KINETICS OF THE COPOLYMERIZATION REACTION OF SALICYLIC ACID ALLYL ESTER WITH MALEIC ANHYDRIDE

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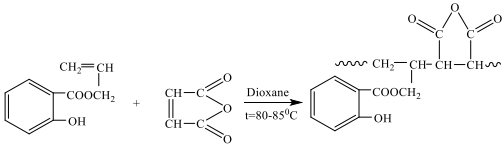
Salicylic acid allyl ester is of interest in free-radical polymerization processes as a reactive monomer containing a functional phenolic group and an unsaturated allyl bond. The presence of both an aromatic fragment and a hydroxyl group in its molecular structure provides the resulting polymer chain with potential biological activity and opportunities for chemical modification. In this regard, its copolymerization with electron-acceptor type monomers is of particular significance.

Maleic anhydride is a vinyl-type monomer with strong electron-acceptor properties and readily forms alternating copolymers with donor-type monomers. The aromatic system of allyl salicylate and the electron-donating effect of its oxygen atoms promote the formation of a donor–acceptor type molecular complex with maleic anhydride. This interaction significantly influences the rate and mechanism of the copolymerization process, as well as the structure of the resulting macromolecule. The study of the kinetic regularities of the free-radical copolymerization reaction between salicylic acid allyl ester and maleic anhydride is of significant scientific and practical importance for the development of polymer materials with functional properties. Since maleic anhydride acts as an electron-acceptor monomer and allyl salicylate as an electron-donor monomer, their interaction leads to the formation of a donor–acceptor type molecular complex, which significantly affects the rate and mechanism of the copolymerization process.



The kinetics of the radical copolymerization of salicylic acid allyl ester (AllST) with maleic anhydride (MA) in the presence of benzoyl peroxide (BP) was investigated in order to establish the main regularities of the process. The reaction was studied by the dilatometric method at 353 K. The kinetic curves obtained at different total monomer concentrations ($[M]_0$ = 0.4–1.0 mol·L^{-1}, $[BP]_0$ = 0.02 mol·L^{-1}) show that the copolymerization proceeds without an observable induction period. An increase in the total monomer concentration leads to an increase in the initial rate of the reaction from 4.18×10^{-4} to 10.7×10^{-4} mol·L^{-1}·min^{-1}. The dependence of lgW_0 on $lg[M]_0$ is linear, and the slope of the straight line is 1.11, indicating a first-order dependence of the process on the total monomer concentration. The effect of initiator concentration was studied at $[AllST]_0 = [MA]_0 = 0.5$ mol·L^{-1} and T = 353 K. The plot of $logW_0$ versus $log[BP]_0$ is linear with a slope of 0.5, which confirms a half-order dependence of the reaction rate on the initiator concentration: $W=k[BP]_{0.5}\cdot([AllST]_0+[MA]_0)$

The rate constants calculated using this equation are $1.85\cdot10^{-3}$, $3.72\cdot10^{-3}$ and $7.54\cdot10^{-3}$ $l^{0.5}\cdot$ mol$^{-0.5}\cdot$ min^{-1} – respectively at 333, 343 and 353 K, respectively. The obtained results indicate that the copolymerization of AllST and MA follows the kinetic regularities typical for radical polymerization of vinyl monomers.