carbons of the polymer backbone (7), i.e. 1,3-diol structure

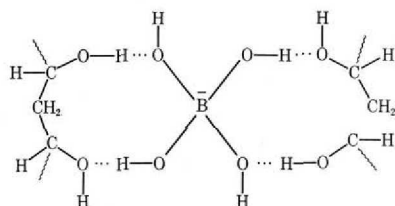


The interaction of long-chain polyols with borate ion is even more interesting than the complexation of boric acid, however, as it leads to the cross-linking of different polymer chains, or sometimes parts of the same chain, in such a way that a three-dimensional structure (network) of connected chains is formed. When the concentration of cross-linked chains is high, solvent is to a large extent immobilized in the network and a semisolid gel results. Examples of networks and gels are rubber and rubber cement, gelatin and rennet desserts, fruit jellies, agar gel media for bacterial culture, soybean curd (tofu), and yogurt. To be an effective cross-linker, a reactant must have at least two available functional groups. In reaction with 1,2-diol structures boric acid meets this minimum requirement, but, since the reaction occurs with adjacent alcohol groups on a single polymer chain, no cross-linking results. Therefore, boric acid alone does not produce polyol gels but must be partially neutralized (or better yet be wholly in the form of the borate ion) to serve as a cross-link agent. Borate ion is tetrafunctional in interaction with alcohol -OH group, and, thus, is particularly effective in creating three-dimensional gel networks from gums or poly(vinyl alcohol). The picture given below, though oversimplified, if extended in space and in three dimensions, may help in visualizing the network complex. One also should not lose sight of the fact that most of the space within the gel is taken up by the water molecules of the solvent environment: the gel in our demonstration is composed 96% of water.



The above representation is misleading in the sense that it seems to imply covalent bonds connecting boron to oxygen to carbon atoms. This cannot be the case, however, if we consider how readily the bonds must form, break, and reform to account for the physical properties of these borate gels. The properties of the poly(vinyl alcohol) borate gel can be rationalized by assuming that the borate cross-linkages are not fixed but break and reform easily, i.e., the system is said to be in a state of dynamic equilibrium (6). The lability and reversibility are demonstrated by the readiness of the gel to turn fluid under mild shear stress and by the complete reversibility of the gelation process when the gel is placed into water. The bonding created by the cross-links is so weak that it can have no semblance of covalent bond character nor, because the cross-links are made and unmade so readily,

can esterification be involved. Borate esters, in fact, require catalysts and energy input for their formation (4). It is likely, instead, that hydrogen bonding interactions are responsible for the observed properties, a view supported by study of the infrared spectra (8). This is a far different case from that of a familiar network polymer, vulcanized rubber, where permanent cross-links are formed by carbon-sulfur-carbon covalent bonds between chains. The structure below indicates schematically how hydrogen bonds might figure in a cross-linked but labile network.



Some aspects of the solubility behavior of poly(vinyl alcohol) are relevant to the gelation by borate and illustrative of the importance of the hydrogen bond (9). Long-chain polyalcohols such as natural gums and synthetic poly(vinyl alcohol) by reason of their high molecular weights and carbonaceous structures would hardly be expected to be water soluble. High solubility in water is conferred on them through the presence of numerous  $-OH$  groups along the main chains, groups which through hydrogen bonding with water molecules maintain the long chains in solution. Indeed, the solubility of poly(vinyl alcohol) is diminished when its solutions are heated to temperatures where hydrogen bonding and water structure are disrupted—an interesting phenomenon in view of the mindset we have that warming the solvent invariably aids dissolution of a solute. The hydrogen bonds between the  $-OH$  group on a polymer chain and water are individually very weak, nowhere near as strong as the covalent bonds between the carbon atoms of the polymer chain. However, the cooperative effect of large numbers of  $-OH$ 's not only accounts for the solubility of the chains but also for the fact that borate cross-links produce a solvated three-dimensional structure (gel) rather than an insoluble precipitated borate complex. The rigidity of the gel at rest arises because the polymer chains, normally flexible and coiled, are stretched and the network distended because of the equilibration of two opposing tendencies: the solvated chains are impelled to disperse in the water, while the cross-links constrain them to remain together. If the cross-links are weak (e.g. hydrogen bonds) the network is easily disrupted by deformation through handling, squeezing, stirring, pouring, or other methods by which shear stress can be applied. It is, however, relatively easy for the bonds to reform because of the propinquity of  $-OH$  groups and borate ions. Extreme dilution with water has the effect of disrupting the weak linkage between  $-OH$  and borate and separating the components so that the gel is not readily reconstituted.

## Preparation and Experimental Details

### Poly(vinyl alcohol)

The success of the experiment depends first of all on using the proper poly(vinyl alcohol). This polymer is manufactured by hydrolyzing poly(vinyl acetate), (7), and for various applications different degrees of hydrolysis are desired. Highly hydrolyzed polymer furnishes the largest number of alcohol  $-OH$  groups in orderly array along the backbone chain, uninterrupted by acetate groups which do not participate in gelation. This maximizes the cooperative action of multiple hydrogen bonds in creating a stable network. Further, high molecular weight of the polymer is important for

good mechanical strength of the network. Therefore use only 99–100% hydrolyzed poly(vinyl alcohol) having a molecular weight of at least 100,000. The material we use may be obtained from Eastman Kodak Co. ((800)-225-5352); it is usually delivered within 1 week of order (viscosity of a 4% aqueous solution at 20°C is reported to be 55–65 cp). A 4% solution calls for adding 40 g of poly(vinyl alcohol), a powdered solid, to about 1 L of tap water. Slowly sprinkling the powder onto the surface of the water while it is stirred will insure that the grains of polymer are individually wetted and will begin the slow process of swelling through imbibition of solvent that precedes the actual dissolution of the polymer. Failure to stir during this addition, and during subsequent slow heating to accelerate the dissolution, will result in a gluey mass of wet polymer which sticks together, settles out, clings to the walls of the vessel, and in general is less than cooperative with attempts to bring it into solution. (This is typical polymer behavior, as experienced polymer chemists know all too well.) Moderate heat (up to 90°C) will help speed dissolution, but do not overheat for two reasons: accelerated evaporation from the surface of the solution leaves a crust or scum of polymer there, and (as mentioned earlier) very high heat interferes with dispersing this material whose solubility is partly a consequence of hydrogen-bonding interaction with the solvent. The finished polymer solution will be clear, nearly colorless, and rather viscous.

### Borax

Any available solid borax [ $Na_2B_4O_7 \cdot 10H_2O$ ] in powder or crystal form may be dissolved in tap water at room temperature to make a 4% by weight borax solution. Note that the volume of this reagent needed to produce the gel is only 1/10 to 1/5 the volume of 4% poly(vinyl alcohol) solution.

### Gel Preparation

One volume of borax will get ten volumes of poly(vinyl alcohol) solution. Add the cross-linking agent to the polymer with rapid and vigorous mixing, continued until the mixture has gelled. The best mixing utensils are stiff, with wide flat surfaces (recall mixing pails of paint!), so ice cream bar stirrers or tongue depressors are advised rather than rod-like stirrers or plastic spoons. Expanded polystyrene or paper drinking cups are suitable vessels.

### Safety Considerations

The stock solutions of polymer and borax will keep for months at room temperature. Handling and transfer is safer if plastic rather than glass bottles are used. On prolonged storage the polymer solution may develop colonies of mold or micro-organisms, and for both esthetic and health reasons it should be discarded when this occurs. Although there are no known toxic effects produced by borax, the polymer itself or the gel, students should wash their hands thoroughly after handling them, as is only good practice. There is no reason not to allow students to take the gel away with them, either in the mixing cup and/or in a plastic bag. They should be warned not to create messes by getting it on clothing or furniture, not to allow young children to play with it, and certainly never to ingest it or leave it anywhere someone else may do so. Cleanup of any residue that may accidentally get onto clothing or desks is easily accomplished with water. Handling the gel contaminated it, leading sometimes to the growth of molds. Clean gel, however, will dry slowly if exposed to air, leaving a transparent glassy film of PVA.

### Variations

Many simple variations and extensions can be done with this experiment. For example, a water-soluble food coloring

can be added to the poly(vinyl alcohol) solution prior to the borate addition. Also, students can write their names with a felt-tip marking pen with water-soluble ink on a piece of ordinary white paper. When the colorless gel is placed on the names, the water-soluble inks will be lifted, and students will see the mirror image of what they wrote appearing in the gel. Fluorescent water-soluble inks (the types found in the common highlighter pens) yield dramatic results especially if an ultraviolet light source is available. A much more fluid gel can be prepared by using a 2% by weight poly(vinyl alcohol) solution. This illustrates the effect of concentration on the consistency of the gel.

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