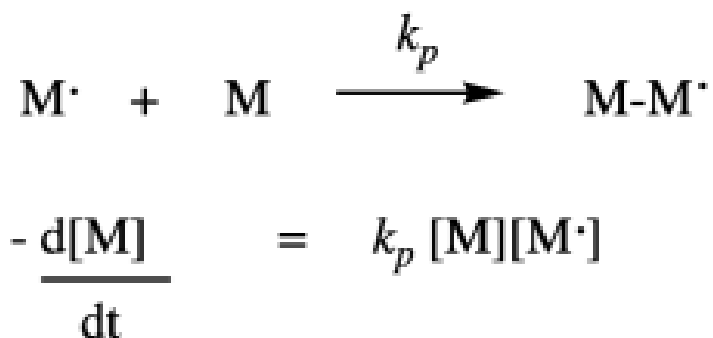


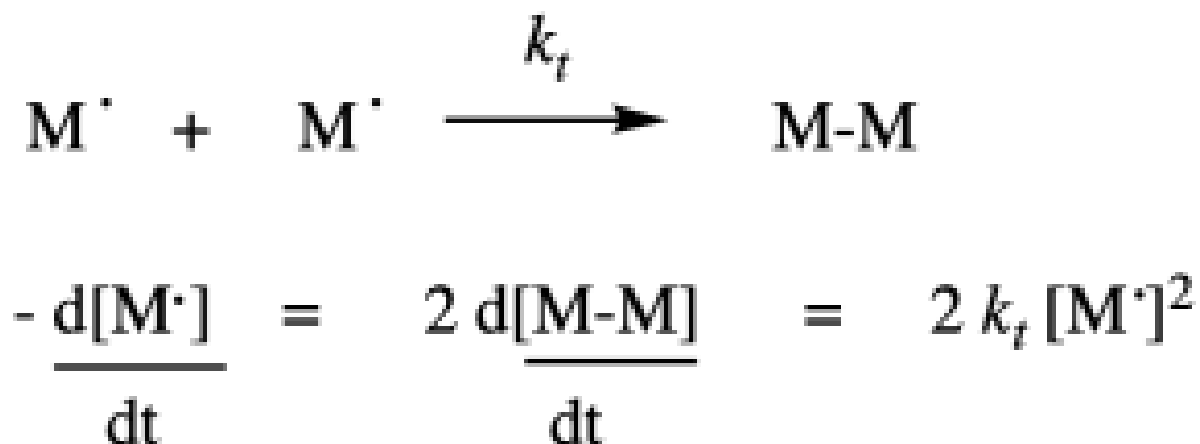
M.Sc. Sem I, CC-2, Physical Chemistry

Kinetics of Chain Polymerization (continued...)

Once the first monomer has been initiated into a radical, it can react with another monomer to enchain it and make a new radical. This is the principal propagation step of the chain reaction. That step will keep repeating, adding more monomers into the chain. The rate constant for this step, k_{prop} or k_p , is identical no matter how many monomers have been enchainned, but is distinct from k_i because of the different nature of the radical intermediates in the two different steps. For example, the radical obtained from addition to styrene looks pretty similar whether it is the first in the chain or the tenth. Each time, the rate of consumption of monomer depends on the propagation rate constant, the concentration of the monomer, and the concentration of the propagating radical. Notice that in the rate law we just write that propagating radical the same way ($M^\bullet$) no matter how long the chain grows.



There is one last process, or group of processes, to complete the chain reaction cycle. In termination, two radicals combine in some way to form closed-shell products. There are a variety of ways that can happen in a radical polymerization. The simplest event conceptually is coupling, in which two radical chains come together and form a bond. That idea is shown below.



Of course, that rate depends on the termination rate constant and the concentrations of both growing chains. The same would be true if the reaction terminated by conproportionation, in which one radical abstracted an alpha hydrogen from the other, forming one saturated and one unsaturated product.

Once again, these last two rates -- of propagation and of termination -- depend on concentrations of reactive intermediates, which we do not typically know. This time we will use a very standard assumption, which is that the concentration of this reactive species remains constant, being consumed as soon as it is generated. The usual way that we apply the steady state approximation is to assume zero change in concentration of the reactive intermediate. That means that the sum of all the rates for processes generating the intermediate equal the sum of all the rates consuming the intermediate. In polymer chemistry, we take a slight shortcut, and just assume that the rate of appearance of the radical in the first place equals its rate of disappearance. We already have expressions for both of those rates.

$$\text{Rate}_{\text{term}} = \text{Rate}_{\text{init}}$$

$$2 k_t [\text{M}\cdot]^2 = 2 f k_d [\text{I}]$$

$$[\text{M}\cdot] = \left(\frac{f k_d [\text{I}]}{k_t} \right)^{1/2}$$

By rearranging, we can get an expression for the reactive chain end concentration. Then we can just substitute the result into our expression for propagation rate:

$$\begin{aligned} - \frac{d[\text{M}]}{dt} &= k_p [\text{M}][\text{M}\cdot] \\ &= k_p [\text{M}] \left(\frac{f k_d [\text{I}]}{k_t} \right)^{1/2} \end{aligned}$$

The result sums up the factors that control the growth rate for the polymer. The growth rate increases linearly with the concentration of monomer, and as the square root of the initiator concentration. The rest of the factors are just constants, so we can think of the rate law as one combined constant and those two concentration dependences. Sometimes an aggregate constant of this type is just designated k' .

Note that the propagation rate varies linearly with the concentration of growing chains, but that the termination rate varies with square of the concentration of growing chains. That difference is significant, and it underlies the strategy of living polymerization, which is to keep the concentration of growing chains low. Doing so has the adverse affect of slowing the rate of propagation, but the effect on the termination rate is much greater, making this trade-off worth it to achieve enhanced molecular weight control.