

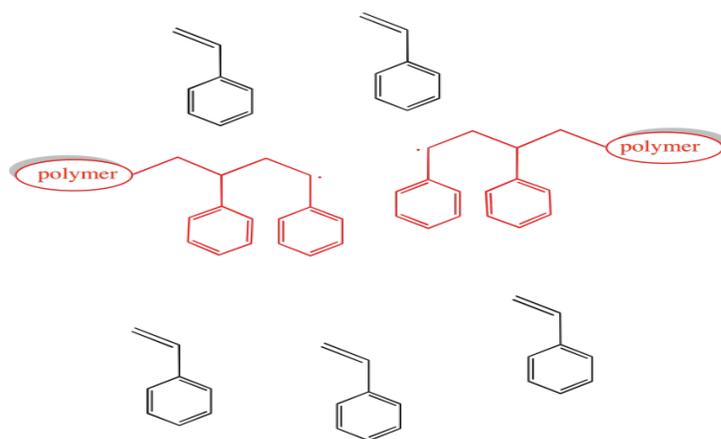
LIVING RADICAL POLYMERISATION

Chain polymerisation reactions result in the efficient conversion of monomers into high molecular weight polymers. However, chain termination events result in a broadening of the polydispersity index of the material. In other words, instead of producing a material composed of molecules that are all about the same molecular weight, a wide range of sizes of molecules result. Some of the chains are very short and others are very long. That's a problem, because the chain length (and the associated property, molecular weight) strongly influence the properties of the material. If the size of the molecules is not controlled, neither are the properties. If the properties are not controlled, the material won't perform reliably in its intended application.

Living polymerisation refers to processes in which unexpected chain termination does not occur. The chain keeps growing and growing as long as more monomer is supplied. In extremely hardy cases, the term "immortal" polymerisation is sometimes used.

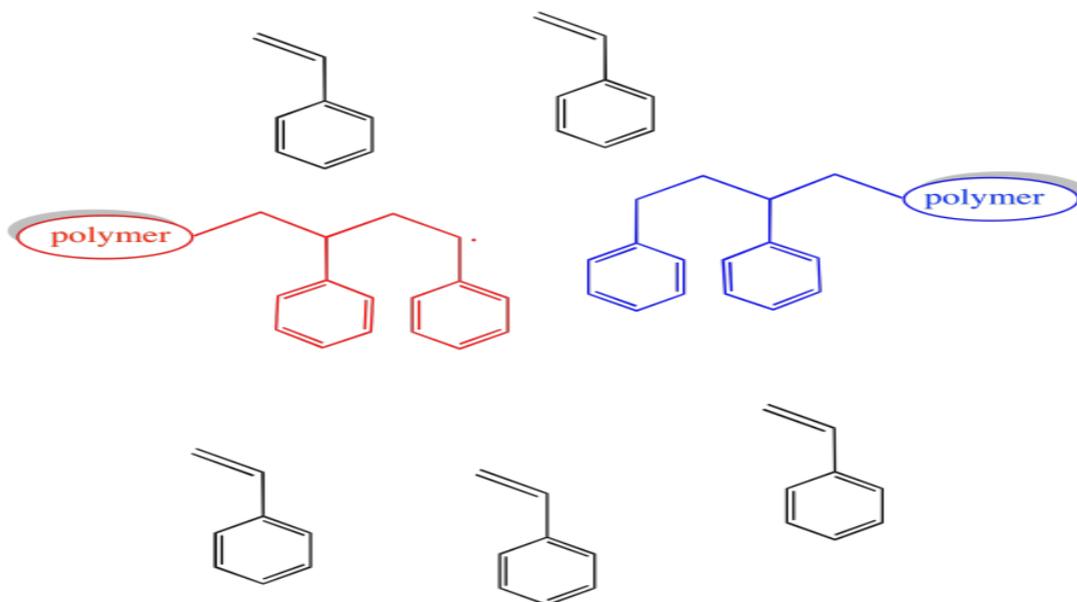
Typically, strategies for living polymerisation involve controlling the reactivity of the intermediates. Frequently, the concentration of the growing chains is kept low. If the concentration of growing chains is kept low, then unexpected side reactions involving the reactive growing chain will be kept to a minimum.

In radical polymerisation, growing chains with radicals at their growing ends will be surrounded by monomers. The radicals devour and enchain the monomers as they move through the reaction medium.



Typical chain-terminating events in radical polymerisation involve the collision of two growing chains. That event could result in head-to-head radical recombination, formation of a double bond via hydrogen abstraction at the head of a chain ("head biting") or formation of a new radical along the backbone of the polymer ("backbiting").

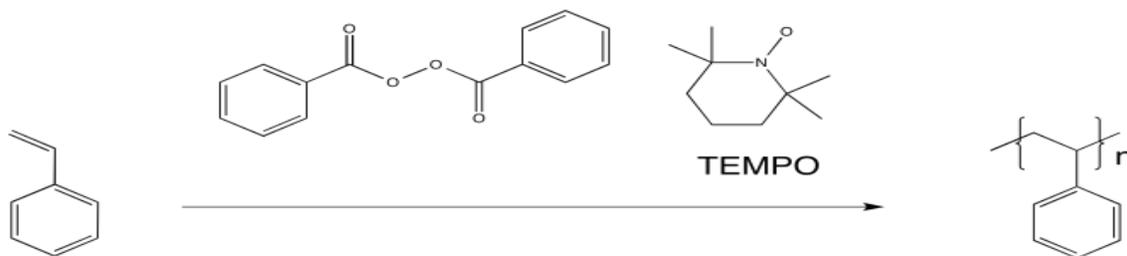
If the concentration of growing chains is limited, then the probability that any of these events will occur is also limited.



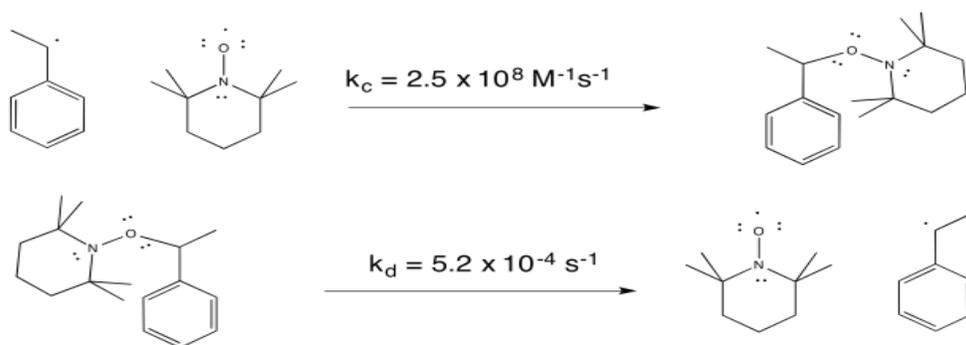
Certainly, the rate of chain growth also slows when the concentration of growing chains is lowered. That is the price to pay for a smooth operation.

The key to living radical polymerisation is to reversibly stop chain growth, sending a polymer chain from an active state into a dormant state. While in the dormant state, the polymer chain is less likely to undergo random chain-termination events. It can't grow, either, until it is brought back into an active state.

Researchers at IBM found that polystyrene polymerisation proceeded much more smoothly when TEMPO, a relatively stable radical, was added to the reaction. The reaction also proceeded more slowly, resulting in overall lower molecular weight of the polymer. However, the distribution of molecular weight was much more uniform. All of the chains were of similar sizes, relatively speaking. As a result, the properties of the material were much more controlled.

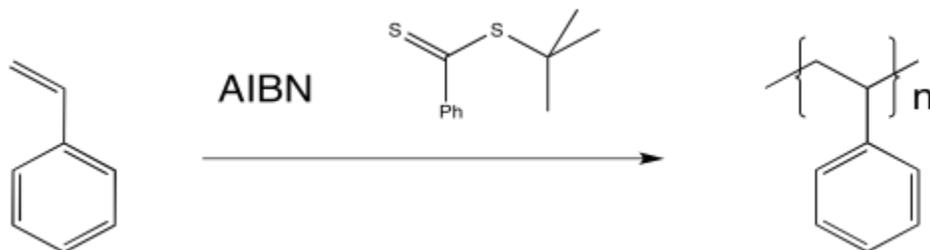


TEMPO helps to control the polymerisation by forming a reversible bond with the growing end of the polymer chain. The radical on TEMPO combines with the radical on the head of the polymer to form a C-O bond. The bond can break again (unusually, for a C-O bond), allowing the polymer chain to resume growing periodically.

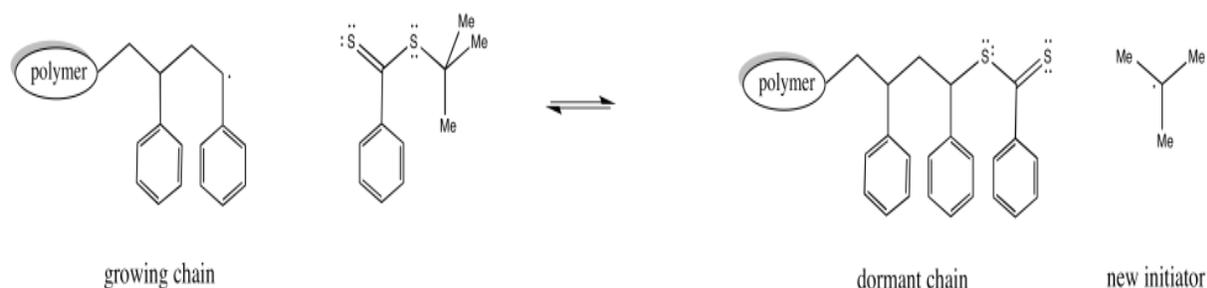


Two of the most common methods of inducing living radical polymerisation are RAFT and ATRP. RAFT stands for radical atom fragmentation polymerisation. Like the TEMPO reaction, it involves a reversible radical recombination to form a covalent bond. RAFT was developed by a group of Australian chemists in the late 1990's, including Enzo Rizzardo, Graeme Moad and San Thang of Australia's national science agency, CSIRO. ATRP stands for atom-transfer radical polymerisation. It was developed in the mid 1990's by Krysztof Matyjaszewski at Carnegie Mellon in Pittsburgh and his post-doctoral associate, Jin-Shan Wang, now at Shanghai Jiao Tong University. An independent discovery of the method was made by Mitsuo Sawamoto at Kyoto University in Japan.

RAFT most commonly employs a thioester (or similar compound) as a chain transfer agent. The chain transfer agent intercepts a growing polymer chain, but does so reversibly.

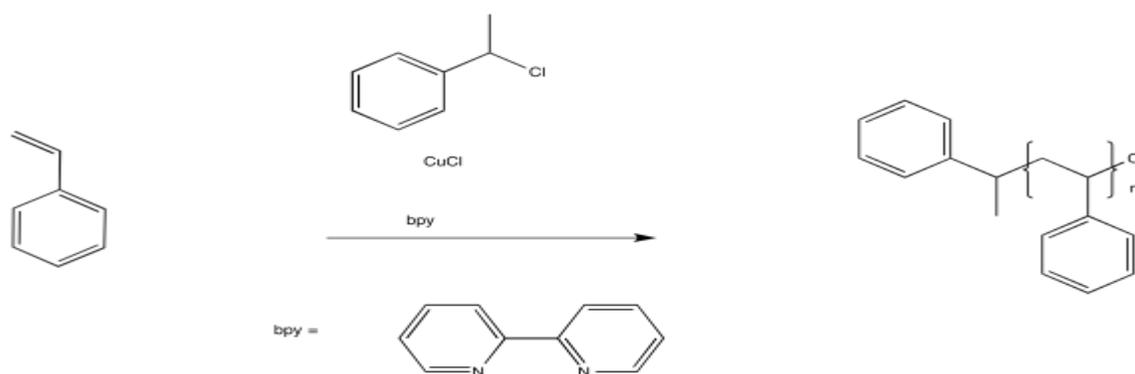


The thioester can react with a radical, placing the growing chain in a dormant state. It can also release a new radical, which can then initiate polymerisation. Eventually, it will regulate the growth of two polymer chains.



In addition, a third species present in equilibrium holds both chains dormant. The chain transfer agent can reversibly release one of these dormant chains at a time.

In ATRP, a similar process works to keep a fraction of the chains in a dormant state. A key component of this method is a copper(I) complex.



The role of the copper(I) complex is to transfer an electron to an inactive species, producing a copper(II) species and a radical. For example, in initiation of the reaction above, the Cu(I) transfers an electron to the alkyl halide to become Cu(II). In turn, the chlorine atom on the alkyl halide becomes chloride anion, Cl^- , and the alkyl portion is left as an initiating radical.



One of the reasons ATRP is so important is that it provides a very reliable and inexpensive way to control polymerisation. In addition, it can be adapted to a wide range of useful processes.

Source: <http://employees.csbsju.edu/cschaller/Reactivity/radical/radicalpolyliving.htm>