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

8.* The polymerization of isobutylene in the presence of superacids

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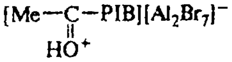
The polymerization of isobutylene in *n*-hexane at −78 °C under the action of the superacid $HBr \cdot 2AlBr_3$ as well as acetyl complexes $MeCOBr \cdot AlBr_3$ and $MeCOBr \cdot 2AlBr_3$ in the presence of $HBr \cdot AlBr_3$ and $HBr \cdot 2AlBr_3$, respectively, was studied. Unlike the superacid providing a quantitative yield of polyisobutylene (PIB) due to protonogenic initiation, the acetyl complexes suppress the proton initiation. In the presence of a mixture of both complexes with the superacid, only macromolecules with the head acetyl fragments MeC(O) are formed, which is evidence for a carbocationic initiation. The data obtained are explained by trapping of protons by the carbonyl groups to form ionic structures of the  $[\mathrm{Me{-}\underset{\underset{HO^+}{\|}}{C}{-}PIB}][\mathrm{Al_2Br_7}]^-$ type (where PIB is polyisobutylene) and to suppress the ionization of the superacids due to the common ion effect.

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

In the previous report,[2] we have shown that in the course of polymerization of isobutylene (IB) induced by the acyl complexes $MeCOBr \cdot AlBr_3$ (Ac-1) and $MeCOBr \cdot 2AlBr_3$ (Ac-2) the addition of 2,6-dimethylpyridine (2,6-DMP) suppresses the reactions of chain initiation and transfer involving free protons and retards the elimination of protons from the growing carbocations. The absence of reinitiation by the eliminated protons was also observed when only the cationogenic initiator Ac-2 was used. This results in the almost 100% functionalization (f) of the polymeric molecules by the acetyl head groups MeC(O) ($f_{C=O} \approx 100\%$) at a sufficiently high content of the tail units with the C=C bonds ($f_{C=C} \approx 50\%$)[3,4] formed due to the elimination of protons. In this connection, several questions arise. How is the reinitiation by eliminated protons suppressed when the complex Ac-2 is used? What are potential possibilities of this mechanism for trapping protons? Why is this mechanism not realized in the system with the protonogenic complex Ac-1?

In order to obtain answers to the questions listed, in this work we studied the polymerization of IB under the action of a mixture of HBr with $AlBr_3$ in a molar ratio of 1 : 2 (protonic superacid) and the complexes Ac-1 and Ac-2 in the presence of these mixtures. These results were compared with the data obtained in the absence of additives of HBr.

Experimental

Purification and drying of the starting reagents and solvent (*n*-hexane), procedures of polymerization in all-sealed glassware, and methods of isolation and analysis of polymers were described previously.[3–5] The efficiency of initiation (E_{in}) was calculated as the ratio of molar concentrations of polymeric chains and an initiator.[4] The degree of functionalization of polymers, *i.e.*, the fraction of macromolecules with the corresponding functional groups ($f_{C=O}$, $f_{C=C}$, and f_{C-Br}), was calculated from the data of the analysis of the content of the groups mentioned in polymeric samples by IR spectroscopy, ozonization and X-ray fluorescence analysis, and from the numerical-mean molecular weights ($\bar{M}_n$) of these polymers determined by gel-permeation chromatography (GPC).[3] It has been established previously[3–5] that only C=C and C—Hal are always the tail groups in the polymeric molecules synthesized under the action of the acyl complexes and precipitated with methanol. Hence, for the polymers synthesized in this work, $f_{C=C} + f_{C=Br} \approx 100\%$. Therefore, the complete analysis of the tail groups was not carried out for all samples. According to the GPC data, the polymeric samples have the unimodal molecular weight distribution.

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Table 1. Polymerization of isobutylene induced by initiating systems involving $AlBr_3$ in *n*-hexane at −78 °C ($[IB]_0$ = 1.25 mol L^{-1}, 20 min)

Entry	Initiator (C/mmol L^{-1})[a]	Conversion (%)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$f_{C=O}$ (%)	$f_{C=C}$ (%)	f_{C-Br} (%)	E_{in} (%)
1	SA-2 (1.2)	91	39	3.9	0	44	55	75—136
2	Ac-1 (1.2)	43	112	5.6	0	49	—	11.4—22.4
3	Ac-2 (1.2)	72	241	3.7	104	41	63	17.4
4	HAc-1 (1.2)	62	276	2.5	99	37	54	13.1
5	HAc-2 (1.2)	50	292	1.9	98	34	—	10.0
6	Ac-2 (4.1)	94	151	3.4	—	26	73	10.7
7	Ac-2 (4.1) + 2.6-DMP (0.5)	99[b]	208	1.6	103	9	—	8.2

[a] [HBr] in entry *1*, [MeCOBr] in other entries.

[b] The duration of polymerization is 50 min.

Methylene bromide was purified and dried by the same procedure as methylene chloride.[5] Dry HBr was obtained by bromination of decalin in the presence of a catalytic amount of $AlBr_3$, passed through paraffinic and calcium chloride traps, condensed in the Schlenk vessel, and dissolved in dry methylene bromide. The content of HBr in solution was determined by the weighing method.

A solution of the superacid $HBr \cdot 2AlBr_3$ (SA-2) in methylene bromide was prepared by mixing calculated amounts of solutions of HBr and $AlBr_3$ with the known concentrations. Solutions of the mixed complexes $HBr \cdot AlBr_3$ + $MeCOBr \cdot AlBr_3$, 1 : 1 (HAc-1) and $HBr \cdot 2AlBr_3$ + $MeCOBr \cdot 2AlBr_3$, 1 : 1 (HAc-2) were prepared similarly. The obtained solutions of initiators were dosed using thin-wall glass balls.[3]

Results and Discussion

The results of studying the polymerization of IB at −78 °C in *n*-hexane under the action of SA-2 and the HAc-1 and HAc-2 mixtures along with the data of the experiments using the Ac-1 and Ac-2 complexes as initiators are presented in Table 1. The kinetic curves of the polymerization processes obtained by the dilatometric method are presented in Fig. 1.

The complex SA-2 efficiently initiates the polymerization of IB: 20 min after, the conversion is greater than 90%. The calculation of the E_{in} value for this and similar experiments is not quite unambiguous, since the macromolecules are formed when the initiation is performed by both the initial superacid and a superacid that appeared due to the elimination of a proton from the growing carbocation. Therefore, in this case, the range of the E_{in} values calculated by the previously described procedure[4] is presented. The greater value corresponding to $E_{in,max}$ was calculated under the assumption that one molecule of the starting initiator HBr was consumed per each macromolecule formed. When $E_{in,max}$ > 100%, this means that the Brønsted acid entered the initiation reaction completely, and an excess number of the polymeric molecules is formed due to the chain transfer. The smaller value $E_{in,min}$ was determined assuming that each act of proton elimination (formation of the terminal C=C bond) was accompanied by reinitiation: $E_{in,min} = E_{in,max} \cdot (f_{C-Br}/100)$. As a whole, the E_{in} values for the experiment with SA-2 (entry *1*) indicate that the absorption of HBr in the initiation of the polymerization of IB is quantitative. This is also reflected by the high polymerization rate (see Fig. 1, curve *1*).

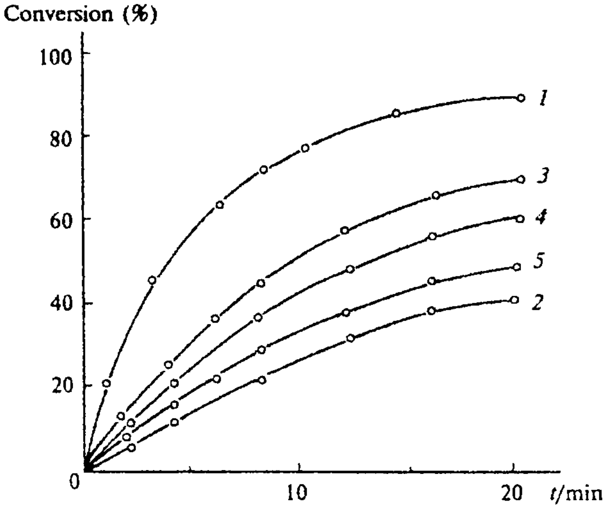


Fig. 1. Kinetics of polymerization of isobutylene in hexane at −78 °C. Numeration of curves corresponds to that of the samples in Table 1 (for conditions, see Table 1).

In entry *1*, the initiating and reinitiating compounds are likely the same (HBr combined with the Lewis acid), unlike entry *2*. In this case, the acyl complex $\mathrm{MeCOBr \cdot AlBr_3}$, although acting as the protonogenic Brønsted acid,[3,4] plays the role of the initiator. The efficiency of this initiator is considerably lower than E_{in} for SA-2 and does not exceed 23% (see Table 1). Therefore, the rate of the polymerization of IB is noticeably lower (*cf.* Fig. 1, curves *1* and *2*). About half the PIB macromolecules formed contain the terminal groups with the C=C bonds (as in entry *1*), and it is quite probable that the protons eliminated during the formation of these groups are completely or partially involved in the reinitiation.

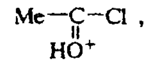
The results of the experiments on the polymerization of IB in the presence of the complex Ac-2, which are similar to entries *3* and *6*, have been discussed in detail in our previous works.[3,4,6] This complex acts as the cationogenic initiator providing the initiation by the acetyl cations $\mathrm{MeC(O)^+}$, and the protons eliminated from the growing carbocations are not able to reinitiate the polymerization of IB.

The initiating effect of HAc-1 (equimolar mixture of HBr, $\mathrm{AlBr_3}$, and $\mathrm{MeCOBr \cdot AlBr_3}$) (entry *4*) unexpectedly turned out to be similar to the behavior of Ac-2. Almost all head groups of the polymeric molecules are the acetyl fragments ($f_{C=O} \approx 100\%$). Therefore, both the initial HBr and HBr formed as a result of elimination of protons ($f_{C=C} = 37\%$) are not involved in the initiation. It is most likely that in this mixture the complex $\mathrm{MeCOBr \cdot AlBr_3}$ is transformed into the complex $\mathrm{MeCOBr \cdot 2AlBr_3}$.

In entry *5*, the presence of the Ac-2 complex, in fact, completely suppresses the protonogenic activity of SA-2, although the superacid exerts a certain effect on both the polymerization rate (see Fig. 1, curve *5*) and the properties of the polymer decreasing E_{in} and the polydispersity and increasing $\bar{M}_n$ (see Table 1).

Let us consider the results and conclusions in the publication[2] devoted to the effect of the additives of 2,6-DMP on the polymerization of IB under the action of the acyl complexes. In these systems, 2,6-DMP served both as the agent stabilizing carbocations and suppressing (although incompletely under the these conditions) the elimination of protons and as the proton trap. The latter effect was especially pronounced during the polymerization of IB in hexane under the action of the protonogenic initiator Ac-1: the activity of the system decreased more than an order of magnitude due to the addition of 2,6-DMP. In this case, the residual activity was explained by the matched ("concert") mechanism of the initiation.[7]

The effect of 2,6-DMP can be illustrated by the comparison of the results of entries *6* and *7* at equal concentrations of Ac-2 presented in Table 1. Since no reinitiation occurs either in the presence or absence of 2,6-DMP ($f_{C=O} \approx 100\%$), it is reasonable to assume that electron donors, which act as proton traps, are present in the systems without 2,6-DMP as well. The carbonyl groups of the acetyl fragments of the $\mathrm{MeC(O)CH_2CMe_2{-}PIB}$ macromolecules seem to be the most probable traps. The interaction of protons with the carbonyl compounds (ketones, esters) is related to superfast reactions;[8] therefore, it is most likely that the carbonyl groups of the macromolecules have time to trap almost all eliminated protons in the system with Ac-2 before they reinitiate the polymerization. Since in all cases $f_{C=O} > f_{C=C}$, the number of these trap groups should be quite sufficient to bind all protons.

Are the Ac-1 and Ac-2 complexes in the form of donor-acceptor complexes or acylium salts[3] and the molecules of free MeCOBr, which could appear in the dissociation of the complexes, the proton traps? Although it has been shown previously[9] that in a medium of strong Brønsted acids ($\mathrm{FSO_3H}$, $\mathrm{ClSO_3H}$, *etc.*) acetyl chloride is capable of reversible protonation at the O atom to form the structure  $\mathrm{Me{-}\underset{\underset{HO^+}{\|}}{C}{-}Cl}$, haloanhydrides of aliphatic acids are related, as a whole, to very weak Lewis bases. For example, according to Gutman, the donor number (*DN*) of acetyl chloride is equal to 0.7 [10] (*DN* is not determined for acetyl bromide but, as a rule, the replacement of chlorine by bromine has a slight effect on this value). For comparison, it should be indicated that *DN* of methyl isobutyl ketone (model of the head fragment of PIB molecules) is equal to 16.[10] It is known that small additives of electron donors with high *DN* (DMSO (29.8),[11] dimethylacetamide (27.8),[11] and 1-methyl-2-pyrrolidone (27.3)[12]) make it possible to suppress efficiently the uncontrolled proton initiation in the course of the cationic polymerization. Ethyl acetate (*DN* = 17.1) is less efficient in this respect.[11] Thus, the lower *DN* of the electron donor, the lower its ability to suppress processes involving free protons. This means that in this case, the carbonyl groups of the head acetyl fragments of the PIB molecules that formed under the action of Ac-2 should be the most efficient proton traps. The other oxygen-containing compounds that are present in these systems (unconsumed acyl complexes, unbound haloanhydrides) are substantially less efficient; otherwise such a strong inhibition effect of 2,6-DMP during the polymerization of Ac-1 would not be observed.[3]

A more complicated situation takes place in the presence of the specially added HBr (entries *4* and *5*). In these systems, the number of the ketone carbonyl groups (head acetyl groups) is *a fortiori* less ($E_{in} = 10{-}13\%$) than the total number of protons that are capable of initiation. Nevertheless, no proton initiation is observed in these experiments ($f_{C=O} \approx 100\%$). It is likely that in this case a different mechanism is realized, which prevents the ionization of HBr even in the presence of the Lewis acid. In order to reveal this mechanism, let us consider the so-called protonic superacids in more detail.

The term "superacid" was probably used for the first time by Olah and coworkers[13] for the systems of the $HF—SbF_5$, $HSO_3F—SbF_5$, *etc.* types, which turned out to be a very convenient medium for studying the structure of carbenium ions at low temperatures (~−100 °C) by NMR spectroscopy. Under these conditions, a noticeable ionization of the systems takes place. The situation changes under milder conditions and for weaker Lewis acids. For example, the solubility of $AlBr_3$ in liquid HBr at −78 °C is very low,[14] and the obtained solutions poorly conduct the current.[15] The conductometric studies have shown that when HCl and $AlCl_3$ are mixed in tetrachloroethylene, some ions are likely formed, but free initial compounds are mainly present.[16]

Taking into account these facts for the $HBr—AlBr_3$ systems (*e.g.*, of the composition 1 : 2), the following series of equilibria can be written:

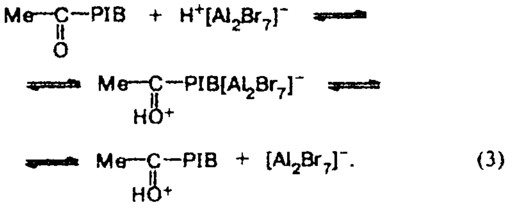
$$HBr + Al_2Br_6 \rightleftharpoons \underset{\text{(nonionized complex)}}{HBr\cdot Al_2Br_6} \rightleftharpoons \underset{\text{(tight ion pair)}}{H^+[Al_2Br_7]^-} \rightleftharpoons \underset{\text{(solvate-separated ion pair)}}{H^+\,[Al_2Br_7]^-_{Sol}} \rightleftharpoons \underset{\text{(free ions)}}{H^+ + [Al_2Br_7]^-} \qquad (1)$$

The authors of some publications suggest supplementing this scheme, for example, with spatially separated pairs,[17] taking into account the specific solvation of the ions by donor or acceptor additions,[18] *etc.* It is important that, according to the published data considered above, in the nonpolar solvent in the $HBr—AlBr_3$ system, these equilibria are shifted to the free components. At the same time, this system assumes the presence (at least a very small amount) of free ions even in nonpolar media. The existence of free ions allows one to apply the Ostwald law of dilution for weak electrolytes and to explain some effects observed in the polymerization of IB. In particular, based on these concepts, it is reasonable to assume that the presence of the carbocationic centers, for which a similar series of equilibria can be written, not only suppress the dissociation of the weaker electrolyte $HBr\cdot Al_2Br_6$, but also shifts the whole system of equilibria (1) to the free components. The complex $HBr\cdot Al_2Br_6$ is a weaker electrolyte than the polymeric growing center[6]

$$PIB—CH_2CMe_2Br\cdot Al_2Br_6 \rightleftharpoons PIB—CH_2CMe_2{}^+[Al_2Br_7]^-, \quad (2)$$

since a proton is considerably worse solvated in the nonpolar solvent than the bulky polyisobutenyl cation.

In essence, the mechanism presented describes the common ion effect.[19] The suppression of the initiating activity of the superacid formed in the elimination of protons from the growing chains during the polymerization of IB under the action of the dicumyl acetate—BCl_3 system in methyl chloride was explained in a similar manner.[20] However, if the suppression of the protonogenic activity is performed only due to the presence of the growing polymeric ion centers, one should expect both the disappearance or a sharp decrease in the initiating activity of the protonogenic complex Ac-1 already at the very beginning of the polymerization and a low E_{in} when SA-2 is used. In fact, in the system with Ac-1, E_{in} increases as the polymeric chains are accumulated[4] and is close to 100% in the case of SA-2 (see Table 1, entry *1*). Perhaps, at the given moment, the true concentration of the ionic form of the growing chains (see Eq. (2)) is very low[6] and cannot exert a noticeable effect on the protonogenic activity of the superacid. Nevertheless, the approach suggesting an important role of the common ion effect in the suppression of the superacid dissociation in the systems with Ac-2 seems to be fruitful. In fact, since the main difference between the systems involving Ac-2 and the systems with Ac-1 is the formation (in the first case) of the head acetyl fragments capable of trapping protons, it is probable that this is precisely their protonation due to which the ion structures capable of dissociation to free ions are formed:



$$\underset{\overset{\|}{O}}{Me—C}—PIB + H^+[Al_2Br_7]^- \rightleftharpoons \underset{\overset{\|}{HO^+}}{Me—C}—PIB[Al_2Br_7]^- \rightleftharpoons \underset{\overset{\|}{HO^+}}{Me—C}—PIB + [Al_2Br_7]^-. \qquad (3)$$

These ion pairs, unlike the growing polymeric ion pairs, cannot "collapse" to form the covalently linked form, and their concentration can exceed significantly the concentration of the polymeric cations thus providing almost the complete suppression of the superacid dissociation and the high content of the $[Al_2Br_7]^-$ ions in the solution. Moreover, it can be supposed that these protonated ion structures also control the concentration of the growing carbocationic centers by a mechanism including the common ion effect. This supposition is favored by the fact that in entries *4* and *5* E_{in} is lower than that in entry *3*, and the decrease in the polymerization rate can be seen in Fig. 1.

Thus, during the polymerization of IB in *n*-hexane under the action of the complex Ac-2, the proton initiation and reinitiation are suppressed due to binding of the protons by the carbonyl groups of the head acetyl fragments of the PIB macromolecules. Although the number of these groups is small, the ion structures formed in their protonation prevent the further ionization of the superacid due to the common ion effect (see equilibria (1) and (3)). As a result, the polymers with $f_{C=O} \approx 100\%$ were obtained in entries *3—6*. Therefore, in these cases, no additional traps of the 2,6-DMP type should be introduced to rule out the uncontrollable (proton) initiation. However, as mentioned previously,[2] another function of 2,6-DMP is likely the stabilization of the carbocations, which is reflected in the considerable decrease in the probability of the elimination of a proton and $f_{C=C}$, narrowing of MWD, and an increase in $\bar{M}_n$.

In the case of the polymerization systems initiated by Ac-1, the equimolar acyl complexes and products of their transformations probably cannot serve as proton traps.

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