Chemically reversible hydrogels have been obtained by combining poly(vinyl alcohol) (PVA) with water-soluble polymers containing a low fraction (~5 mol%) of units with phenylboronic acid (PBA) functionality. Interpolymer association occurs via formation of boronate esters between the PBA units of the water-soluble polymer and the diol groups of PVA. Compared to the classical gels formed by PVA and sodium borate, the present systems form stronger gels (higher elastic modulus, longer relaxation time) over a broader pH range. Pronounced viscoelastic behaviour was observed even at pH ~ 6, i.e. well below the pH range in which the PVA/sodium borate system works. The higher efficiency of the present systems is mainly attributed to the multi-functional character of the PBA-appended chains which can connect several PVA chains at the same time.

The properties of our systems depend strongly on the nature of the PBA-appended polymer. Four types of water-soluble backbones have been tested: poly(N,N-dimethylacrylamide) PDMAM, poly(N-isopropylacrylamide) PNIPAM, poly(allylamine) PAA, and poly(ethylene-imine) PEI. PAA was found to be the most efficient in inducing gelation with PVA. This was attributed to the presence, along the linear PAA chain, of primary amine groups contributing to the stabilization of the boronate esters. On the other hand, PEI which also has amino groups but is highly branched is less efficient in forming gels with PVA. Finally, PNIPAM which exhibits LCST behaviour in aqueous solvents, forms thermoreversible gels when mixed with PVA. The viscolelastic behaviour of these systems was further tuned by adjusting the fraction of PBA units incorporated to the water-soluble polymer.

Schematic representation of the inter-polymer association via boronate ester formation.