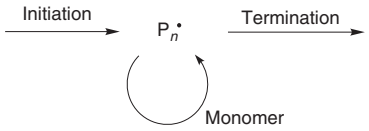
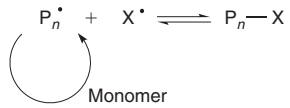
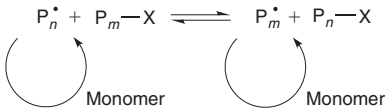


Scheme 1.



Scheme 2. Reversible deactivation.



Scheme 3. Reversible chain transfer.

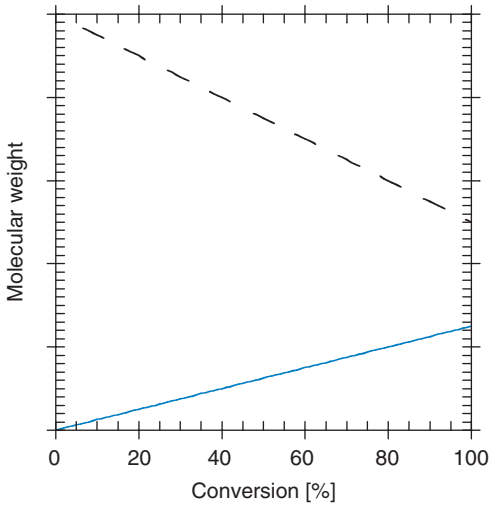


Fig. 1. Evolution of molecular weight with monomer conversion for a conventional radical polymerization with constant rate of initiation (– – –) and a living radical polymerization (—).

the synthesis of blocks, stars, or other polymers of complex architecture. New materials that have the potential of revolutionizing a large part of the polymer industry are beginning to appear. Possible applications range from novel surfactants, dispersants, coatings, and adhesives, to biomaterials, membranes, drug delivery media, and materials for microelectronics.

To understand how RAFT and other forms of living radical polymerization work, we first need to consider the mechanism of the conventional process.[1] Radical polymerization is a chain reaction. The chains are initiated by radicals (formed from an initiator) adding to monomer. Chain propagation then involves the sequential addition of monomer units to the radical ($P_n^{\bullet}$) so formed. Chain termination occurs when the propagating radicals react by combination or disproportionation. A much simplified mechanism is shown in Scheme 1.

In conventional radical polymerization, the steady-state concentration of propagating species is about 10^{-7} M, and individual chains grow for 5–10 s before terminating. Chains are continuously formed, propagate, and are terminated by radical–radical reaction. The molecular weight of chains formed in the early stages of polymerization is high and will reduce with conversion because of monomer depletion (Fig. 1). The breadth of the molecular-weight distribution and polydispersity is governed by statistical factors. The polydispersity, expressed in terms of the ratio of weight to number average molecular weights,* is broad ($\overline{M}_w/\overline{M}_n > 1.5$; see Fig. 2).

In an ideal living polymerization, all chains are initiated at the beginning, grow at the same rate, and survive the polymerization (there is no termination). The propensity of free radicals to undergo radical–radical termination means that, for the case of radical polymerization, all chains cannot be simultaneously active. To confer living character on a radical polymerization, it is necessary to suppress or render insignificant all processes that terminate chains irreversibly. Thus, living radical polymerization only becomes possible in the presence of reagents that react with the propagating radicals ($P_n^{\bullet}$) by reversible deactivation (Scheme 2) or reversible chain transfer (Scheme 3) so that the majority of chains are maintained in a dormant form (P_n—X). The average concentration of the active propagating species in a living radical polymerization may be similar to that for the conventional process although the cumulative lifetime of an individual chain as an active species will be lower. Rapid equilibration between the active and dormant forms ensures that all chains possess an equal chance for growth and that all chains will grow, albeit intermittently. Under these conditions, the molecular weight increases linearly with conversion (Fig. 1) and the molecular weight distribution can be very narrow (e.g. $\overline{M}_w/\overline{M}_n \approx 1.1$, Fig. 2).

The living radical polymerization techniques that have recently received greatest attention are nitroxide-mediated polymerization (NMP), atom-transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer (RAFT). The NMP technique was devised in our laboratories in the early 1980s,[10] and in recent years has been exploited extensively for the synthesis of narrow molecular-weight distribution homopolymers and block copolymers of styrene and acrylates.[2,11,12] Recent developments have made NMP applicable to a wider, though still restricted, range of monomers.[2] ATRP is substantially

*The number average molecular weight or molar mass is simply the total weight of the sample divided by the number of molecules in the sample: $\overline{M}_n = \sum n_i M_i / \sum n_i = \sum w_i / \sum n_i$, where n_i is the number of chains of length i, w_i is the weight of chains of length i, and M_i is the molecular weight of a chain of length i. The weight average molecular weight is the sum of the weights of chains of each molecular weight multiplied by their molecular weight divided by the total weight of the sample: $\overline{M}_w = \sum w_i M_i / \sum w_i = \sum n_i M_i^2 / \sum n_i M_i$. The weight average is always greater than the number average molecular weight. The polydispersity is the ratio of the weight average to the number average molecular weight and, for an ideal radical polymerization, will be 2 for termination by disproportionation or chain transfer, or 1.5 for termination by combination.