“Did you know? July-September 2026"

Did you know ..... that chain transfer agents (CTA) arc used to limit the extent of crosslinking in emulsion polymerizations (EP) of synthetic rubbers (think polybutadiene, PBd)? These rubbers gain their elasticity via the crosslinking that naturally occurs in the /at/er portions of the latex reaction. This issue of our •"Did you know .... "Presentations is the 5th in a multi-part series that collectively discusses the molecular weights typically produced in both batch and semi-batch emulsion polymerization (EP) processes. the effectiveness of chain transfer agents (CTA) in both process types~ and the possibility of polymer chain branching and cross-linking in the latex particles. In the current issue we address the mechanism by which the CTA limits the crosslink density of synthetic rubbers produced in latex form.

In general, linear polymer chain lengths produced in free radical polymerizations depend upon the rate of propagation of the polymer radical and the rate at which chain growth is stopped (due to termination or chain transfer). the so-called initiation, propagation, termination sequence. This is certainly true in EP. Here we have latex particles constantly receiving oligomeric radicals (typically containing ~3-6 monomer units) from the aqueous phase - some of these radicals grow into high M\V polymer and some terminate other polymer radicals already in the particles. When butadiene is the monomer (often with a small amount of styrene or acrylonitrile comonomer) and the latex reaction is carried out as a batch process, the probability of crosslinking reactions occurring increases as the monomer concentration in the latex particles decreases (as you may know, this monomer reduction proceeds uniformly during the last -60% of the batch reaction). Should the producer wish to limit the extent of crosslinking from its uncontrolled value~ the addition of CTA can accomplish that task.

The mechanism of crosslinking involves a series of chemical reactions. The first, of course, is the production of linear chains propagating within the latex panicle that already contains dead polymer chains. The second involves proton transfer from the propagating chains to the backbone of the existing dead polymer chains, thus creating a '"mid-chain radical'· on the otherwise dead polymer chain. Eventually, this mid-chain radical adds a monomer unit and a branched, radical chain is created that propagates with time. At last, two of these propagating branched chains terminate by recombination, linking the two original dead (and maybe linear) chains. Although the detailed mechanism can be more complicated than this, the above description will serve adequately to now introduce the role of a CTA in altering the probability of one or more of the above reactions taking place.

There are 2 types of polymer radical chains in the latex particle at any point in time - linear chains and branched chains. The CTA can interact with both of these~ but the ones leading to crosslinking control are the branched. radical chains. When that happens. the branch is terminated by proton abstraction with the CTA (e.g. C12H21SH) and the possibility of that branch leading to crosslinking is eliminated. In that W:t) the suppression of crosslinking from its unmodified level (that without CTA) can be controlled by the type and level of the CTA in the latex recipe. This has been known for more than 80 years the famous GRS Rubber Latex recipe developed in the 1940s for the production of automotive tires is shown below.

Water 180 parts
1-3 butadiene 75 parts
Styrene 25 parts
"Soap" 5 parts
Mercaptan (t-dm) 0.5 parts
Potassium persulfate 0.3 parts
Ferrous sulfate 0.1 parts

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