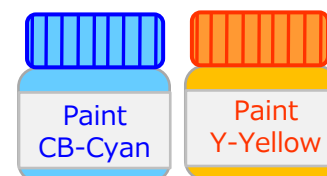


ESR of Materials –Photopolymerization 3 -

Product used : Electron Spin Resonance (ESR)

Many of the plastics we use in our daily lives are produced using radical polymerization reactions. If it were possible to directly observe this radical polymerization reaction, a great deal of useful information could be obtained. With ESR, only the unpaired electrons at the free end of a polymer chain can be observed; but, by making good use of this, it is possible to obtain a variety of information, such as molecular size (chain length) and mobility, in spite of seeing only a small portion of the molecule.



■ Radical Polymerization

Radical polymerization is a reaction in which macromolecules are synthesized by successively adding radicals to monomers. This is mainly used to polymerize vinyl monomers. It is a chain reaction with initiation, propagation and termination reactions.

(1) Initiation

The polymerization initiator (I) decomposes and generates the primary radical (R·). This primary radical (R·) reacts with the monomer (M) to generate the initiating radical (R-M·).

(2) Propagation

The initiating radical (R-M·) reacts with the monomer (M) and generates the polymer radical (P·). The polymer radical (P·) repeats the additive reaction with the monomer (M) as the polymerization reaction progresses. The main chain of the polymer is formed through this process.

(3) Termination

This is the process in which the propagating radical (P-M·) reacts with the chemical species of the polymerization system and loses its reactivity. This can be either a combination of 2 propagating radicals with each other (P-P), or the transfer of hydrogen between the 2 propagating radicals (P(+H) + P(-H)) in a disproportionation reaction.

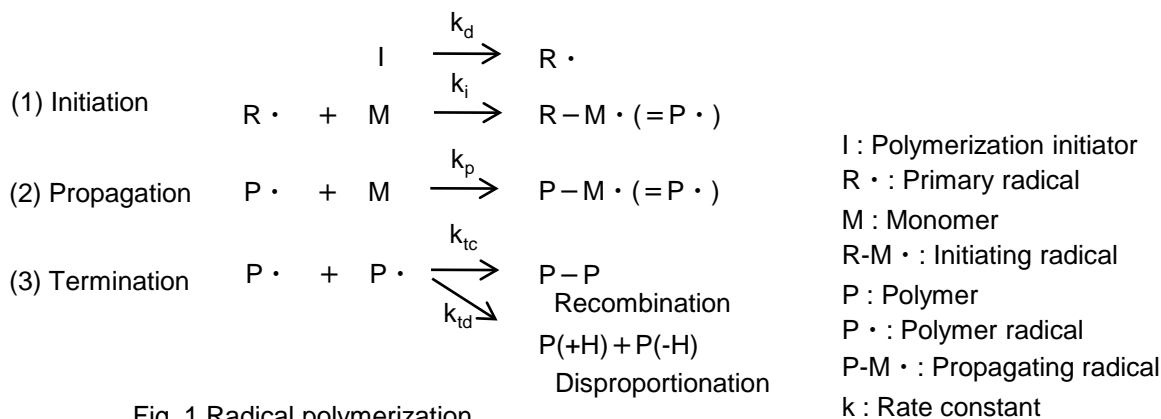


Fig. 1 Radical polymerization

The initiation, propagation, and termination all start simultaneously when the polymerization system is exposed to light, and the length of the polymer (degree of polymerization) is affected by the polymerization condition. Since the polymerization initiator is decomposed when exposed to the light and can be used immediately for the next reaction, depending on the sample, the lifespan of the primary radical (R·) may be quite short, so it may not be possible to detect this with ordinary ESR measurements. In the subsequent propagation reactions, as the polymerization process progresses, the generation of propagating radicals also progresses, which can be observed as an ESR signal. As the number of propagating radicals increases, their interactions of combination or disproportionation (termination reactions) will also proceed. When the rate of radical creation from the polymerization reactions equals the rate at which the radicals disappear due to the termination reactions, the intensity of the ESR signal will become constant (steady state).

