Summary

Living radical polymerization represents a number of techniques which have drawn considerable scientific interest over the last few years, because they allow the preparation of complex polymer architectures in a relatively simple way and starting from a broad range of monomers. One of the latest of these techniques is RAFT polymerization (Reversible Addition–Fragmentation chain Transfer). Its reversibe deactivation mechanism is based upon a transfer reaction rather than a termination reaction which characterizes a number of other popular polymerization techniques. This has several important consequences for the polymerization kinetics and process. A conventional initiator can be used while the steady state concentration of radicals is determined by the equilibrium between initiation and termination, similar to a conventional free-radical polymerization. For this reason, a RAFT agent can be added to an existing recipe without any drastic changes in the polymerization procedure. The resulting polymer, however, will have a predetermined molar mass and monomer sequence distribution.

One of the most prominent kinetic parameters in RAFT polymerization is the transfer constant. Its effect on the molar mass distribution is illustrated by a number of computer simulations. These simulations indicate that a minimum transfer constant of ten is required to prepare low polydispersity material in a batch reaction. The evolution of the concentrations of a series of oligomers was analysed using high performance liquid chromatography. Comparison of these concentration profiles with computer simulations allowed an estimate to be obtained for the transfer rate coefficient of dormant polystyryl RAFT agents based on the dithiobenzoate moiety. Its value was found to be 1,000 to 10,000 times larger than the propagation rate coefficient, which ensures living characteristics under nearly all circumstances.

The radical concentration in RAFT polymerization should be the same as in a similar recipe without RAFT according to the mechanism, that is proposed in the literature. In practice, however, retardation is observed, which was investigated with the aid of computer simulations. This revealed that the explanations that are proposed in the literature are unrealistic. Termination of the intermediate radical, which is formed in the transfer reaction, is then proposed as an alternative explanation. Simulations demonstrate that this additional reaction pathway can explain the retardation without affecting the molar mass distribution, as is observed in practice.

Besides, accepted values can be used for the kinetic parameters in the polymerization scheme while the concentration of the intermediate radical agrees with experimental data reported in the literature.

The robustness and versatility of the RAFT process is further illustrated by the controlled copolymerization of styrene and maleic anhydride. The anhydryde monomer could not be polymerized in a controlled manner by other living radical techniques, but the application in RAFT polymerization allowed the preparation of low polydispersity copolymers of predetermined molar mass. A macromolecular polyolefin-based RAFT agent allowed the formation of poly(styrene-*block*-[ethylene-*co*-butylene]) and poly([styrene-*co*-maleic anhydride]-*block*-[ethylene-*co*-butylene]), polymers which are expected to show interesting properties, *e.g.* as compatibilizers.

It was shown that the labile colored dithiobenzoate group could be removed from the polymer chain quantitatively by photolysis. After this process, the molar mass distribution not only showed signs of the bimolecular combination product, but also of the terminated intermediate radical with a triple molar mass. The absence of monomer during photolysis allowed this species to be detected, thereby providing experimental evidence for the occurrence of this reaction.

The application of RAFT in emulsion polymerization is an important aspect when it comes to industrial acceptance. This application is also interesting from a scientific point of view as compartmentalization of the radicals leads to a reduction of termination, thereby improving the quality of the living process.

Both seeded as well as *ab initio* batch emulsion polymerizations are characterized by colloidal instability, a low RAFT efficiency, inhibition and retardation. These effects were first attributed to transport phenomena concerning the RAFT agent as the consumption rate of highly reactive transfer agents is known to be limited by the interphase transfer rate in many emulsion systems. Similar problems were observed, however, in miniemulsion polymerization in which phase transfer phenomena are essentially eliminated. A more thorough kinetic analysis of the emulsion polymerization demonstrated that the shift of the radical chain length distribution towards lower values increases the radical exit rate leading to a slower polymerization, while also particle formation is hindered. The key factor behind the instability in miniemulsion polymerization appears to be of a more thermodynamic nature. Droplet nucleation disturbs the metastable equilibrium between the droplets and causes a small number of droplets in which the RAFT agent has been transformed into dormant oligomers to attract monmer from the unnucleated droplets. This hypothesis is, however, based upon elimination of alternative explanations and has not yet een verified experimentally.

When anionic surfactants were replaced by nonionics, the efficiency of the RAFT agent in miniemulsion polymerization was enhanced. Although stability problems could not be completely overcome, they were reduced to such an extent that they were no longer of importance on the polymerization timescale. This allowed living radical polymerizations to be conducted in a heterogeneous medium with the advantage of radical compartmentalization, leading to well-defined homopolymers (of methyl, butyl and 2-ethylhexyl methacrylate) but also allowed the preparation of 'designer-latices'. Depending on the process conditions (batch *vs.* semi-continuous), surfactant concentration and initiator, either exceptionally pure block copolymer latices could be synthesized (poly(2-ethylhexyl methacrylate-*block*-[methyl methacrylate-*co*-methacrylic acid])), or latices with an interesting bimodal particle size distribution could be obtained, consisting of a large number of small poly(methyl methacrylate) hard spheres and a smaller number of large poly(methyl methacrylate-*block*-2-ethylhexyl methacrylate) soft spheres of controlled molar mass.

All in all it may be concluded that the increased insight obtained in the mechanism of RAFT polymerization in (mini)emulsion has led to strongly improved microstructural control of the (co)polymers prepared.