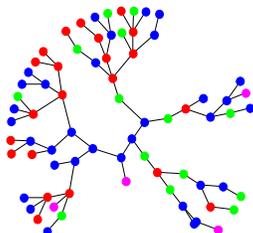


seminar 20-1-2010

Statistics of random branched polymers,  
stepwise polymerization of polyfunctional monomers bearing A and B coreactive groups.



Schematic drawing of a single branched polymer molecule.

One of the reaction mechanisms with which in the chemical industry polymers are produced, is stepwise polymerization of so-called polyfunctional monomers. These monomers are rather simple molecules and form the building blocks of much larger polymer molecules. Each monomer bears one or more reactive atom groups of type A (e.g.  $-\text{COOH}$ ) and/or of type B (e.g.  $-\text{NH}_3$ ). An A group on one monomer might react with a B group on another monomer, thus forming a bond between the two monomer units. Reactions on the same polymer molecule lead to ever larger molecules. Two A groups do not react with each other, neither two B groups. Monomers with three or more reactive groups, that is with functionality  $\geq 3$ , act as branch points in a polymer molecule (if all groups have reacted).

During the reaction, a byproduct (e.g.  $\text{H}_2\text{O}$ ) is formed. By removing this byproduct from the reactor vessel, the degree of conversion – that is the fraction of reactive groups which have actually reacted – can be controlled.

The chemical reaction is a random process; each reactive group has equal probability to react. Small, large and very large polymer molecules are formed. We are interested in the statistical properties of the quasi infinite set of molecules: i.e. the molecular size distribution, the molecular weight distribution, the average number of branch points per molecule, the average length of the linear segments between two branch points, the radius of gyration, etc. To a large extent, these properties determine the visco-elastic behavior of the polymer. It is cost effective to replace laborious experimentation by modelling calculations.

The polymer molecules can be considered as “trees” from graph theory. We have derived a set of three coupled polynomial equations for the three generating functions “generating” the molecules. The corresponding set of recursive relations can be solved – within a practically feasible amount of computer time - for molecules of moderate size, that is comprising 1000 or less monomer units. Asymptotic methods from analytic combinatorics have come to rescue to obtain the statistical properties of the very large molecules, and just these molecules – although relatively few in number – have large influence on the performance of the polymer.

We will present the set of coupled polynomial equations for the three generating functions, derive the asymptotics and discuss further problems and applications.