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The influence of small additives of arenes on low-temperature isobutylene polymerization in an aliphatic solvent

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Isobutylene polymerization in hexane at −78 °C initiated by the methanol—aluminum bromide and *tert*-butyl chloride—aluminum bromide systems in the presence of minor additives (to 10 mmol L^{-1}) of arenes (benzene, chlorobenzene, toluene, and mesitylene) was studied. The addition of the arenes to a monomer solution has virtually no effect on the polymer yield, whereas the preliminary interaction of a concentrated solution of the Lewis acid with benzene and chlorobenzene sharply increases the monomer conversion and initiation efficiency. The results are interpreteted within a mechanism involving the participation of arene σ- and π-complexes in initiation. The concentration of the complexes is determined by the order of arene addition, and the activity and stability are related to their nature. In these experiments, hexafluorobenzene unexpectedly exhibited a pronounced inhibiting ability.

Key words: isobutylene, arenes, methanol, *tert*-butyl chloride, aluminum bromide, cationic polymerization.

In our previous study of the cationic polymerization of isobutylene (IB), we have found that minor additives of some nonpolymerized compounds have a pronounced effect on the polymerization and parameters of the polymers formed. For example, it has been shown[1] that the very low activity of the aluminum iodide complex with isopropyl alcohol in hexane at −45 and −78 °C increases dramatically when organic electron acceptors (di- and trinitrobenzene, chloranyl, and others) are added. A similar influence of electron acceptors was found when the additives were introduced to the system involving the initiating mesitoyl complex $MesCOBr \cdot 2AlBr_3$ (Mst-2; Mes = 2,4,6-$Me_3C_6H_2$). Moreover, even the initiation-inactive equimolar ionic complex $MesCOBr \cdot AlBr_3$ (Mst-1) became active upon introduction of these additives. Meanwhile, we failed to activate in a similar way the nonionic equimolar complexes of aluminum bromide with pivaloyl chloride or benzoyl chloride.[2] In all the cases, the concentrations of the complexes and additives were low (~1 mmol L^{-1}) and comparable. The activation effect of organic electron acceptors resembles that appeared due to the addition of the excess Lewis acid. We proposed a general mechanism of activation of these systems, which suggests a decrease in the nucleophilicity of the counterion.[2] An important role of anion solvation by the electron acceptor additives for successful cationic polymerization has been demonstrated.[3]

The subsequent experiments showed that some aromatic compounds, also taken in very low concentrations, can exhibit an unexpectedly strong activation effect. In this work, we studied the influence of small arene additives on cationic IB polymerization by the systems on the basis of aluminum bromide in hexane at −78 °C and on the parameters of initiation efficiency of these systems.

Experimental

Hexane was treated with concentrated H_2SO_4, washed with a NaOH solution and water, and dried with $CaCl_2$, molecular sieves, and a potassium-sodium alloy. Arenes (benzene, toluene, mesitylene, chlorobenzene, and hexafluorobenzene) were purified and dried similarly (the two latters were not treated with alkali metals). Isobutylene was stored for several days above granulated KOH, additionally dried with CaH_2, molecular sieves, and butyllithium, and recondensed. *tert*-Butyl chloride was dried with $CaCl_2$ and molecular sieves and distilled. Methanol was treated with metallic sodium and distilled. Anhydrous aluminum bromide was heated in a dry argon flow for 1 h at 150 °C and twice sublimed *in vacuo.* The final stages of purification and drying of all the substances, preparation of solutions, and dosing in ampules and thin-walled glass balls were carried out in a whole-sealed glassware with the use of a deep vacuum.[4,5]

Isobutylene was polymerized in a whole-sealed vacuum setup with two initiating systems: aluminum bromide—methanol and aluminum bromide—*tert*-butyl chloride. The polymerization kinetics was studied by dilatometry. In all experiments, the induction period was absent, and the monomer conversion (Q) increased monotonically in time, which allowed the use of the Q value, reached within a specified time, as the activity parameter of the system. Solutions of components of the initiating system, arenes, and the monomer were introduced into the setup in thin-walled glass balls or in ampules with thin glass membranes. The balls and membranes were broken by glass-sealed steel rods. The "bullets" were manipulated by small permanent magnets. The same "bullets" were used as stirring bars in the setup.

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Two variants were applied for the introduction of aromatic additives into the system. According to variant I, arene was pre-added to a relatively concentrated (~0.05 mol L^{-1}) solution of aluminum bromide (usually the molar ratio was ~8 : 1), and the prepared solution was dosed in balls. According to variant II, arene was introduced beforehand into a monomer solution in hexane. In all the experiments, aluminum bromide or its mixture with an aromatic additive was last to be introduced, and this moment was taken as the beginning of polymerization.

When a total conversion of the monomer was reached, the polymers were precipitated by excess cooled methanol and dried *in vacuo* to a constant weight.

The molecular weights and molecular-weight distribution of polymers were determined by GPC.[5,6] The number of the double C=C bonds in polymers was found by the ozonization method using an ADS-4 instrument. Using these results and taking into account $^{-}M_{\rm n}$, we calculated the degree of functionalization of macromolecules by double bonds $f_{\rm C=C}$, *i.e.*, the fraction of the polymer molecules containing C=C bonds. The formulas for calculation of the minimum and maximum initiation efficiency ($E_{\rm in}$) and their substantiation are presented below.

Table 1. Influence of arenes on IB polymerization in the presence of the methanol—aluminum bromide (1 : 1) initiating system at −78 °C

Entry	Arene	Variant of introduction	C^a AlBr$_3$	Ar	IB	$M_{\rm n}^{b,c}$	Q_{30}^d	$f_{\rm C=C}^c$	$E_{\rm in}^c$
							%		
	—	—	0.80	—	1.83	358	7	45	36—20
2	C_6F_6	I	1.05	8.4	1.92	—	0	—	—
3	PhCl	I	0.88	7.0	1.83	121	92	40	96—58
4	C_6H_6	I	0.82	6.5	1.62	175	53	35	63—41
5	$PhCH_3$	I	0.80	6.4	1.69	256	17	48	46—24
6	$C_6H_3Me_3$	I	0.81	6.5	1.69	169	9	72	69—19
7	C_6F_6	II	1.05	1.0	1.92	486	12	24	21—16
8	C_6H_6	II	0.87	8.0	1.62	137	9	79	76—16
9	C_6H_5Me	II	0.81	8.0	1.62	125	11	85	90—14
10	$C_6H_3Me_3$	II	0.80	8.0	1.62	53	13	90	214—21

[a] Concentration of AlBr$_3$ and Ar in mmol L^{-1}, and that of IB in mol L^{-1}.
[b] The $M_{\rm n} \cdot 10^{-3}$ values are presented.
[c] The $M_{\rm n}$, $f_{\rm C=C}$, and $E_{\rm in}$ values were determined for the samples isolated upon the quantitative conversion of the monomer ($Q \approx 100\%$).
[d] Conversion within 30 min.

Table 2. Isobutylene polymerization by the *tert*-butyl chloride—aluminum bromide system in the presence of minor arene additives at −78 °C

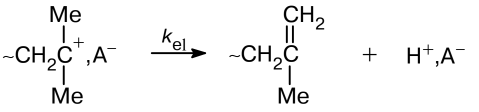
Entry	Arene	Variant of introduction	C^a AlBr$_3$	Ar	IB	$M_{\rm n}^{b,c}$	Q_{30}^d	$f_{\rm C=C}^c$	$E_{\rm in}^c$
							%		
11	—	—	0.80	—	1.81	109	50	31	93—64
12	C_6F_6	I	0.96	7.6	1.81	—	0	—	—
13	PhCl	I	0.97	7.7	1.83	89	80	22	111—87
14	C_6H_6	I	0.95	7.6	1.83	106	69	18	102—84
15	$PhCH_3$	I	0.95	7.6	1.58	107	52	49	87—44
16	$C_6H_3Me_3$	I	0.95	7.6	1.58	105	56	56	89—39
17	C_6F_6	II	0.96	1.0	1.81	230	59	14	46—40
18	C_6H_6	II	0.95	8.0	1.81	96	44	55	111—50

[a] Concentration of AlBr$_3$ and Ar in mmol L^{-1}, and that of IB in mol L^{-1}.
[b] The $M_{\rm n} \cdot 10^{-3}$ values are presented.
[c] The $M_{\rm n}$, $f_{\rm C=C}$, and $E_{\rm in}$ values were determined for the samples isolated upon the total conversion of the monomer ($Q \approx 100\%$).
[d] Conversion within 5 min.

Results and Discussion

Estimation criteria of the system. The monomer conversions Q (or polymer yields) reached within a specified time (Tables 1 and 2) are often compared to compare the activities of the polymerization systems. However, almost all reactions that occur during polymerization affect this parameter, and its use is insufficient, in some cases, for the estimation of the activity of initiators. An additional fruitful information for this estimation can be obtained from the determination of the initiation efficiency $E_{\rm in}$, although this parameter cannot always be calculated unambiguously. In the absence of chain transfer, $E_{\rm in}$ is simply found by the division of the concentration of polymer molecules into the molar concentration of the initiator. For cationic IB polymerization, in the general case, several chain transfer reactions may occur through proton elimination from the growing carbocation:

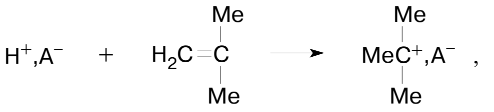
— proton elimination for the A^- counterion to form the superacid



$$\sim\!CH_2\overset{Me}{\underset{Me}{C^+}},A^- \xrightarrow{k_{el}} \sim\!CH_2\overset{CH_2}{\underset{Me}{\overset{\|}{C}}} + H^+,A^-$$

(1a)

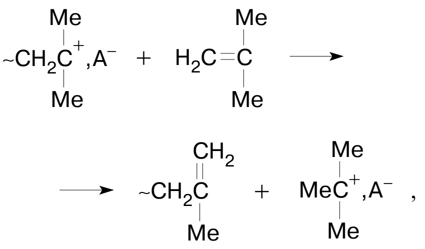
($k_{\rm el}$ is the elimination constant) followed by proton reinitiation



$$H^+,A^- + H_2C{=}\overset{Me}{\underset{Me}{C}} \longrightarrow Me\overset{Me}{\underset{Me}{C^+}},A^- ,$$

(1b)

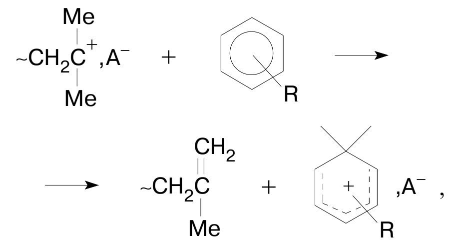
— direct transfer to the monomer



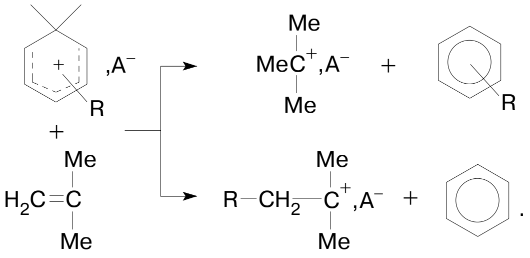
$$\sim\!CH_2\overset{Me}{\underset{Me}{C^+}},A^- + H_2C{=}\overset{Me}{\underset{Me}{C}} \longrightarrow \sim\!CH_2\overset{CH_2}{\underset{Me}{\overset{\|}{C}}} + Me\overset{Me}{\underset{Me}{C^+}},A^- ,$$

(2)

— chain transfer to the arene


(3a)

also accompanied by proton reinitiation (or cationation)


(3b)
(3c)

According to traditional views on the mechanism of cationic polymerization (see, *e.g.*, Refs. 7 and 8a), the second stages of processes (1) and (3) (*i.e.*, reactions (1b), (3b), and (3c)) occur completely. Hence, these reactions can be considered as chain transfer (termination of the material rather than kinetic chains). In this case, E_{in} can easily be calculated from the content of terminal double C=C bonds in the polymer, *i.e.*, $f_{\text{C=C}}$. In fact, for some systems the situation is most likely more complicated. Our results on IB low-temperature polymerization initiated by the 1 : 2 acyl halide complexes with aluminum bromide demonstrated the virtually complete absence of reaction (1b). This fact was attributed to the appearance of proton traps, the head ketone groups entered with the initiator fragment, in the structure of polymeric molecules.[9,10] Our data also indicate that reaction (2) does not occur under the chosen conditions (low temperature, nonpolar solvent). It is most likely that the direct chain transfer to the monomer (2) is not characteristic at all of low-temperature IB polymerization in an aliphatic solvent, therefore, it can be ignored in subsequent discussion.

As for the reinitiation activity of the aromatic protonated products of reaction (3a), if these products are sufficiently stable, their activity also can be expected to be at least considerably decreased. Therefore, under specific conditions, the second stages of reactions (1) and (3) ((1b), (3b), and (3c)) can be absent at all (or occur partially), and the first stages ((1a) and (3a)) can be considered, in this case, as termination stages of material and kinetic chains as well.

It follows from the aforesaid that the contribution of chain transfer reactions into the formation of new macromolecules can be estimated with a satisfactory accuracy only when quantitative data on the content of head and terminal groups of this or another type are available; the use of acyl initiators is very convenient in this respect.[2,5,9,10] The relative content of the head groups appeared by the primary initiation and due to chain transfer cannot be determined for initiation by protons of aliphatic carbocations. Correspondingly, the E_{in} value cannot be calculated exactly. Nevertheless, the obtained data (see Tables 1 and 2) make it possible to find the limiting values of initiation efficiency. The maximum initiation efficiency $E_{\text{in}}^{\text{max}}$ can be calculated on the basis of the absence of reinitiation by eliminated protons

$$E_{\text{in}}^{\text{max}} = [\text{M}_0](Q/100)/(DP_{\text{n}}[\text{In}]),$$

where $[\text{M}]_0$ is the initial concentration of the monomer, Q (%) is the conversion, DP_{n} is the average degree of polymerization, and In is the initiator. In this work, the initiator concentration was accepted to be equal to the initial concentration of methanol or *tert*-butyl chloride because the participation of a residual moisture in initiation can be neglected under the used "superdry" conditions.

The minimum initiation efficiency is calculated under the assumption that all eliminated protons participate in the initiation of new polymeric chains

$$E_{\text{in}}^{\text{min}} = E_{\text{in}}^{\text{max}}(100 - f_{\text{C=C}})/100.$$

The true E_{in} values should lie between these two limiting values. However, as will be shown below, even such an estimation parameter as the interval of limiting values ($E_{\text{in}}^{\text{max}} - E_{\text{in}}^{\text{min}}$) is very useful, in some cases, to reveal the influence of these or other factors on the activity of initiators.

Initiating system aluminum bromide—methanol. Let us consider the situation that takes place when low amounts of arene are added (variant II, see entries *1* and *7—10* in Table 1). No substantial change in the activity of the system due to the addition of aromatic compounds was observed: the polymer yield for 30 min remained rather low (~10%). A very high $E_{\text{in}}^{\text{max}}$ value in entry *10* (>200%) shows that at least in the system with mesitylene a considerable part of macromolecules is unambiguously formed due to reinitiation by ion products formed through proton elimination in reactions (1a) and/or (3a). Compounds capable of preventing reinitiation are absent, most likely, under these conditions. In this case, it seems reasonable that the true E_{in} value is close to $E_{\text{in}}^{\text{min}}$, which is almost the same in these experiments and amounts to 15—20%.

Hexafluorobenzene (1 mmol L^{-1}) also has no noticeable influence on the activity. However, at higher concentrations (~8 mmol L^{-1}) it inhibits the process (see, *e.g.*, entries *2* in Table 1 and *12* in Table 2).

When an aromatic compound is pre-added to a concentrated solution of aluminum bromide (variant I, entries *2—6* in Table 1), the picture changes drastically: benzene and the more so chlorobenzene increase sharply the activity of the system. The shift of the E_{in} intervals toward higher values indicates that the acceleration is due, in particular, to an increase in the degree of using the initiator. The acceleration effect of toluene is much lower and is virtually absent in the case of mesitylene. In the presence of hexafluorobenzene, as mentioned above, polymerization does not occur under the indicated conditions.

Initiating system aluminum bromide—*tert*-butyl chloride. This system provides a higher polymerization rate than the aluminum bromide—methanol combination under the same concentrations of the components: already after 5 min the polymer yield even in the absence of modifying arenes was 50% (see entry *11* in Table 2). For this reason, in this series (see entries *11—18* in Table 2) we restricted our consideration by precisely this duration of the process to compare the polymer yields.

As in experiments with methanol, the addition of benzene or a small amount of hexafluorobenzene to the blend (variant II) slightly affects the activity of the system. The data obtained in entries according to variant I qualitatively resemble the results for the system with methanol: acceleration in the presence of chlorobenzene is again most pronounced, benzene exhibits a weaker activation effect, and toluene and mesitylene do not virtually activate the system. Hexafluorobenzene at a concentration of 7.6 mmol L^{-1} inhibits polymerization.

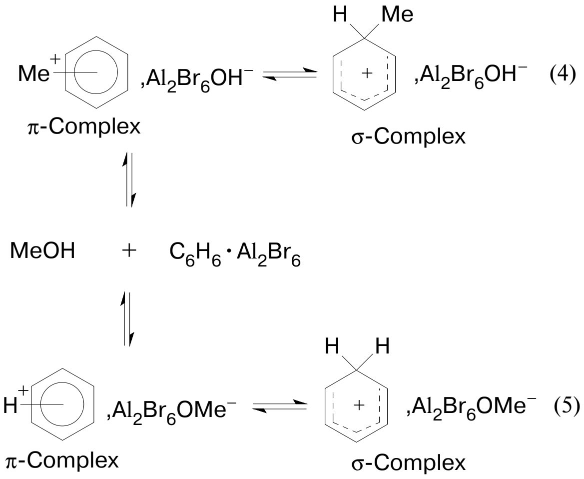
For the most experiments illustrated in Table 2, the E_{in} intervals overlap, which impedes an unambiguous estimation of the influence of modifying additives on this parameter. We can only mention its lower values in entry *17* with hexafluorobenzene. In addition, the E_{in}^{max} values exceeding 100% in entries *13*, *14*, and *18* indicate again a considerable contribution of reinitiation by eliminated protons.

The results presented in Tables 1 and 2 show that for both initiating systems (aluminum bromide—methanol and aluminum bromide—*tert*-butyl chloride) the additives of aromatic compounds have a qualitatively similar effect, which, however, is determined to a great extent by the order of introduction of the additive. The starting nonmodified systems can differ in the nature of initiating species. Combinations of the Lewis acids with *tert*-butyl chloride are usually considered as typically cationogenic initiating systems, and *tert*-butyl chloride is attributed to the most efficient initiators of IB polymerization due to the resemblance of structures of the *tert*-butyl cation and growing polyisobutenyl cation.[11] The corresponding tertiary carbocations are also formed when the Lewis acids are combined with such alcohols as *tert*-butyl alcohol or triphenylmethylcarbinol.[12] This is also evidenced by quantum-chemical calculations.[13] The situation with methanol is less evident,[14,15] but it can be assumed that, when it is used, proton initiation can make some contribution depending on the conditions of the process. (Below we will return to the question about the nature of initiating species in the system with methanol.) Nevertheless, resemble responses of both systems to the nature of modifying arenes and the order of their introduction indicate that a possible difference in the types of primarily formed positively charged particles has no qualitative effect on the general picture of the process.

The pre-contact of arenes with aluminum bromide in a relatively concentrated solutions (conditions of variant I) in several cases (Ar is benzene or chlorobenzene) has a very strong effect on the activity of the polymerization system, which suggests the appearance due to this contact of some new compounds, whose formation in dilute solutions is much less probable. It is most likely that these interactions can afford only rather weak intermolecular $Ar \cdot Al_2Br_6$ complexes (1 : 2; Ar is benzene, toluene, and, probably, weaker aromatic π-donors), and in the case of stronger electron donors, $Ar \cdot AlBr_3$ (1 : 1; in particular, if Ar is mesitylene). A detailed information on these complexes and factors influencing their formation was generalized in the monograph.[16] However, data on the thermodynamic parameters of solutions of these complexes in poorly polar liquids are limited and their reliability casts some doubt because of a low degree of drying of the components and solvent.[16] Therefore, we performed a study of the aluminum bromide complexes with benzene by ^{27}Al NMR spectroscopy using the drying methods applied for polymerization procedures in a whole-sealed evacuated glassware (see Experimental). The obtained results[17] allowed the determination of the equilibrium constants of the $C_6H_6 \cdot Al_2Br_6$ complex within the temperature range from +20 °C (0.72 L mol^{-1}) to −80 °C (8.55 L mol^{-1}). The calculation that took into account the latter value showed that at −78 °C in a relatively concentrated solution where aluminum bromide was pre-mixed with benzene the main part (~90%) of the Lewis acid was bound to form a complex. Meanwhile, in a polymerization solution, *i.e.*, at the concentrations indicated in Tables 1 and 2, in the equilibrium state only ~8% aluminum bromide participates in complex formation with benzene (even when the consumption of Al_2Br_6 for complex formation with the monomer and formation of active sites is ignored). These values should be somewhat higher for stronger electron donors, and for weaker electron donors they, by contrast, should decrease.

Thus, although complexes of the πv-type are attributed to weak intermolecular complexes,[16] the fraction of the complex form can considerably be increased due to the temperature decrease and an increase in the concentration of the components. These are precisely these conditions, which favor bounding of the Lewis acid to form a complex with arene, that are created by mixing according to variant I. This results, most likely, in differences observed when the order of arene introduction is changed. It should be emphasized that many stages in olefin cationic polymerization occur with very high rates.[18] Probably, under our conditions, some interactions between the components have time to occur until the system is completely homogenized. Since at least several seconds are required for mixing the system according to the procedure used (see Experimental), the initial stages of the process are nonequilibrium under the conditions of variant I, *i.e.*, they involve a solution containing the arene—Lewis acid complexes in high concentrations.

Taking into account the assumption of the reason for the difference in activities at different orders of arene introduction, let us consider the main reactions between the components, which can involve the donor-acceptor arene—Lewis acid complexes or occur without them (reactions (4)—(8)).



$$2\ \mathrm{MeOH} + \mathrm{Al_2Br_6} \rightleftharpoons 2\ [\mathrm{MeOH \cdot AlBr_3}] \qquad (6)$$

$$2\ [\mathrm{MeOH \cdot AlBr_3}] \rightleftharpoons 2\ \mathrm{HBr} + \mathrm{Al_2Br_5OMe} \qquad (7)$$

$$2\ [\mathrm{MeOH \cdot AlBr_3}] \rightleftharpoons 2\ \mathrm{MeBr} + \mathrm{Al_2Br_5OH} \qquad (8)$$

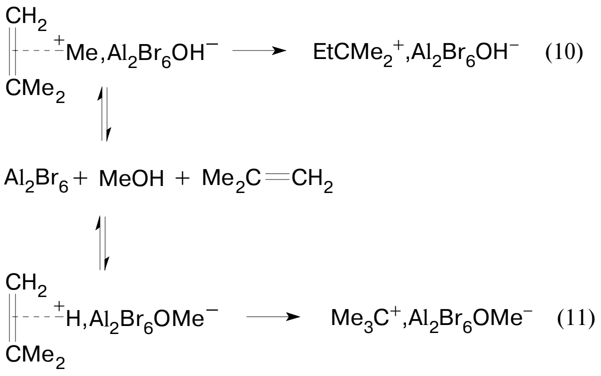
In the presence of the donor-acceptor complexes, the arenium complexes of the π- and σ-types can directly be formed (reactions (4) and (5)). These complexes are capable of initiating IB polymerization due to protonation (cationation by the methyl cation cannot either be excluded). Although the composition of the arenonium complexes, presumably formed under our conditions, is unknown, they probably resemble in structure the Gustavson complexes, which found use as the catalysts for polymerization and telomerization.**[8b,19]** The π-form of the complex is most likely the real initiator because, as reported previously,**[8c]** the products of the addition of arenonium ions to the monomer were not observed when IB polymerization was initiated by the proton-containing onium complexes based on polystyrene and its derivatives.

The reaction of alcohol with aluminum bromide in the absence of arenes affords the intermediate 1 : 1 complexes (reaction (6)); the heat of formation of these complexes is**[20]** ~40 kcal mol^{-1}. Although calculations show that even for primary alcohols (methanol, ethanol, *etc.*) the carbocation should be an initiating species when these complexes are used, it was assumed in these calculations that the counterion in the initiating ionogenic structure can contain only one molecule of the Lewis acid**[8d,14]** (in our case, $\mathrm{AlBr_3OH^-}$ should be this counterion). However, our studies with the mesitoyl complexes**[2]** showed that in the systems involving aluminum bromide, at least in low-polar media (*e.g.*, hexane or methylene dichloride), these "monomeric" counterions are too nucleophilic and do not allow monomer addition: polymerization does not occur. Therefore, the alcohol—aluminum bromide (1 : 1) complex itself is probably inactive in the process initiation. Its decomposition *via* reaction (8) results in the primary haloalkyl: these compounds cannot function as initiators. Hence, this route corresponds to the nonproductive consumption of methanol. Reaction (7) produces HBr, which reacts subsequently with the aluminum bromide dimer and is capable of forming the active sites. Another way of the formation of initiating sites can be the activation of the $\mathrm{CH_3OH \cdot AlBr_3}$ complex by free aluminum bromide, which is present in the dimeric or monomeric forms. The latter is formed when the dimer dissociates in the reaction

$$\mathrm{Al_2Br_6} \rightleftharpoons 2\ \mathrm{AlBr_3}, \qquad (9)$$

which is favored by the dilution of the system. We cannot conclusively say whether the Lewis acid-activated $\mathrm{CH_3OH \cdot AlBr_3}$ complex is capable of manifesting the cationogenic or protonogenic activity. However, note that the boron trifluoride etherate $\mathrm{Et_2O \cdot BF_3}$, which is often used for the initiation of cationic polymerization, usually contains a considerable amount of the $\mathrm{EtOH \cdot BF_3}$ and even $\mathrm{H_2O \cdot BF_3}$ complexes. This allows some authors**[21]** to consider the etherate as a virtually protonogenic initiator. In any case, the mechanism of initiation by the Lewis acid—primary alcohol system is rather sophisticated and requires more detailed study. Nevertheless, the low E_{in} values for the nonmodified system (see entry *1*, Table 1) are worth mentioning. They can be compared with the corresponding values (76—135%) obtained**[22]** for the HBr—$\mathrm{Al_2Br_6}$ system under similar conditions (hexane, −78 °C, $[\mathrm{IB}]_0 = 1.25$ mol L^{-1}, $[\mathrm{HBr}] = [\mathrm{Al_2Br_6}] = 1.2$ mmol L^{-1}). Such a low initiation efficiency is stipulated, most likely, by the high strength of the $\mathrm{MeOH \cdot AlBr_3}$ complex and its nonproductive consumption *via* reaction (8). This conclusion can be supported by the data for the system with *tert*-butyl chloride (see entry *11*, Table 2). For the last case, no reaction of type (8) can be assumed, and haloalkyl complexes with the Lewis acids are much less stable**[23—25]** than the alcohol complexes and, therefore, the initiation efficiency with this initiator is much higher.

Let us consider one more possible direction of the formation of active sites, which assumes the direct participation of the olefin—Lewis acid complexes, using the "methanol" system as an example (reactions (10) and (11)).

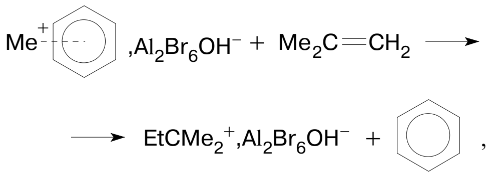


These reactions formally resemble reactions (4) and (5) involving arene, although it is significant that the second stages of reactions (10) and (11) are irreversible unlike the corresponding stages of reactions (4) and (5). This distinction has already been mentioned previously.[8e] Meanwhile, reactions (10) and (11) result in the direct formation of active sites of growth, whereas reactions (4) and (5) give only species probably capable of the initiation of polymerization. Therefore, it is necessary to explain how the overall increase in the process rate and the initiation efficiency is achieved due to the additional participation of reactions (4) and (5) in the case of using benzene or chlorobenzene additives.

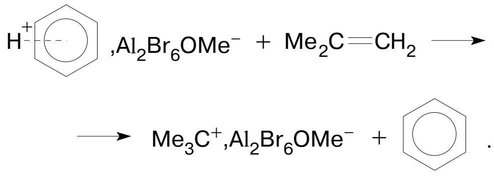
In our opinion, this increase is reasoned by the fact that the formation of the π-complexes in reactions (4) and (5) is facilitated by a low decrease in entropy upon complex formation: protons or carbocations during complex formation can virtually freely remove along the chain of conjugated π-bonds of the aromatic ring.[26] This is confirmed by the data[27] that the entropy loss ($-\Delta S^\circ$) upon the formation of the π-complexes with a proton for the phenol—naphthalene, phenol—phenanthrene, and phenol—benzene pairs is 2.8, 1.0, and 4 cal deg^{-1} mol^{-1}, respectively, whereas it is 10—18 cal deg^{-1} mol^{-1} for the phenol—alkyl vinyl ester pair.

A low polarity of the medium is an additional factor that should determine the preferential formation of the arenonium π- and σ-complexes compared to the corresponding olefin adducts. Arene complexes are more bulky and have a more delocalized charge and, hence, they are less demanding for the solvating capability of the solvent. By contrast, the formation of the intermediate π-complexes *via* reactions (10) and (11) in low-polar media is hindered according to some data. The authors[28,29] found a decrease in the rate of IB polymerization initiated by trifluoromethanesulfonic acid or aluminum bromide at elevated monomer concentrations. They explained this effect by bounding of the main amount of the Brönsted or Lewis acid to form inactive complexes with the monomer. Similar anomalous dependences of the polymerization activity on the monomer concentration have been found for several acyl and alkyl initiating systems.[4] If the previously proposed[28,29] explanation is valid, it should be accepted that the transition states appeared in reactions (10) and (11) (for example, π-complexes) differ in structure from the corresponding states appeared during initiation by the initiator—coinitiator complex and their formation is more hindered.

The second stages of reactions (4) and (5) describe the monomolecular transformation of the π-complexes into σ-complexes. Since, as already emphasized,[8c] the arenonium ions themselves do not add to IB, their potential initiating ability should be determined by the easiness of the inverse transition to the π-complexes. In this sense, the σ-complexes can be considered as species that are potentially capable of initiation. The introduction of electron-donating alkyl substituents into the aromatic ring and an increase in their number favor the formation of arenonium complexes stabilizing the positive charge of the ring. At the same time, the increase in the stability should decrease the initiating ability of the complexes, *i.e.*, their activity in the reactions



(12)



(13)

Most likely, due to the opposite directivity of these two tendencies, only for relatively weak aromatic electron donors, benzene and chlorobenzene, the most pronounced activation effect was found among several studied arenes.

Isolation of the starting arene in reactions (12) and (13) makes it possible to consider aromatic compounds as "catalysts for the initiation stage" favoring the transformation of the starting initiator into ionic structures and thus preventing competing reactions, which lead to a less efficient consumption of the initiator.

Thus, we can interpret the influence of small additives of arenes on the activity of low-temperature IB polymerization in a nonpolar medium and the initiation efficiency as follows. When these additives are introduced into a solution of the monomer, they do not affect, as a rule, the above parameters. The pre-mixing of relatively concentrated solutions of benzene or chlorobenzene and the Lewis acid, which favors the formation of donor-acceptor complexes of the πv-type, enhances the polymer yield and initiation efficiency. This is especially pronounced for the methanol—aluminum bromide initiating system. It is assumed that this activation is reasoned by the formation of the π- and σ-arenonium complexes capable of intertransforming and functioning in the future as initiating sites. Analysis of the reactions allowed the consideration of these arenes as catalysts of initiation. The stronger aromatic electron donors, toluene and mesitylene, should prone to even a greater extent to the transformation into these arenonium complexes. However, the σ-complexes formed with their participation are more stable and, as a consequence, less active in the protonation or cationation of the monomer, due to which the activation effect of the two last arenes is virtually aligned. When mesitylene is used with the *tert*-butyl chloride—aluminum bromide system, the σ-arenonium complexes cannot probably be formed because of steric hindrances. The most electron-withdrawing arene, hexafluorobenzene, even in a concentration of ~8 mmol L^{-1} inhibits completely polymerization. Presently, reasons for such an influence of this compound remain unclear.

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