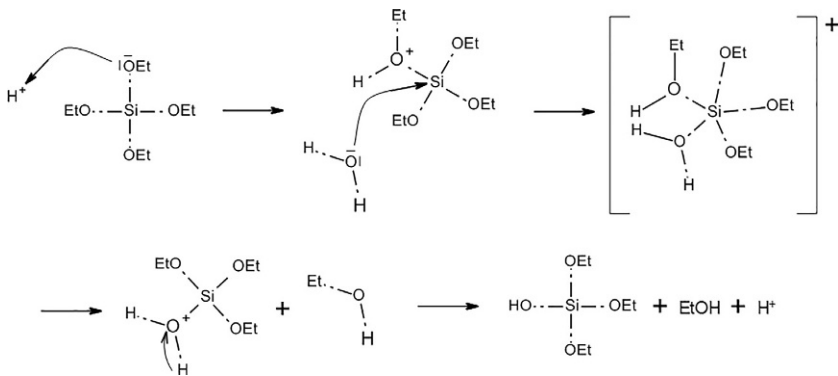


enthalpy at a so-called glass transition temperature ( $T_g$ ). At  $T_g$ , the glass is thus obtained. If  $T_g$  is exceeded, the thermal agitation, which has become too great, leads to the destruction of the amorphous network by releasing the bonding energy. This phenomenon is visible by an exothermic peak on DTA analysis, corresponding to the crystallization temperature ( $T_c$ ) of the compound. During cooling, the amorphous character of the material is no longer conserved and a new crystallized arrangement of the atoms can be observed by X-ray diffraction. As the temperature increases, the ion diffusion is increased and the last gaseous compounds occur. They are visible on Thermogravimetric Analysis (TGA). The expansion of the material also increases with temperature. If microscopic cracks exist in the gel, they will then become macroscopic during the heat treatment, which often reduces the massive samples into small fragments.

To allow the formation of perfectly amorphous sol-gel glasses, the kinetics of the formation of the gels must be understood. The hydrolysis-condensation reactions, which take place in the sol during gelation, are of the second-order nucleophilic substitution type (SN2) (Brinker, 1988). The length of the carbon chains of the organic substituents of the alkoxides will thus have an influence on the reactivity, as well as on the electronic configuration of the central atom. This latter parameter is strongly influenced by the pH of the reaction mixture, thus allowing the use of acids (Balamurugan et al., 2006) and bases (Pope and Mackenzie, 1986) as catalysts for the gelation of TEOS and PET.

The hydrolysis of TEOS in an acid medium leads to a positive reaction intermediate, unstable and poorly solvated in the alcoholic medium as schematized:



So, TEOS is never fully hydrolyzed. This partial hydrolysis of the precursor has a consequence on the structure of the aggregates condensing in the sol: the molecules align themselves on a linear structure, close to that which can be observed for a conventional polymerization in organic chemistry (Pohl et al., 1985). Chains grow in the sol over time and become longer and longer. The gel point is reached when the chains end up tangling with each other: a vitreous network is formed and densifies.