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Abstract

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STUDY OF THE KINETICS OF HOMOGENEOUS AND HETEROGENEOUS POLYMERIZATION OF α,β-FLUORO-SUBSTITUTED STYRENES

In the works of a number of authors it has been shown that, in the process of emulsion polymerization, the chemical role of the adsorption layers of the emulsifier is very great (^{1}). At the same time it is known that the use of such initiating systems as make it possible to combine the properties of the hydrocarbon and aqueous phases in adsorption layers considerably increases the rate of polymerization. The synergism of initiator action in emulsion polymerization apparently should be observed with the simultaneous use of two initiators soluble in water and in the organic phase. Up to the present time, polymerization in emulsion has been studied in detail for the particular case: polymerization of styrene in the presence of persulfates (^{2}).

In our experiments (^{3}) emulsion polymerization was carried out in an aqueous medium (80%). Initiation was effected by means of potassium persulfate (0.5%) and azobisisobutyric acid dinitrile (0.5% of the weight of monomer). The emulsion was stabilized with sodium oleate (2.5%). Sodium pyrophosphate (0.1%) was chosen as regulator.

Table 1

Kinetic characteristics of homogeneous and heterogeneous polymerization of fluoro-substituted styrenes and styrene

Monomer	$(K)_{60^\circ}$, $\sec^{-1}$	E, kcal/mol	K, (l/mol · sec)$^{1/2}$	$[\eta]$, dl/g	$(K_p/K_0)_{60^\circ}$, (l/mol · sec$^{1/2}$)
α,β,β-trifluorostyrene	$0.4 \cdot 10^{-6}$	19.7	$3.5 \cdot 10^7$	0.05	–

Monomer	$(K)_{60^\circ}$, $\sec^{-1}$	E, kcal/mol	K, (l/mol · sec)$^{1/2}$	$[\eta]$, dl/g	$(K_p/K_0)_{60^\circ}$, (l/mol · sec$^{1/2}$)
4-methyl-α,β,β-trifluorostyrene (in solution)	$0.9 \cdot 10^{-6}$	20.5	$2.6 \cdot 10^{6}$	0.08	$0.4 \cdot 10^{-2}$
4-methyl-α,β,β-trifluorostyrene (in emulsion)	$2.7 \cdot 10^{-6}$	24.0	$1.2 \cdot 10^{10}$	0.41	–
styrene (in solution)	$3.2 \cdot 10^{-6}$	21.2	$3.7 \cdot 10^{9}$	0.28	$2.2 \cdot 10^{-2}$
styrene (in emulsion)	$16 \cdot 10^{-4}$	22.0	$6.0 \cdot 10^{11}$	2.9	–

Under these conditions the kinetics of emulsion polymerization of 4-methyl-α,β,β-trifluorostyrene and styrene were studied. The rate of emulsion polymerization varies regularly with temperature; therefore the values of the activation energy (E) and of the pre-exponential factor (K) of the overall reaction were calculated (Table 1).

For comparison, the kinetics of initiated polymerization in toluene solution of 4-methyl-α,β,β-trifluorostyrene, α,β,β-trifluorostyrene, and styrene were studied (Table 1). The initiator of homogeneous polymerization was likewise azobisisobutyric acid dinitrile.

The magnitude of the molecular weight of the polymers obtained was judged qualitatively from the results of viscometric measurements.

An attempt was made to determine the rates of the elementary stages of the polymerization process of 4-methyl-α,β,β-trifluorostyrene. From the magnitude of the induction period caused by the presence of diphenylpicrylhydrazyl, the ratio (K_p/K_0) at 60° was calculated for 4-methyl-α,β,β-trifluorostyrene during polymerization in solution (Table 1), where K_p and K_0 are, respectively, the rate constants of the propagation and termination reactions.

It is evident from the results obtained that, both in solution and in emulsion, the polymerization rate decreases sharply when hydrogen in the vinyl group of styrene is replaced by fluorine; the degree of polymerization thereby decreases by a factor of 30–80.

However, the polymerization rate in emulsion is 4–5 times greater than in solution. The difference between the rates of the heterogeneous and homogeneous polymerization reactions increases on going to more active monomers. The molecular weight of the polymers obtained in emulsion is considerably higher than that of samples polymerized in solution at the same temperature.

The mechanism of emulsion polymerization under conditions of double initiation differs substantially not only from homogeneous polymerization, but also from emulsion polymerization initiated by potassium persulfate. The activation energies for the polymerization of styrene in emulsion and in solution coincide (Table 1).

Thus, the synergism of initiation of emulsion polymerization is manifested in an increase in the rate and degree of polymerization; however, along with these factors, an increase in the activation energy of the overall reaction is observed. The synergistic action of polymerization initiators in emulsion on individual stages of the reaction and on the sites at which they occur remains as yet unexplained.

A study of the overall polymerization reaction in emulsion and in solution of fluorine-substituted styrenes, as well as preliminary data on determining the rate constants of the elementary polymerization reactions, shows that the presence of electrophilic substituents in the vinyl group of styrene increases the rate of the termination reaction, lowering the gross polymerization rate. This is understandable if it is assumed that the conjugation of the π bond of the vinyl group with the benzene ring for α,β-fluorine-substituted styrenes is considerably less than for styrene.

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