

A Review of Redox and Thermal Initiation in Free Radical Polymerization

Sahar Bayat^{1,*} - Seyyed Alborz Majzoob Hosseini²

¹ Abadgaran Construction Chemicals Manufacturer Email address: sahariii_bayat@yahoo.com, telephone number:00989122681493 ² Abadgaran Construction Chemicals Manufacturer Email address: Alborz @abadgarangroup.com, telephone number:00982187754

ABSTRACT

Generation of free radical species is an essential element of all free-radical polymerization reactions. A lot of organic molecules are stable at moderate and elevated temperatures. Therefore, in some reactions the addition of stable free radical which shows very little or almost no tendency in self-combination is of great importance, as free radical species are aimed to initiate reactant molecules in a specific reaction.

The radical species differ in a wide range from organic to inorganic chemicals. These molecules are chosen based on monomers and desired reactions. There are a vast range of organic peroxides and azo compounds as well as redox pairs that are important in resin and polymer industries. The way to generate these free radicals varies from mild to harsh conditions. In this review, giving some examples of thermal and redox pair initiators, some newly employed metal-ion-organic –compound redox systems for polymerizations in aqueous media are presented.

Keywords: polymerization, all free-radical polymerization, radical species, azo, *peroxides, redox pairs, metal-ion-organic*

1. RADICAL INITIATORS

Radical initiators are molecules bearing one or several weak bonds with BDE ~100-200 kJ.mol-1. When the temperature of the reaction is sufficiently high, the initiator decomposes with homolysis of the weakest bond and produces free radicals. These free radicals initiate a chain or non-chain free radical reaction [1]

A variety of initiator systems can be used to bring about the radical polymerization including 1) Thermal Decomposition of Initiators, 2) Redox Initiation, 3) Photochemical Initiation, 4) Initiation by Ionizing Radiation, 5) Pure Thermal Initiation, and 6) Other Methods of Initiation.

1.1 Thermal Decomposition of Initiators

There are generally two types of free radical initiators that are used commercially in the polymer and resin industries, organic peroxides (ROOR[^]) and aliphatic azo compounds (R-N=N-R[^]).2 Both types decompose thermally to produce free radicals. Organic peroxides decompose by initial cleavage of oxygen-oxygen bond to produce free radicals and the azo compounds decompose by cleavage of two carbon-nitrogen bonds to produce nitrogen and two alkyl radicals [2]to[3]

$$\mathbf{ROOR'} \xrightarrow{\Delta} \mathbf{RO} + \mathbf{OR'}$$

 $\mathbf{R} - \mathbf{N} = \mathbf{N} - \mathbf{R}' \xrightarrow{\bigtriangleup} \mathbf{R} \cdot + \mathbf{N}_2 + \mathbf{N}'$

1.1.1 Peroxides

Organic peroxides are compounds possessing one or more oxygen–oxygen bonds. They have the general structure ROOR or ROOH, and decompose thermally by the initial cleavage of the oxygen–oxygen bond to produce two radicals. Depending on the peroxide class, the rates of decompositions of organic peroxides can be enhanced by specific promoters or activators, which significantly decrease the energy necessary to break the oxygen–oxygen bond. Such accelerated decompositions occur well below peroxide's normal application temperatures and usually result in

1