Physical Chemistry

E. B. Lyudvig, A. R. Gantmakher, Academician S. S. Medvedev

1964

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

E. B. Lyudvig, A. R. Gantmakher, Academician S. S. Medvedev

On the Mechanism of Cationic Polymerization in the Presence of Metal Halides

In studies of the initiation mechanism and the nature of active centers in cationic polymerization with metal halides and BF_3, it has been shown for many systems that cocatalysis by proton-donor additives or alkyl halides is necessary (the results of these studies are summarized in (1)).

However, a number of facts—the decrease in the molecular weight of polymers upon addition of H_2O and HCl to metal halides (2,3), the increase in the polymerization rate with increasing catalyst concentration (C) and constant cocatalyst concentration (B) at $C/B > 1$, and S-shaped kinetic curves in the polymerization of some monomers (1–7)—have not found a satisfactory explanation within the framework of the existing ideas about the mechanism of the process in the presence of a catalyst-cocatalyst system.

It should be noted that, although there existed a tendency to regard the mechanism of cocatalysis as common to all cationic polymerization processes, as was indicated in (8,9), in a number of systems where, according to (10), the role of the cocatalyst could be fulfilled by the solvent—an alkyl halide—the necessity of cocatalysis by proton-donor additives was not demonstrated.

Fig. 1. Effect of water additives on the rate of polymerization of styrene (M_1) with $SnCl_4$ at various

$$\frac{[\mathrm{SnCl_4}]}{[\mathrm{H_2O}]} = N.$$

$[M_1] = 1.5$ mol/l, $[\mathrm{SnCl_4}] = 0.016$ mol/l.
1—$N = 1$; 2—$N = 6$; 3—$N = 16$; 4—$N = 40$; 5—$N = 100$.

The aim of the present work was to elucidate the mechanism of cationic polymerization in the presence of metal halides and the role of proton-donor additives in this process.

The systems chosen as objects of study were $SnCl_4$—styrene or α-methylstyrene in ethyl chloride solution. Polymerization was carried out at 20° under condi-

Fig. 2

Figure 2: Fig. 2

tions of thorough purification of the starting substances. Thus, for example, a new procedure was used for purifying the monomers (after the purification employed earlier, the monomer was additionally treated in vacuum with lithium ethyl). It was shown that under these conditions polymerization of styrene and α-methylstyrene does not occur without addition of the cocatalyst.

In this connection, the study of the polymerization process of styrene and α-methylstyrene was carried out in the presence of water additives over a wide range of ratios

$$[\mathrm{SnCl_4}]_0 : [\mathrm{H_2O}]_0^* = N \quad (N = 0.5 — 100).$$

Water was introduced in the form of a solution in benzene; the water content was monitored with lithium ethyl by the method developed in our laboratory by D. K. Polyakov**. At concentrations greater than 0.003 mol/l, water was dosed in ethyl chloride solution.

The kinetics of polymerization was studied at 20° by the dilatometric method. The concentrations of monomer, catalyst, and water were varied, and the molecular weights of the polymers were determined.

As can be seen from Fig. 1, the reproducible data obtained in the polymerization of styrene confirmed the previously expressed assumption about the na—

···of two directions of the process: I—when $[\mathrm{H_2O}]_0 \geq [\mathrm{SnCl_4}]_0$; under the adopted conditions, at this ratio of the catalyst components the polymerization proceeds with a rate decreasing with time (Fig. 1, 1), and II—in the presence of relatively small additions of water, $N > 5$, when the polymerization proceeds with an increasing rate with time (Fig. 1, 2-5). (It had previously been assumed ($^{2,3,5-8}$) that processes II proceed without a cocatalyst.)

Fig. 2. Effect of the concentration of catalyst (1, 2) and monomer (3, 4, 5) on the rate of polymerization of styrene (M_1). 1, 2 –$[\mathrm{H_2O}] = 0.0004$ mol/l, $[M_1] = 1.5$ mol/l. $[\mathrm{SnCl_4}] = 0.032$ mol/l, 2 –0.008 mol/l, 3, 4, 5 –$[\mathrm{H_2O}] = 0.001$ mol/l, $[\mathrm{SnCl_4}] = 0.016$ mol/l. $[M_1]$ equals: 2.5 (3); 1.5 (4), 1 mol/l (5).

At constant $[\mathrm{H_2O}]_0$, the induction period decreases with the introduction of additions of monomer and catalyst, with increasing $[M]_0$ and $[\mathrm{SnCl_4}]_0$ (Fig. 2), and also with methylstyrene (Fig. 3). An increase in the monomer concentration at $N > 5$ (Figs. 1, 2) promotes the preferential occurrence of process II.

---

* Here and below, the subscript 0 denotes the initial concentration; absence of a subscript denotes the concentration at time t.

** Accuracy of determination of $[\mathrm{H_2O}] \cong \pm 2.5\%$.

Fig. 3

Figure 3: Fig. 3

The fact that, in the presence of low values of $[H_2O]_0$, polymerization ceases at low conversions indicates that water is consumed during the process. Moreover, in case II $[H_2O]_0 \ll [Mn]$, where $[Mn]$ is the concentration of polymer chains at 100% yield, i.e., under conditions II, the molecular weight of the polymers is predominantly regulated by molecular-chain termination reactions with regeneration of the cocatalyst.

In agreement with (^{2,5}), it was established that the molecular weight of the polymers increases on passing from processes I to processes II. Under the same conditions, when N is changed from 0.5 to 13, $[\eta]$ increases from 0.215 to 0.373.

Comparison of the rates of polymerization and the molecular weights of the polymers formed shows that acceleration of polymerization is accompanied by an increase in the initiation rate.

As follows from Fig. 3, polymerization of α-methylstyrene over a wide range of values of N proceeds without an increase in the rate with time. The observed results can be explained by taking into account the possible formation of different types of complexes involving the catalyst. In the system $SnCl_4$—H_2O—monomer (M), taking into account that

Fig. 3. Rates of polymerization of α-methylstyrene (M_3) (1, 2) and styrene (M_1) in the presence of additions of M_3 (3, 4) and additions of polystyrene (M_2) (6), $[SnCl_4] = 0.016$ mol/l, $[M_3] = 1.5$ mol/l (1, 2); $[H_2O]$ equals: 0.016 (1), 0.0005 (2), 3, 4, 5, 6 –0.001 mol/l, $[M_1] = 1.5$ mol/l. $[M_3]$ equals: 0.06 (3), 0.035 (4), 0 (5), 54 (6).

the coordination number of Sn^{IV} is 6, the formation of the complexes $SnCl_4 \cdot 2H_2O$ and $SnCl_4 \cdot M{\cdot}H_2O$ is possible. The ratio between these complexes is determined by the following scheme

$$SnCl_4 \underset{K_1}{\overset{H_2O}{\rightleftarrows}} SnCl_4 \cdot H_2O \begin{cases} \xrightarrow[K_2]{H_2O} SnCl_4 \cdot 2H_2O, \\ \xrightarrow[K_3]{M} SnCl_4 \cdot M \cdot H_2O. \end{cases} \tag{1}$$

(K_1, K_2, K_3 are the equilibrium constants of the corresponding reactions). It is assumed that for styrene (M_1), under equilibrium conditions,

$$[SnCl_4 \cdot M_1 \cdot H_2O] \ll [SnCl_4 \cdot 2H_2O]. \tag{2}$$

From (1) and (2) it follows that

$$[\mathrm{SnCl_4 \cdot M_1 \cdot H_2O}] = K_3'(K_1/K_2)^{1/2}[\mathrm{SnCl_4}]_c^{1/2}\left[\frac{\mathrm{H_2O}}{2}\right]^{1/2}[\mathrm{M_1}], \tag{3}$$

where

$$[\mathrm{SnCl_4}]_c = \left([\mathrm{SnCl_4}]_0 - \frac{[\mathrm{H_2O}]}{2}\right). \tag{4}$$

It is further assumed that the role of the molecule M can be played not only by monomer molecules, but also by polymer molecules with terminal double bonds, formed in the course of polymerization. These molecules (M_2) should be more active in complex formation (greater electron density at the double bond) than styrene molecules.

In accordance with scheme (1), two catalytic complexes are formed in the system $\mathrm{SnCl_4}$–$\mathrm{H_2O}$–M: I–$\mathrm{SnCl_4 \cdot 2H_2O}$ and II–$\mathrm{SnCl_4 \cdot M \cdot H_2O}$, and the polymerization of styrene proceeds in the following directions

$$\text{I –initiator I –}\mathrm{SnCl_4 \cdot 2H_2O}$$

$$\mathrm{SnCl_4 \cdot 2H_2O} + M_1 \xrightarrow{K_{\mathrm{in}\,1}} \overset{+}{\mathrm{H}}M_1[\overline{\mathrm{SnCl_4 \cdot OH \cdot H_2O}}] \quad \text{initiation} \tag{5}$$

$$\overset{+}{\mathrm{H}}M_{1n}[\overline{\mathrm{SnCl_4 \cdot OH \cdot H_2O}}] + M_1 \xrightarrow{K_{p1}} \overset{+}{\mathrm{H}}M_{1n+1}[\overline{\mathrm{SnCl_4 \cdot OH \cdot H_2O}}] \quad \text{chain growth} \tag{6}$$

$$\overset{+}{\mathrm{H}}M_{1n+1}[\overline{\mathrm{SnCl_4 \cdot OH \cdot H_2O}}] \xrightarrow{K_{01}} \mathrm{H}M_{1n+1}\mathrm{OH} + \mathrm{SnCl_4 \cdot H_2O} \quad \text{chain termination} \tag{7}$$

According to (7), in mechanism I water is irreversibly consumed during termination of the chain.

$$\text{II –initiator II –}\mathrm{SnCl_4} \cdot M_1 \cdot \mathrm{H_2O}$$

$$\mathrm{SnCl_4} \cdot M_1 \cdot \mathrm{H_2O} + M_1 \xrightarrow{K_{\mathrm{in}\,2}} \overset{+}{\mathrm{H}}M_1[\overline{\mathrm{SnCl_4} \cdot M_1 \cdot \mathrm{OH}}] \quad \text{initiation} \tag{8}$$

$$\overset{+}{\mathrm{H}}M_{1n}[\overline{\mathrm{SnCl_4} \cdot M_1 \cdot \mathrm{OH}}] + M_1 \xrightarrow{K_{p2}} \overset{+}{\mathrm{H}}M_{1n+1}[\overline{\mathrm{SnCl_4} \cdot M_1 \cdot \mathrm{OH}}] \quad \text{chain growth} \tag{9}$$

$$\mathrm{R{\sim}C-\overset{+}{C}{<}\ [\overline{\underset{|}{S}nCl_4 \cdot \mathit{M}_1 \cdot OH}]} \xrightarrow{K'_{02}} \mathrm{R{\sim}C=C{+}SnCl_4{\cdot}\mathit{M}_1{\cdot}H_2O} \quad \text{chain termination} \tag{10}$$

$$\mathrm{R{\sim}C-\overset{+}{C}{<}\ [\overline{\underset{|}{S}nCl_4 \cdot \mathit{M}_1 \cdot OH}]} \xrightarrow{K_{02}} \mathrm{R{\sim}C{-}C{-}OH{+}SnCl_4{+}\mathit{M}_1} \quad \text{chain termination} \tag{11}$$

Terminal double bonds may also be formed in the reaction of chain transfer through monomer.

Here, from a comparison of rates (Fig. 1) and molecular weights it follows that $K_{\mathrm{in}\,2} \gg K_{\mathrm{in}\,1}$. From the molecular-weight data, taking into account that $[\mathrm{H_2O}]_0 \ll [M_{\mathrm{in}}]$, one may conclude that $\underline{K_{02} \ll K'_{02}} < K_{01}$. This is apparently due to the fact that the counterion $[\overline{\mathrm{SnCl_4} \cdot M \cdot \mathrm{OH}}]$ is more stable than $[\overline{\mathrm{SnCl_4} \cdot \mathrm{OH} \cdot \mathrm{H_2O}}]$.

In polymerization by mechanism II, as a result of the chain-termination reaction (10), polymer molecules with terminal double bonds (M_2) are formed, which, upon coordination with $\mathrm{SnCl_4}$, are capable, in accordance with the above considerations, of forming stronger complexes than styrene and of displacing water molecules from the $\mathrm{SnCl_4} \cdot 2\mathrm{H_2O}$ complexes, with the formation of $\mathrm{SnCl_4} \cdot M_2{\cdot}\mathrm{H_2O}$ complexes highly active in initiation.

In connection with the progressive increase of (M_2) with the depth of polymerization

there should be an increase in $[\mathrm{SnCl_4} \cdot M_2 \cdot \mathrm{H_2O}]$ (see (3)) and in the polymerization rate with time.

From the above consideration it may be concluded that the induction period is associated with the accumulation of a certain amount of M_2, which causes an increase in $[\mathrm{SnCl_4}{\cdot}M_2{\cdot}\mathrm{H_2O}]$, in the initiation rate, and in the polymerization rate. In this connection the dependence of the induction period on $[M]_0$, $[\mathrm{SnCl_4}]_0$, and $[\mathrm{H_2O}]_0$ must be the inverse of the dependence of the rate of process II on these parameters (3), (8)–(11), which is in agreement with the experimental data (see Figs. 1 and 2).

The increase in the rate is limited by the limiting value $[\mathrm{SnCl_4}{\cdot}M_2{\cdot}\mathrm{H_2O}] = [\mathrm{H_2O}]$ and by the consumption of the components (M_1 and $\mathrm{H_2O}$) in the course of the process.

Confirmation of the above assumptions is provided by the established influence on the process of additions of polystyrene (M_2), obtained under conditions in which mechanism II predominates ($N = 100$), and also of α-methylstyrene (M_3).

As follows from Fig. 3, , in the presence of additions of such a polymer the process proceeds at a high rate without an induction period.

According to Fig. 3, the introduction of small additions of M_3 sharply lowers the induction periods while preserving high rates of styrene polymerization, since in this case the role of M_2 is performed by the molecules M_3.

The kinetics of the homopolymerization of α-methylstyrene is also readily explained by its high activity in complex formation with Lewis acids, owing to which the main mass of the catalyst is present from the very beginning in the form of the complex $[SnCl_4 \cdot M_3 \cdot H_2O]$, which leads to the absence of an induction period and to high rates of the process, despite the relatively low (for steric reasons) rate of chain growth.

Additions of isobutylene have an analogous influence on the process ([7]).

In the course of polymerization, at $N > 1$, especially at deep stages of the process, when $[M_2]$ has increased and $[M_1]$ has decreased, the molecules M_2 can participate in chain-growth acts, which should lead to an increase in molecular weight in comparison with that expected (cf. (11)).

Thus it has been shown that S-shaped kinetic curves in the polymerization of a number of monomers are due not to a decrease in the rate of chain termination as a consequence of an increase in the viscosity of the system ([12,13]) and not to the exhaustion of impurities ([14]), but to a change in the nature of the catalytic centers and of the mechanism of the process with the depth of polymerization.

It follows from the results of this work that a feature of catalytic systems based on halides of group IV metals (Sn, Ti) is the ability of the catalyst, owing to coordination number 6, to form two types of complexes possessing different catalytic activity.

In this connection, depending on the conditions under which the process is conducted—the temperature, solvent, concentrations of the components, the nature of the catalyst, cocatalyst, monomer, and depth of polymerization—one or the other type of complex and the corresponding mechanism of the process predominates in the system, which explains the difference in the kinetic regularities observed in the polymerization of different monomers by different authors ([1]).

Physical-Chemical Institute
named after L. Ya. Karpov

Received
3 III 1964

CITED LITERATURE

1. *The Chemistry of Cationic Polymerization*, P. H. Plesch, Ed., London—N. Y., 1963.

2. A. R. Gantmakher, S. S. Medvedev, ZhFKh, **23**, 520 (1949).
3. A. R. Gantmakher, S. S. Medvedev, ZhFKh, **25**, 1328 (1951).
4. Overberger, R. Ehrig, R. Marcus, J. Am. Chem. Soc., **80**, 2456 (1958).
5. A. R. Gantmakher, S. S. Medvedev, ZhFKh, **26**, 173 (1952).
6. T. E. Lipatova, A. R. Gantmakher, S. S. Medvedev, ZhFKh, **30**, 1752 (1956).
7. E. B. Lyudvig, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **1**, 1342, 1333 (1959).
8. V. Longworth, P. Plesch, DAN, **127**, 97 (1959).
9. A. R. Gantmakher, S. S. Medvedev, E. B. Lyudvig, DAN, **127**, 100 (1959).
10. R. Colclough, F. Dainton, Trans. Farad. Soc., **54**, 886 (1958).
11. W. Longworth, P. Plesch, *Symp. über Makromoleküle*, Wiesbaden, 1959, **3**, All.
12. R. Norrisch, K. Russell, Nature, **160**, 543 (1947).
13. P. Plesch, *The Chemistry of Cationic Polymerization*, P. H. Plesch, Ed., London—N. Y., 1963, p. 179.
14. R. Cundell, ibid., p. 586.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.