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

10.* The influence of the composition of complexes of mesitoyl bromide with aluminum bromide on their ability to initiate isobutylene polymerization

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The ionic complex of mesitoyl bromide with aluminum bromide in a 1 : 1 composition (Mst-1) does not initiate the isobutylene polymerization in *n*-hexane or methylene dichloride at −78 °C. The corresponding ionic complex of the 1 : 2 composition (Mst-2) acts as a cationogenic initiator of the polymerization. The addition of excess Lewis acid or introduction of organic electron acceptors increases the initiating activity of the Mst-1 complex and activates acyl complexes of the 1 : 2 composition including Mst-2. The results are discussed in terms of the effect of specific solvation on the nucleophilicity of counteranions, which makes the addition of the monomer to the carbocation possible.

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

In the previous works,[1—3] we have demonstrated the substantial effect of the composition of the acyl halide complexes with aluminum bromide $RCOX \cdot nAlBr_3$ (R = Ac, Ph; X = Cl, Br; *n* = 1, 2) on their ability to initiate isobutylene (IB) polymerization and on the initiation mechanism. The acetyl $MeCOBr \cdot 2AlBr_3$ (Ac-2) and benzoyl $PhCOCl \cdot 2AlBr_3$ (Bn-2) complexes in *n*-hexane at −78 °C act as cationogenic initiators of the formation of polyisobutylene (PIB) macromolecules with head ketonic groups (functionalization degree $f_{C=O} \approx$ 100%). This behavior of the 1 : 2 complexes agrees with the fact that they can exist in the form of the acylium salt even in low-polar solvents.[4] The 1 : 1 complexes in the majority of solvents (except strong protic acids) exist in the form of donor-acceptor complexes.[5] When the latter contain proton-donor groups such as $MeCOBr \cdot AlBr_3$ (Ac-1), they act as protonogenic initiators.[1,2,6] The $PhCOCl \cdot AlBr_3$ (Bn-1) complex, which does not contain these groups, does not initiate the IB polymerization.[3]

^{13}C and ^{27}Al NMR spectral studies established that, unlike the other acyl complexes, the mesitoyl bromide (MesCOBr, Mes = $2,4,6\text{-}Me_3C_6H_2$) complexes with aluminum bromide, $MesCOBr \cdot AlBr_3$ (Mst-1) and $MesCOBr \cdot 2AlBr_3$ (Mst-2),[7] exist in solutions only in the form of acylium salts. As supposed,[8] this is due to steric hindrances, which are created by the substituents in positions 2 and 6 of the aromatic ring for the coordination of the Lewis acid to the O atom (MesC(Br)=O→Lewis acid) and prevent the formation of donor-acceptor complexes. The positions of the signals in the ^{13}C NMR spectra differ slightly (by not more than 0.7 ppm) for the complexes with the $AlBr_4^-$ and $Al_2Br_7^-$ anions. The composition of the anions corresponds to the initial molar ratio of the reagents, which is supported by the ^{27}Al NMR spectra.[7] Thus, the mesitoyl complexes give a unique opportunity to study the effect of the counterion composition on the ability of carbocations to initiate cationic polymerization.

In this work, we studied the activity of the mesitoyl complexes (Mst-1 and Mst-2) in the initiation of the cationic polymerization of IB.

Experimental

Procedures for purification and drying of the starting reagents and solvents, polymerization in all-sealed glassware, and isolation and analysis of polymers have been described in our previous works.[2,6,9,10] Mesitoyl complexes were obtained

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*For Part 9, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 52—56, January, 1998.

Table 1. Results of studying IB polymerization under the action of acyl complexes at −78 °C

Entry	Experimental conditions						Polymer			
	Complex*	R in RCOBr	[RCOBr] /mmol L^{-1}	Solvent	[IB] /mol L^{-1}	Time /min	Yield (%)	$\bar{M}_n$/10^3	$f_{C=C}$ (%)	E_{in} (%)
1	Mst-1	Mes	1.8	n-C_6H_{14}	1.02	120	0	—	—	0.0
2	Mst-2	Mes	1.8	n-C_6H_{14}	1.02	20	9	20.1	27	14.2
3	Mst-1	Mes	2.5	CH_2Cl_2	0.80	120	0	—	—	0.0
4	Mst-2	Mes	2.5	CH_2Cl_2	0.80	30	52	22.2	21	42.0
5	Ac-2	Me	1.8	n-C_6H_{14}	1.02	20	88	170.0	37	16.4
6	Ac-2	Me	8.6	CH_2Cl_2	0.80	20	100	5.2	27	99.4

* Mst-1 = $MesCOBr \cdot AlBr_3$, Mst-2 = $MesCOBr \cdot 2AlBr_3$, Ac-2 = $MeCOBr \cdot 2AlBr_3$.

by the known procedure.[7] The functionalization degree of polymers, *i.e.*, the fraction of macromolecules with the corresponding functional groups ($f_{C=O}$, $f_{C=C}$), were calculated from the data of the determination of the content of these groups in the polymer samples by IR spectroscopy and the ozonization method and from the values of the numerical-mean molecular weight $\bar{M}_n$ of the polymers determined by gel penetration chromatography (GPC).[2] According to the GPC data, the polymer samples had the unimodal molecular weight distribution (MWD).

Ethylaluminum dichloride was pre-distilled under dry argon, evacuated, and sealed in thin-walled glass balls. Organic electron-acceptor compounds (dichloroquinone, chloranil, and dibromodicyanoquinone) were recrystallized from benzene, dried and placed in the same glass balls. The reagents dosed in the balls were used for the preparation of solutions with known concentrations.

Results and Discussion

The results in Table 1 show that at −78 °C in both n-hexane and CH_2Cl_2 (entries *1* and *3*) the equimolar Mst-1 complex does not initiate the IB polymerization. In the presence of Mst-2 in n-hexane (entry *2*), the yield of the polymer is quite noticeable already in 20 min, and in CH_2Cl_2 (entry *4*) the polymerization rate and the efficiency of initiation (E_{in}) are higher. The acetyl Ac-2 complex is much more active under similar conditions (*cf.* Table 1, entries *2* and *5*, *4* and *6*). Almost all macromolecules of PIB obtained in the presence of Mst-2 contain head fragments of the cationogenic initiator RCO ($f_{C=O} \approx 100\%$). This composition is characteristic of the majority of IB polymers formed due to the initiation by the 1 : 2 acyl complexes.[2,3,6] Only the Ac-2 complex in CH_2Cl_2 gives the polymeric product with $f_{C=O} < 100\%$, which can be explained by the contribution of the donor-acceptor complex, which acts as a protonogenic initiator, to the initiation.[9,10]

The Mst-1 complex, which is incapable of initiation, becomes active in the presence of excess $AlBr_3$ when $AlEtCl_2$ or organic additives of the electron-acceptor type are introduced. The results of these experiments are presented in Table 2. The polymerization begins immediately after the introduction of the additive. When the nature of the electron acceptor changes, the yield of the polymer and E_{in} increase in parallel. In the presence of organic electron-acceptor compounds, the activity of Mst-1 reaches that of the Mst-2 complex and even can exceed it. The latter fact is likely due to the high molar ratios of the components of the initiating system in our experiments: organic electron acceptor/MesCOBr ≈ 3.3. The polymerization rate and the E_{in} value also increase when chloranil or excess $AlBr_3$ is added to the system with Mst-2 (entries *12* and *13*). The polymers obtained in entries *7*—*11* are characterized by $f_{C=O} \approx 100\%$, *i.e.*, the "modified" Mst-1 complex is similar to the 1 : 2 acyl complexes, in particular, Mst-2, in the cationogenic character of the initiation and the absence of the chain transfer. The qualitatively similar effect of different electron-acceptor additives suggests that the mechanism of

Table 2. Activation of acyl complexes by additives of Lewis acids and organic electron-acceptor compounds (n-hexane, [IB] = 1.02 mol L^{-1}, [RCOX] = 1.8 mmol L^{-1}, [additive] = 6.0 mmol L^{-1}, −78 °C, 20 min)

Entry	Complex[a]	Additive[b]	Polymer				
			Yield (%)	$\bar{M}_n$/10^3	$f_{C=O}$ (%)	$f_{C=C}$ (%)	E_{in} (%)
7	Mst-1	DCQ	11.5	38.8	100	27	9.4
8	Mst-1	CA	24	45.0	100	25	16.9
9	Mst-1	DBDCQ	39	56.2	100	14	22.0
10	Mst-1	$AlEtCl_2$	71	53.1	100	49	42.4
11	Mst-1	$AlBr_3$	77	47.7	100	31	51.2
12	Mst-2	CA	35	40.3	100	17	27.5
13	Mst-2	$AlBr_3$	100	41.9	100	51	75.6
14	Bn-1	CA	0[c]	—	—	—	0.0
15	Pv-1	CA	0[c]	—	—	—	0.0
16	Ac-1	—	57	91.5	0	49	—
17	Ac-1	CA	66	166.0	0	40	—
18	Ac-1	DBDCQ	79	190.0	0	31	—
19	Ac-2	CA	94	169.0	100	24	17.6
20	Ac-2	DBDCQ	100	132.0	100	17	24.0

[a] Bn-1 = $PhCOCl \cdot AlBr_3$, Pv-1 = $Me_3CCOCl \cdot AlBr_3$, Ac-1 = $MeCOBr \cdot AlBr_3$.

[b] DCQ is dicyanoquinone, CA is chloranil, DBDCQ is dibromodicyanoquinone.

[c] Duration of the experiment is 2 h.

their activating effect on the mesitoyl complexes is similar to the mechanism of activation by excess $AlBr_3$.

It is noteworthy that organic electron-acceptor compounds cannot activate the 1 : 1 benzoyl chloride and pivaloyl chloride complexes with $AlBr_3$ (Bn-1 and Pv-1), which exist only in the form of donor-acceptor complexes and are not independent initiators[3,11] (see Table 2, entries *14* and *15*), but increase noticeably the rate of the polymerization initiated by the protonogenic Ac-1 (entries *16—18*) and cationogenic Ac-2 complexes (see Tables 1 and 2, entries *5*, *19*, and *20*).

It has been previously shown[7] that despite the pronounced similarity of the spectral parameters of the cations in the Mst-1 and Mst-2 complexes, their activities in the cleavage of alkanes and isomerization of trimethylenenorbornene are quite different. For example, Mst-2 at room temperature for 0.5—3 h cleaves completely *n*-octane and *n*-dodecane, and for 5—8 h it provides the transformation of *exo*-trimethylenenorbornene into adamantane in 37—54% yield. Under the same conditions, in the presence of Mst-1, these substrates did not noticeably change. To explain the sharp difference in the activities of these complexes in the reactions of alkane cleavage and isomerization of trimethylenenorbornene, the activity of the 1 : 2 complex was assumed[7] to be due to the formation of the dicationic structures $[RC^{2+}—O—AlX_3^-]AlX_4^-$, in which the C atom possesses a high electrophilicity. The possibility of the existence of such compounds was confirmed by the quantum-chemical MNDO calculations for the $MeCOCl \cdot nAlCl_3$ (n = 1—3) complexes.[12] They cannot be detected by spectral methods due to a very low equilibrium concentration, although the MS analysis allows one to observe[13] the acetyl $C_2H_4O^{2+}$ dication. A very high electrophilicity of similar dications (or, in the general case, multications) can facilitate their fast interaction even with such weak nucleophiles as paraffins[7] or nonactivated arenes.[13] For example, acetyl cations have been established[13] in weak acidic media (for example, in CF_3COOH) to acylate very slowly benzene and almost cannot acylate chlorobenzene. The acylation rates increase sharply on going to a more acidic medium (CF_3SO_3H). These results were explained by the fact that in these cases, the highly electrophilic protonated acyl $MeC^+=O^+H$ cations are acylating species. More detailed information about the multications and their possible role in acylation reactions is presented in the reviews.[5,14]

Although the activities of the mesitoyl complexes are very similar in the low-temperature alkane cracking or isomerization of trimethylenenorbornene, on the one hand, and in the initiation of the IB polymerization, on the other hand (Mst-1 is inactive, and Mst-2 exhibits a sufficiently high activity), the concepts on the determining role of dications in the activity of these complexes are not likely necessary to explain the data obtained by us for the polymerization. In fact, if the capability of Mst-2 and similar 1 : 2 acyl complexes of initiating is determined by the presence of highly electrophilic dications, one should expect a considerably higher rate of the IB polymerization under the action of these complexes than that of the processes initiated by normal "classic" cationic species. In fact, this is not true. For example, under identical conditions, the rates of polymerization under the action of Ac-2 and the protonogenic Ac-1 initiator do not differ very much.[2] Moreover, the $H_2O—AlBr_3$ and Bu^tHal—Lewis acid systems, which cannot produce dicationic species, are usually more active in the initiation of the IB polymerization than the 1 : 2 acyl complexes.[15] The difference between the nucleophilicities of the substrates is a reason for the difference in the behavior of the species in the low-temperature alkane cracking or isomerization of trimethylenenorbornene and that in the initiation of the IB polymerization: the highly nucleophilic IB readily reacts with normal "classic" cationic species. A similar conclusion was drawn by the authors of Ref. 13, where they showed that, unlike benzene and chlorobenzene, the more nucleophilic ("activated") toluene can be rapidly acylated even in weak acidic media by normal acyl cations. In our opinion, different effects of the $AlBr_4^-$ and $Al_2Br_7^-$ counterions on the reactivity of the mesitoyl cations should be a reason for the sharply different activities of the Mst-1 and Mst-2 complexes in the initiation of the IB polymerization.

In nonpolar and moderately polar media (the dielectric constants of *n*-hexane and CH_2Cl_2 are 1.9 and 9.0, respectively), ionic compounds are mainly present as ion pairs.[16] This is also related to the mesitoyl complexes under consideration. Some increase in the distance between the components of the ion pair should occur prior to the addition of the monomer to the initiating cation (in this case, the mesitoyl cation). (Quantum-chemical analysis of the elementary act of the monomer insertion to the carbocation—counterion bond has been given in Ref. 16.) Since the smaller the sizes of the ions, the stronger the bond between ions in ionic associates,[17] the monomer can more easily separate ions in Mst-2 than in Mst-1. Therefore, the less nucleophilic[18] $Al_2X_7^-$ anion can be expected to create the more favorable conditions for the chain initiation and growth than the more nucleophilic AlX_4^-.

Let us examine the results obtained from the viewpoint of solvation interactions in the system under study. In dihalomethanes (CH_2Cl_2 and CH_2Br_2), the solvation of ion pairs by solvent molecules is insufficient to decrease the nucleophilicity of the AlX_4^- (X = Br) counterion to the extent necessary for the initiating effect of the Mst-1 complex. By contrast, even small additives of strong electron acceptors (Lewis acids or organic electron-acceptor compounds) activate this complex. The interaction of these additives with counterions (specific solvation) is energetically favorable, because of the competition between the additive molecules and excess solvent molecules for the position in the coordination sphere (the difference between the concentrations of the solvent and additive is ~3 orders of magnitude). An important role of the solvation of anions by the electron-acceptor additives for the successful cationic polymerization has been demonstrated by several authors (see, *e.g.*, Ref. 19). A similar effect of the sharp acceleration of the reaction due to the addition of small amounts of specifically interacting compounds to the solvent is often observed for other, not polymerization processes. This effect usually does not correlate to a change in the dielectric constant of the medium; hence, it has been called[20] a "small additive effect." (Of course, a specific mechanism of the effect of these additives can operate in each particular case.).

Is the specific solvation of counterions accompanied by a change in the state of ionic associates, for example, by the transformation of contact ion pairs into solvent-separated pairs? As far as we know, for cationic initiators, data on the reliably established differences in the activities of these two types of the pairs are scarce. However, this difference was demonstrated for the carbanionic salts, in particular, fluorenyl salts,[21] using UV-VIS spectroscopy. Only a peak at 346 nm was observed in the spectrum of fluorenyllithium in dioxane. On going to the more polar solvents (THF and 1,2-DME), this peak partially or completely disappears, but a new peak at 373 nm appears. In the study of the concentration dependences of the intensities of these peaks, the first of them was assigned to contact pairs and the second peak was assigned to the solvent-separated ion pairs rather than to free ions. The specific solvation of cations, which is also accompanied by the transition to solvent-separated pairs, was also observed when a small amount of the strong electron donor DMSO was added.[21] The comparison of the spectral parameters to the data on the kinetics of the styrene polymerization suggested[21] a considerably higher activity of the solvent-separated ion pairs than that of the contact ion pairs.

Data on the state of ionic associates of mesitoyl salts in different media are lacking. At the same time, the replacement of, *e.g.*, the nucleophilic AlX_4^- counterion by the less nucleophlic $Al_2X_7^-$, when one equivalent of $AlBr_3$ (or another Lewis acid) is added to the Mst-1 complex, cannot likely be considered as the transformation of the contact ion pair into the solvent-separated pair. It is noteworthy that the authors of Ref. 22 observed another type of solvation: the specific peripheral solvation for the diphenylsodium—polyether system, which was not accompanied by the spatial separation of the components of the ion pair but affected the interaction of the charges.

Taking into account all data listed, we assume that the nucleophilicity of the counterion should be sufficiently decreased to provide the activity of the carbocation salt in the initiation of the polymerization. To control the nucleophilicity of the counterion, it is especially efficient to use small amounts of electron-acceptor type additives, which provide the specific solvation. An excessive amount of these additives favors to a greater extent a decrease in the nucleophilicity of the counterions, which is reflected in an increase in the yield of the polymer and E_{in} (*cf.* Tables 1 and 2, entries *2*, *12*, and *13*). A decrease in the counterion nucleophilicity should, in principle, favor the transformation of contact ion pairs into solvent-separated pairs, *i.e.*, an increase in the degree of the ion separation is a consequence of a decrease in the anion nucleophilicity. However, this does not mean that a direct or unambiguous dependence should exist between the activity of the carbocation in the reaction of addition to olefins and the degree of ion separation.

The nucleophilicity of the already formed counterions can be decreased by the addition of both organic electron-acceptor compounds and an excess of the Lewis acid, but organic electron-acceptor additives cannot transform donor-acceptor complexes inactive in initiation to the active acylium salts.

The results obtained testify that the monomer cannot add to the mesitoyl cation in the original Mst-1 complex (*i.e.*, initiation does not occur); however, the additional solvation of the anion makes this initiation possible. In the case of the Mst-2 complex containing the $Al_2Br_7^-$ counterion, the primary addition of the monomer becomes possible, and the activity of the mesitoyl cation can be increased due to the additional solvation of the counteranion. As mentioned above, the data of entries *2*, *12*, and *13* indicate that the E_{in} value increases when chloranil or excess $AlBr_3$ is added (*i.e.*, the activity in the initiation increases). In addition, the comparison of the results of these experiments shows that the additional solvation also favors an increase in the activity of growing centers (*i.e.*, the effective constant of the growth rate). This conclusion is based on the fact that the yield of the polymer increases more than the E_{in} value (*cf.*, entries *2* and *13*).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-32825a).

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Received May 19, 1997;
in revised form July 10, 1997