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Cationic polymerization of hydrocarbon monomers induced by complexes of acyl halides with Lewis acids

9.* Peculiarities of the mechanism of isobutylene polymerization initiated by the $MeCOBr \cdot AlBr_3$ complex

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Polymerization of isobutylene in *n*-hexane at −78 °C initiated by $MeCOBr \cdot AlBr_3$ was studied. The results obtained were compared with the corresponding data for $RCOX \cdot 2AlBr_3$ complexes (R = Me or Ph, X = Cl or Br). The main peculiarities of the polymerization mechanism under the action of $MeCOBr \cdot AlBr_3$ were established. The rate constants of proton elimination and of chain termination and chain growth were determined experimentally.

Key words: isobutylene, polyisobutylene, molecular weight, end groups; Lewis acids; cationic polymerization.

Previously,[2,3] we found that the acyl halide/Lewis acid ratio has a pronounced effect on the polymerization of isobutylene (IB) initiated by $MeCOBr \cdot AlBr_3$ (Ac-1) and $MeCOBr \cdot 2AlBr_3$ (Ac-2) complexes. Thus, the number-average molecular weight $\bar{M}_n$ and the polydispersity index $\bar{M}_w/\bar{M}_n$ of polyisobutylene (PIB) increase as the degree of conversion (Q) increases, while the efficiency of the initiator (E_{in}) remains constant when Ac-2 is used. Almost all the head groups in the PIB macromolecules are acetyl fragments (degree of functionalization $f_{C=O} \approx 100\%$) even at high degrees of polymerization, despite the fact that an appreciable amount of superacid $HBr \cdot 2AlBr_3$ forms as a result of elimination of protons from the growing carbocations. The reasons for the inability of the superacid to participate in reinitiation in this system have been considered in Ref. 1. The system with Ac-2 is, as a whole, similar in many properties to "living" polymerization systems, which have a constant, but less then 100% E_{in} (type II according to Kennedy[4]), despite a pronounced tendency to lose active centers because of elimination of protons. When the initiating complex $PhCOCl \cdot 2AlBr_3$ (Bn-2) is used, it is possible to prevent proton elimination to a large extent.[5] It is likely that each polymeric chain in systems with complexes of composition 1 : 2 repeatedly undergoes reversible termination, which manifests itself in halogenation of the polymeric carbocation (a collapse of the ionic pair).[6]

A different picture is observed when the protonogenic initiator, complex Ac-1, is used: E_{in} increases as the degree of polymerization increases, the $\bar{M}_w/\bar{M}_n$ value changes slightly with a relatively broad molecular weight distribution (MWD), while $\bar{M}_n$ gradually decreases. The macromolecules contain no acetyl groups ($f_{C=O} = 0$).[2,3] However, many aspects of the mechanism of polymerization under the action of this complex are still unclear. In particular, it is not clear whether irreversible termination occurs in the system, what the role of reversible termination is, and if reversible termination occurs.

The presence of double C=C bonds in the macromolecules can be associated with two processes: a bimolecular one-step chain transfer to the monomer

$$\text{PIB—CH}_2\text{—CMe}_2{}^+\text{,A}^- + \text{CH}_2\text{=CMe}_2 \xrightarrow{k_{tr}} \text{PIB—CH}_2\text{—C(=CH}_2\text{)Me} + \text{Me—CMe}_2{}^+\text{,A}^-, \quad (1)$$

where PIB is the polyisobutylene, A^- is the counterion, and k_{tr} is the rate constant of bimolecular chain transfer to a monomer, and monomolecular proton elimination

$$\text{PIB—CH}_2\text{—CMe}_2{}^+\text{,A}^- \xrightarrow{k_{el}} \text{PIB—CH}_2\text{—C(=CH}_2\text{)Me} + \text{H}^+\text{,A}^-, \quad (2)$$

where k_{el} is the rate constant of proton elimination.

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* For Part 8, see Ref. 1.

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In the general case, the superacid H^+,A^- formed as a result of the latter reaction can initiate the formation of new active centers

$$H^+,A^- + CH_2{=}CMe_2 \longrightarrow Me{-}CMe_2^+,A^-. \qquad (3)$$

In this case the combination of reactions (2) and (3) describes two-step chain transfer to the monomer. No one-step transfer (reaction (1)) occurs for systems with acyl initiating complexes of composition 1 : 2 (Ac-2, Bn-2), while two-step transfer is terminated after the first stage (reaction (2)). In this work, an attempt has been made to elucidate whether any of these variants of chain transfer occur in systems with Ac-1.

Experimental

The procedures for purifying and drying the reagents and the solvent (*n*-hexane), preparing the initiating complexes, and performing the polymerization, isolation, and analysis of the polymers have been described previously.[1—3,5] The maximum efficiency of initiation ($E_{in,max}$) was calculated as the ratio of the mole concentrations of the polymer and initiator, while the minimum $E_{in,min}$ was determined assuming that each act of proton elimination (reaction (2)) is accompanied by reinitiation *via* reaction (3): $E_{in,min} = E_{in,max} \cdot (f_{C-Br}/100)$, where f_{C-Br} is expressed in per cent.

Results and Discussion

As follows from the data listed in Tables 1 and 2, a considerable portion of the PIB molecules formed *via* initiation by complex Ac-1 contains end C=C groups ($f_{C=C}$ = 29 to 51%). Since in the systems with Ac-2 these groups are only formed as a result of monomolecular proton elimination (2),[1—3] one can assume that this reaction is also of considerable importance when Ac-1 is used. Therefore, one must first establish the probability of the completion of chain transfer through a counterion, *i.e.*, the initiation of polymerization by the superacid formed in systems with Ac-1 (reaction (3)). If no such reinitiation occurs, then, as in the case of Ac-2, chain transfer degenerates into the loss of active centers.[6] In our previous works[7] we showed that the initiating activity of Ac-1, caused by the protonogenic character of this complex, is sharply suppressed in the presence of the proton trap, 2,6-dimethylpyridine (2,6-DMP); the contribution from the "concerted" mechanism of initiation in the polymerization of IB is no more than 5—10% independently of the presence of the proton trap. Therefore, unlike systems involving Ac-2 and Bn-2,[3] this system in the absence of 2,6-DMP is incapable of trapping free protons and terminating two-step chain transfer through a counterion after the first stage. For this reason, the $E_{in,min}$ values (see Table 1) calculated assuming that all superacid H^+,A^- formed *via* reaction (2) participates in the formation of new polymeric chains and taking into account its high initiating activity[1] seem to be even more reliable than the $E_{in,max}$ values.

The nearly linear kinetic dependences for the polymerization of IB in a fairly wide range of concentrations of Ac-1 (1.3—7.5 mmol L^{-1}) shown in semilogarithmic coordinates (Fig. 1, $[M]_0$ and $[M]$ are the initial and the current concentrations of the monomer, respectively) correspond to first order with respect to the current concentration of the monomer when the concentration of active centers is constant over time. Since elimination of protons from the growing carbocations in this system does not result in a loss of active centers, while E_{in} (judging by both limiting values) increases slowly in the course of the process and does not exceed several per cent (see Table 1), the steadiness of the number of active centers over time can only be achieved by irreversible termination, at a rate that must be

Table 1. Effect of the degree of conversion of the monomer (Q) on the PIB characteristics and E_{in} (*n*-hexane, −78 °C, $[M]_0$ = 1.25 mol L^{-1}, [Ac-1] = 9.7 mmol L^{-1})

t /min	Q (%)	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$f_{C=C}$ (%)	f_{C-Br} (%)	$E_{in,max}$ (%)	$E_{in,min}$ (%)
2	22	138.7	6.15	29.4	—	1.1	0.8
10	68	119.4	6.24	36.7	—	4.1	2.6
20	96	106.5	6.47	41.4	60.1	6.5	3.8

Table 2. Dependence of the molecular weight of PIB on the concentration of Ac-1 (*n*-hexane, −78 °C, $[M]_0$ = 1.64 mol L^{-1}, 30 min)

[Ac-1] /mmol L^{-1}	Q (%)	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w \cdot 10^{-3}$	$f_{C=C}$ (%)
1.30	44	130	733	51
2.82	61	119	590	47
7.50	79	108	541	46

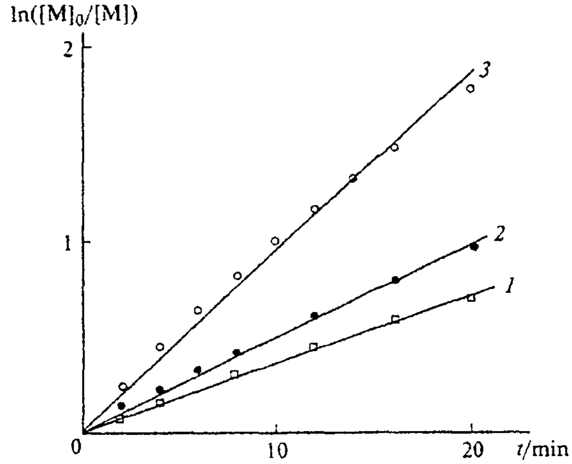

Fig. 1. Semilogarithmic anamorphoses of the kinetic curves of polymerization of IB under the action of Ac-1 (*n*-hexane, −78 °C, $[M]_0$ = 1.64 mol L^{-1}); [Ac-1]/mmol L^{-1} = 1.30 (*1*), 2.82 (*2*), 7.50 (*3*).

equal to the rate of initiation (a quasi-steady state is realized).

Since for all PIB samples synthesized with Ac-1 ($f_{C=C} + f_{C-Br}$) ≈ 100% (see Table 1 and the data of previous works[1,2]), it is obvious that in this case only collapse of the ionic pair (k_t is the rate constant of termination) can serve as the reaction of irreversible termination:

$$\mathrm{PIB{-}CH_2{-}CMe_2^+,A^-} \xrightarrow{k_t} \mathrm{PIB{-}CH_2{-}CMe_2{-}Br} + \text{Other nonionic products.} \qquad (4)$$

The similar collapse reaction in polymerization systems initiated by acyl complexes of composition 1 : 2 is likely to be reversible.[5,6]

The halogen anhydride fragment left after initiation can be a constituent of the counterion (A^-):

$$\mathrm{MeCOBr\cdot AlBr_3 + CH_2{=}CMe_2} \longrightarrow \mathrm{[Me{-}CMe_2]^+[CH_2COBr\cdot AlBr_3]^-}. \qquad (5)$$

Then the composition of the products of reaction (4) will be determined by the character of the decomposition of the species formed as a result of the release of a halide ion from the counterion A^-. It is very likely that $AlBr_3$ will also be present among these products.

Equation (5) describes the initiation process in the general form. In fact, the rate of this reaction appears to be independent of the concentration of monomer. Otherwise, the rate of polymerization would be second order with respect to the monomer, which is inconsistent with the experimental data presented in Fig. 1. Then, taking into account the fact that the rate of initiation is directly proportional to [Ac-1]:

$$R_{in} = k_i[\text{Ac-1}],$$

and the rate of termination (reaction (4)) is directly proportional to the concentration of active centers $[n^*]$:

$$R_t = k_t[n^*],$$

in the case of equality of these rates we get

$$[n^*] = (k_i/k_t)[\text{Ac-1}],$$

and the initial rate of polymerization (W_0) should be first order with respect to both the initiator and the monomer:

$$W_0 = (k_{pr}k_i/k_t)[\text{Ac-1}][\mathrm{M}]_0,$$

where k_{pr} is the rate constant for chain propagation. The first order curves with respect to the monomer were shown above (see Fig. 1). The dependence of W_0 on the concentration of Ac-1 (Fig. 2) shown in logarithmic coordinates allowed us to determine that the order of this reaction with respect to the initiator is truly equal to 1.0, which confirms the correctness of the above mentioned concepts. Note that in the case of Ac-2 and Bn-2 the reaction orders are equal to 0.5 and 2, respectively.[5]

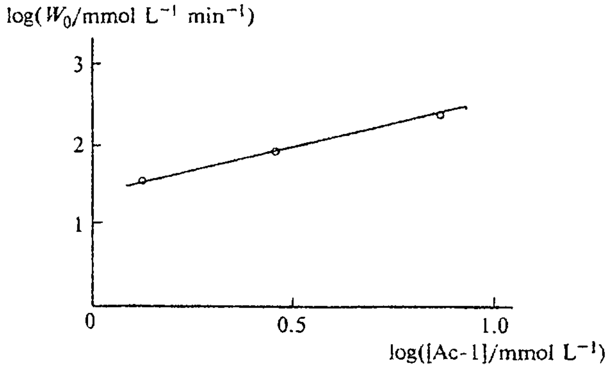

Fig. 2. Determination of the order of the initial rate of polymerization W_0 from the concentration of Ac-1 (*n*-hexane, −78 °C, $[\mathrm{M}]_0$ = 1.64 mol L^{-1}).

At least two reasons for the irreversibility of reaction (4) in the systems involving Ac-1 can be suggested:

1) $AlBr_3$ (which like, for instance, BCl_3[8,9] can be present among the products of this reaction) is incapable of re-abstraction of the covalently bonded halogen atom from the aliphatic polymeric chain under the given conditions or it fails in doing this because it quickly bonds to unreacted species of complex Ac-1. The possibility of this type of bonding has been demonstrated previously[1] in the conversion of a mixture of superacid ($HBr+AlBr_3$) with Ac-1 into complex Ac-2. At the same time, the concentration of $AlBr_3$ released is too small (E_{in} does not exceed several per cent) to form an appreciable number of Ac-2 molecules. Therefore it is almost impossible to detect the appearance of macromolecules with head acetyl fragments formed as a result of initiation by complexes of Ac-2.

2) In the nonionic product of reaction (4), $AlBr_3$ turns into a weak Lewis acid or even into a compound that exhibits no acid properties.

In this case, the "irreversibility" of termination means that the probability of re-formation of active carbocationic centers from PIB molecules with an end halogen atom within the period of polymerization is close to zero[10] under the experimental conditions, although these macromolecules can act as polymeric initiators when the conditions are changed (for instance, when excess Lewis acid is added). If for all that, a fraction of macromolecules is capable of growing further under our conditions, then the number of re-activated molecules will characterize the fraction of reversible termination. It is very difficult to find evidence for reversible termination (if it does occur) in this system judging by the kinetic data (see Fig. 1) and the small change in the polydispersity index $\bar{M}_w/\bar{M}_n$ (see Table 1).

To estimate the contributions from different chain limiting reactions, one can use the Mayo equation, which should be used in the integral form[11] at $R_{in} = R_t$ and at a degree of conversion higher than 10%:

$$\frac{1}{\overline{DP}_n} = \frac{k_{tr}}{k_{pr}} + \frac{k_{el} + k_t}{k_{pr}} \cdot \frac{\ln[100/(100-Q)]}{[M]_0 \cdot Q/100},$$

where $\overline{DP}_n$ is the number-average degree of polymerization, $Q(\%)$ is the degree of conversion; notations of the other terms of the equation were indicated earlier. This equation is valid in the case when no chain transfer to the initiator occurs, as, for instance, in "inifer" systems:[8,9]

$$[\mathrm{PIB{-}CH_2{-}CMe_2}]^+.\mathrm{A^-} + \mathrm{MeC(Br){=}O{\rightarrow}AlBr_3} \longrightarrow$$

$$\longrightarrow \mathrm{PIB{-}CH_2CMe_2{-}Br} + [\mathrm{MeC(O)}]^+.\mathrm{A^-} \xrightarrow{\mathrm{CH_2{=}CMe_2}}$$

$$\longrightarrow [\mathrm{Me{-}C(O){-}CH_2{-}CMe_2}]^+.\mathrm{A^-} \xrightarrow{\mathrm{CH_2{=}CMe_2}} \text{Chain propagation.} \quad (6)$$

The weak effect of Ac-1 concentration on the molecular weight of the polymers (see Table 2) points to the absence of this type of transfer. The slight decrease in molecular weight that occurs as the concentration of Ac-1 increases can be explained by taking into account the different degrees of conversion (*cf.* data in Table 1). In addition, reaction (6) should lead to macromolecules with head acetyl groups, which were not detected in the polymers ($f_{C=O} = 0$).

The $1/\overline{DP}_n$ values for the PIB samples obtained at [Ac-1] = 1.2 to 9.7 mmol L^{-1} and $[M]_0$ = 0.40 to 2.35 mol L^{-1} are shown in Fig. 3 in the coordinates of the integral Mayo equation. Apart from the two extreme right-hand points (point *1* corresponds to relatively low $[M]_0$ (0.40 mol L^{-1}) while point *2* corresponds to high conversion (96%) at moderate $[M]_0$ (1.25 mol L^{-1})), all the points are close to the straight line. Due to the scatter of points caused, for instance, by experimental errors, it is impossible to make the unambiguous statement that the straight line issues from the origin, *i.e.*, $k_{tr}/k_{pr} = 0$. At the same time, the absence of direct chain transfer to the monomer in the polymerization of IB under analogous conditions in the presence of Ac-2,[3] Bn-2,[5] or with the use of the initiating system cumylchloride/BCl_3 in a mixture of methylene chloride with cyclohexane[12] can be considered as a point in support of the absence of direct chain transfer to the monomer ($k_{tr} \approx 0$) also in the system with Ac-1. Moreover, if direct chain transfer to the monomer (reaction (1)) plays an important role in the formation of the double C=C bonds in the polymeric molecules, one would expect a decrease in $f_{C=C}$ as the degree of conversion increases, since the competing termination reaction (4) is zero order with respect to the monomer. In fact, (see Table 1) this value becomes somewhat greater as the degree of polymerization increases.

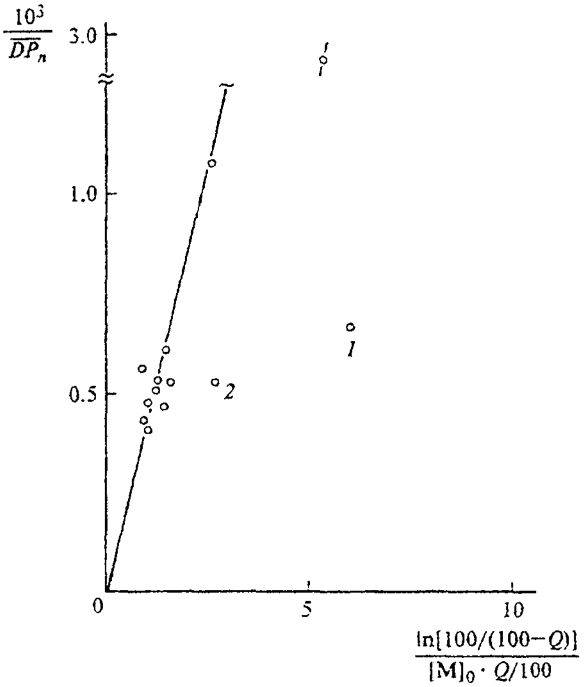

Fig. 3. The Mayo plot for the PIB samples synthesized in the presence of the initiating complex Ac-1 (*n*-hexane, −78 °C, [Ac-1] = 1.2−9.7 mmol L^{-1}, $[M]_0$ = 0.40−2.35 mol L^{-1}); points: *1*, $[M]_0$ = 0.40 mol L^{-1}; *2*, $[M]_0$ = 1.25 mol L^{-1}.

Assuming $k_{tr} \approx 0$, it is possible to determine the $(k_{el} + k_t)/k_{pr}$ ratio from the slope of the straight line in Fig. 3. It was found to be equal to $4.16 \cdot 10^{-4}$ mol L^{-1}. The k_{el}/k_{pr} ratio calculated previously[13] is equal to $1.30 \cdot 10^{-4}$ mol L^{-1}. Hence, $k_t/k_{pr} = 2.86 \cdot 10^{-4}$ mol L^{-1}, while the ratio $k_{el}/k_t = 0.45$, *i.e.*, in this case termination plays a more important role in limiting chain growth than transfer through the counterion. At the same time, the slight increase in $f_{C=C}$ mentioned above that occurs as the degree of conversion increases (see Table 1) is likely due to a change in the k_{el}/k_{pr} value in the later stages of polymerization.

Thus, the mechanism of polymerization of IB in the presence of Ac-1 essentially differs from that of polymerization in the presence of acyl complexes of composition $RCOX \cdot 2AlBr_3$. Polymerization initiated by Ac-1 is characterized by the following main features:

1) Ac-1 is a protonogenic initiator;

2) initiation proceeds slowly in the course of polymerization, as indicated by an increase in E_{in};

3) the initial rate of polymerization is first order with respect to the concentration of the initiator;

4) the carbonyl groups present in the system cannot act as proton traps;

5) chain termination, consisting in the collapse of the ionic pair, is irreversible (or almost irreversible);

6) in addition to chain termination, chain transfer through the counterion plays an important role in limiting the chains.

To estimate the ability of cationic polymerization systems to enter chain limiting reactions, we proposed the criteria of "similarity to a living system".[13] These criteria were first established for systems initiated by acyl complexes of composition 1 : 2 (Ac-2, Bn-2, *etc.*) and allowed one to estimate the role of reactions resulting in the appearance of C=C bonds in the polymeric molecules (reactions (1) and (2)). (No irreversible termination occurs in these systems). The first criterion,

$$(\mathrm{C{=}C})_{\mathrm{rel}} = f_{\mathrm{C=C}}/\overline{DP}_n$$

can be used regardless of the mechanism of the formation of the C=C bonds in the macromolecules. However, to compare different systems using this criterion, it is essential to have data obtained at close $[\mathrm{M}]_0$ and Q. The second criterion,

$$\frac{k_{\mathrm{el}}}{k_{\mathrm{pr}}} = \frac{f_{\mathrm{C=C}}}{\overline{DP}_n} \cdot \frac{[\mathrm{M}]_0}{10^4} \cdot \frac{Q}{\ln[100/(100-Q)]}$$

makes it possible to compare data obtained at different $[\mathrm{M}]_0$ and Q; however, it is valid only if $k_{\mathrm{tr}}/k_{\mathrm{pr}} \approx 0$. (For more detail, see Ref. 13.)

For the systems with Ac-1, irreversible termination is a predominant reaction of chain limitation. For systems of this type, it is appropriate to use an additional criterion that allows one to estimate the tendency for a system to undergo irreversible termination. This criterion can be obtained from the Mayo equation in the integral form. If $k_{\mathrm{tr}} \approx 0$ (as in the case of Ac-1), then one can first calculate the generalized criterion taking into account the contribution from irreversible termination as well as those from chain transfer (or chain loss) caused by proton elimination:

$$\frac{k_{\mathrm{el}} + k_{\mathrm{t}}}{k_{\mathrm{pr}}} = \frac{[\mathrm{M}]_0}{100\overline{DP}_n} \cdot \frac{Q}{\ln[100/(100-Q)]} \ .$$

A comparison of this formula with the above equation for the second criterion allows one to easily calculate the $k_{\mathrm{t}}/k_{\mathrm{pr}}$ ratio:

$$\frac{k_{\mathrm{t}}}{k_{\mathrm{pr}}} = \frac{(100 - f_{\mathrm{C=C}})}{\overline{DP}_n} \cdot \frac{[\mathrm{M}]_0}{10^4} \cdot \frac{Q}{\ln[100/(100-Q)]} \ .$$

Note that for all analyzed PIB samples synthesized with acyl complexes Ac-1 and Ac-2,[2,3] $f_{\mathrm{C-Br}} \approx 100 - f_{\mathrm{C=C}}$. This fact confirms that the collapse of the ionic pair does correspond to the irreversible termination in the system with Ac-1.

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