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

12.* The polymerization of isobutylene initiated by mixtures of complexes of acetyl bromide and benzoyl chloride with aluminum bromide

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The polymerization of isobutylene in hexane at −78 °C in the presence of the $MeCOBr \cdot AlBr_3 + PhCOCl \cdot AlBr_3$ and $MeCOBr \cdot 2AlBr_3 + PhCOCl \cdot 2AlBr_3$ mixtures was investigated. It was established that only acetyl bromide shows an initiating activity, while benzoyl chloride seems to be part of a counterion, which markedly increases the "viability" of growing carbocationic centers. Possible mechanisms for the formation of initiating centers in mixed complexes are discussed.

Key words: isobutylene, polyisobutylene, acetyl bromide, benzoyl chloride, aluminum bromide, complexes, cationic polymerization.

Earlier,[2] it was shown that on addition of acetyl complexes $MeCOBr \cdot nAlBr_3$ (n = 1 or 2) to mixtures of HBr with $AlBr_3$, systems capable of initiating the polymerization of isobutylene (IB) are formed. The combined action of these initiators does not match the contributions from the effects made by individual initiators. Thus, mixing of the $MeCOBr \cdot AlBr_3$ complex with equimolar amounts of HBr and $AlBr_3$ completely suppresses the protonogenic activity, and this mixture exhibits the properties of the cationogenic initiator $MeCOBr \cdot 2AlBr_3$. One can assume that mixtures of other complexes will also change the polymerization process characteristic of individual complexes and the properties of resulting polymers. To verify this assumption, we studied the polymerization of IB in the presence of mixtures of acetyl and benzoyl complexes, *viz*., $MeCOBr \cdot AlBr_3 + PhCOCl \cdot AlBr_3$ (the AcBn-1 system) and $MeCOBr \cdot 2AlBr_3 + PhCOCl \cdot 2AlBr_3$ (the AcBn-2 system), and determined the characteristics of the polymeric products.

Experimental

Purification and drying of the starting compounds and solvents and procedures for polymerization, isolation, and analysis of polymers were described earlier.[2–5] Complexes were mixed directly in a solution of monomer. *n*-Hexane was used as solvent. The AcBn-1 system was prepared by mixing equimolar amounts of complexes $MeCOBr \cdot AlBr_3$ (Ac-1) and $PhCOCl \cdot AlBr_3$ (Bn-1). The AcBn-2 system was prepared by mixing the corresponding 1 : 2 complexes (Ac-2 and Bn-2). Polymerization was carried out at −78 °C. The degree of conversion of monomer (Q) was monitored by dilatometry or from the dry residue in tests with samples withdrawn during the process.

The degree of functionalization of polymers, *i.e.*, the fraction of macromolecules bearing the corresponding functional groups ($f_{C=O}$, $f_{C=C}$, and $f_{C-\text{halogen}}$), was calculated from the data of IR spectroscopy, X-ray fluorescence analysis, and ozonization with consideration of $\overline{M}_n$ of these polymers (determined by gel-permeation chromatography (GPC)).[3] According to GPC data, polymer specimens had unimodal molecular-weight distribution (MD).

^1H and ^{13}C NMR spectra were recorded on a Bruker WP-200SY spectrometer (200 and 50.3 MHz, respectively). Solutions of complexes were prepared in CH_2Br_2, which was used as the internal standard. The δ values obtained were converted to the Me_4Si scale.

Results and Discussion

It is known[6,7] that acyl complexes can exist in solution in the form of donor-acceptor complexes (DAC), acylium salts (AS), or their mixtures (DAC + AS). For example, the existence of DAC in a solution of the Ac-2 complex is confirmed by ^1H and ^{13}C signals at δ 3.5 and 210.0, respectively, while appropriate signals at δ 4.65 and 152.0 suggest the presence of a salt form[3] (Table 1). The NMR spectrum of the benzoyl Bn-2 complex exhibits no signals from a salt form, but a signal at δ 192—194 from DAC is split,[5] probably, because of halogen exchange.[11] A low content of AS correlates with a low efficiency of this cationogenic initiator in the polymerization of IB.[5]

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Table 1. Composition and characteristic signals of ^1H and ^{13}C from complexes of acyl halides with aluminum bromide

Composition of complex	δ ^1H	δ ^{13}C	Structure	Reference
$MeCOBr \cdot AlBr_3$ (Ac-1)	3.5	210.0	DAC	2,7—9
$MeCOBr \cdot 2AlBr_3$ (Ac-2)	3.5, 4.65	210.0, 152.0	DAC +AS	2,7—9
$PhCOCl \cdot AlBr_3$ (Bn-1)	—	190.0	DAC	4
$PhCOCl \cdot 2AlBr_3$ (Bn-2)	—	193.4, 192.2	DAC + AS[b]	4
$MeCOBr \cdot AlBr_3$[a] + $PhCOCl \cdot AlBr_3$ (AcBn-1)	3.5, 4.65	—	DAC + AS	The present work
$MeCOBr \cdot 2AlBr_3$[a] + $PhCOCl \cdot 2AlBr_3$ (AcBn-2)	3.5, 4.65	—	DAC + AS	The present work

[a] The presence of a small amount of an acylium salt was deduced from the splitting of a signal from DAC.[4]

[b] Equimolar mixture.

The ^{13}C NMR spectra of mixed systems contain a large number of signals in the range δ 150—210, which precludes a conclusion about the composition and structure of products of a reaction between the initial complexes. However, the ^1H NMR spectrum of the AcBn-1 system (see Table 1) unambiguously indicates the presence of a salt form including a $MeC(O)^+$ cation, which is characteristic of the Ac-2 complex.

The reaction between acetyl and benzoyl complexes is additionally confirmed by the characteristics of products of the polymerization of IB initiated by such mixtures and individual complexes (Tables 2). The Bn-1 complex does not initiate the polymerization of IB.[5] Polymers obtained under the action of mixed complexes are almost entirely composed of macromolecules with head acetyl groups MeC(O)— ($f_{C=O}$ ~100%). The absence of PhC(O)— groups characteristic of polymerization products formed under the action of Bn-2 was shown by IR and UV spectroscopy. Therefore, an equimolar mixture of Ac-1 and Bn-1 nearly completely loses the protonogenic activity,[12] probably, owing to transformation into another acetyl complex capable of cationogenic initiation. However, the available data cast doubt on the statement that such a transformation goes to completion because nearly full suppression of protonogenic activity is possible even in the presence of minor amounts of head carbonyl groups in polymeric molecules.[2] Apparently, the reaction of Ac-1 with Bn-1 yields the Ac-2 complex and free PhCOCl:

$$MeCOBr \cdot AlBr_3 + PhCOCl \cdot AlBr_3 \rightleftharpoons$$
$$\rightleftharpoons MeCOBr \cdot Al_2Br_6 + PhCOCl \qquad (1)$$
$$\updownarrow$$
$$MeCO^+,\ Al_2Br_7^-.$$

Table 2. Results of the polymerization of isobutylene under the action of acyl complexes in hexane at −78 °C[a]

Complex or mixture	Polymer: Q (%)	$\bar{M}_n \cdot 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$f_{C=C}$ (%)	$f_{C=O}$ (%)	Initiating particle	E_{in} (%)	k_{ei}/k_p /mol L^{-1}
Ac-1	75	9.86	5.20	43	0	H^+	—[b]	$3.1 \cdot 10^{-4}$
Ac-2	~100	16.90	4.10	39	~100	$MeC(O)^+$	10.6	$6.6 \cdot 10^{-5}$
Bn-2	82	25.20	1.48	3	~100	$PhC(O)^+$	5.7	$7.5 \cdot 10^{-6}$
AcBn-1	71	33.70	1.61	6	~100	$MeC(O)^+$	3.7	$1.3 \cdot 10^{-5}$
AcBn-2	~100	12.40	2.01	10	~100	$MeC(O)^+$	14.1	$2.3 \cdot 10^{-5}$

[a] Polymerization conditions: $[IB]_0$ = 2.35 mol L^{-1}; [RCOX] = 7.5 mmol L^{-1}; reaction time = 15 min.

[b] Under similar conditions (except for $[IB]_0$ = 1.25 mol L^{-1} and [MeCOBr] = 9.7 mmol L^{-1}); E_{in} increases with increasing degree of conversion (E_{in} = 3.8—6.5% at Q = 96%).[11] This index cannot be calculated more precisely because of an uncertain contribution from chain transmission reactions in the presence of this protonogenic initiating complex.

In the case of a mixture of Ac-2 and Bn-2, reactions between the acetyl and benzoyl components can also be assumed since the Bn-2 complex loses its initiating power.

To gain a better understanding of the behavior of mixtures of acetyl and benzoyl complexes, we studied the two-step polymerization of IB initiated by these systems as well as the effect of the concentration of acyl halides on the polymerization rate and the characteristics of resulting polymers. Insofar as the initiator in these mixed systems is actually acetyl bromide, the efficiency of initiation was calculated relative to the concentration of this reagent, and the concentration of active centers $[n^*]$ was determined by the equation $[n^*] = E_{in} \cdot [\mathrm{MeCOBr}]$.

Data in Tables 3—5 show a close similarity of polymerization processes occurring in the presence of the mixture of Ac-1 with Bn-2 and the individual Ac-2 complex.[3,4] In one- and two-step processes, the molecular weight grows and the degree of conversion of the monomer increases, while the relative fraction of molecules with terminal C—halogen bonds ($f_{\mathrm{C-halogen}}$) is reduced. In addition, the molecular-weight distribution becomes broader (the polydispersity index $\bar{M}_w/\bar{M}_n$ increases), and E_{in} decreases with increasing concentration of initiator. Such features were also noted for mixtures of Ac-1 with Bn-1. This suggests that, in both cases, the centers of chain initiation and growth are structurally similar and the polymerization processes follow similar mechanisms.

Table 3. Results of the two-step polymerization of IB in the presence of the AcBn-1 mixture

t /min	Q (%)	$\bar{M}_n \cdot 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$f_{\mathrm{C-halogen}}$ (%)	E_{in}	$[n^*]$ /mmol L^{-1}
			First stage			
2	16	8.36	1.50	97	5.1	0.118
5	38	18.2	1.61	99	5.9	0.135
12	67	30.4	1.42	104	5.0	0.115
20	84	39.3	1.55	96	6.5	0.130
			Second stage			
24	14	52.2	1.64	87	6.7	0.154
48	69	76.2	1.69	82	6.8	0.156

Note. Polymerization conditions: $[\mathrm{IB}]_0$ = 1.25 mol L^{-1}, [MeCOBr] = 2.3 mmol L^{-1}.

Table 4. Influence of the concentration of acyl halide on the polymerization of IB in the presence of the AcBn-1 mixture

[MeCOBr] /mmol L^{-1}	Q (%)	$\bar{M}_n \cdot 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$f_{\mathrm{C-halogen}}$ (%)	E_{in}	$[n^*]$ /mmol L^{-1}
			AcBn-1			
4.9	~100	31.8	1.64	97	4.5	0.220
3.6	~100	36.9	1.52	104	5.3	0.190
2.3	86	43.6	1.55	96	6.0	0.138
1.3	74	45.0	1.56	101	8.8	0.115
0.45	47	47.0	1.70	94	15.6	0.070
			AcBn-2			
4.9	~100	8.16	1.90	92	17.5	0.858
3.6	~100	9.58	2.05	90	20.3	0.730
1.3	~100	15.7	2.10	85	34.2	0.445
0.45	73	20.8	2.20	77	54.7	0.246

Note. Polymerization conditions: $[\mathrm{IB}]_0$ = 1.25 mol L^{-1}, 40 min.

Our data indicate that the activity and efficiency of the initiating systems AcBn-1, AcBn-2, and Ac-2 are essentially different. Different also are the characteristics of polymers formed in their presence (see Table 2). For example, in the two-step polymerization initiated by AcBn-1, the number-average molecular weight ($\bar{M}_n$) of resulting polymer is an almost linear function of the yield of the polymer, whereas in the presence of AcBn-2 its increase begins to deviate substantially from linearity once the second portion of the monomer is added. Earlier,[13] we showed that the "living" character of cationic initiating systems can be estimated by using the criterion for "closeness to the living state," in particular, from the ratio of the rate constant of proton elimination to that of chain growth, k_{el}/k_p. A lower ratio corresponds to a decrease in the relative role of a side reaction of chain restriction, *i.e.*, to an enhancement of the viability of active centers. Among the three above-mentioned systems capable of generating acetylium cations, the viability is the highest for AcBn-1 and the lowest for Ac-2. The benzoyl Bn-2 complex provides even more living centers, whereas in the system with protonogenic Ac-1, active centers often eliminate the proton. Because elimination of the proton is accompanied by chain termination caused by the collapse of ion pairs,[12] the Ac-1 complex functions as an initiator of "dead" cationic polymerization.

The results obtained support the previous assumptions that the nature of head groups and the composition of a counterion are important for the development of side reactions of chain restriction.[2,5,12,13] Earlier,[5] a detailed analysis of the polymerization of IB under the action of

Table 5. Results of the two-step polymerization of IB in the presence of the AcBn-2 mixture

t /min	Q (%)	$\bar{M}_n \cdot 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$f_{\mathrm{C=C}}$ (%)	E_{in}	$[n^*]$ /mmol L^{-1}
			First stage			
2	19	2.93	1.45	1.5	34.9	0.454
5	41	6.47	1.52	4	34.1	0.443
12	74	11.6	1.62	9	34.5	0.449
20	89	14.1	1.58	14	34.0	0.442
			Second stage			
24	29	12.2	1.67	21	57.1	0.742
48	92	17.4	1.81	27	59.4	0.772

Note. Polymerization conditions: $[\mathrm{IB}]_0$ = 1.25 mol L^{-1}, [MeCOBr] = 1.3 mmol L^{-1}.

the benzoyl Bn-2 complex allowed us to determine that one of the molecules of this complex produces an initiating acylium cation, while the second is part of a counterion, thus increasing the viability of active centers. The involvement of two molecules of Bn-2 in the formation of active centers correlates well with the second order of the polymerization rate (with respect to the concentration of PhCOCl). An order close to second (1.85) was previously reported also for the polymerization of THF in the presence of a complex of benzoyl chloride with antimony pentachloride.[14] This gives grounds to assume that, in the mixed complexes AcBn-1 and AcBn-2 as well, a portion of the adducts $PhCOCl \cdot AlBr_3$ and $PhCOCl \cdot 2AlBr_3$ will be part of a counterion, thus providing a more "living" polymerization.

This explanation is in better agreement with most of the experimental facts than the assumption that benzoyl complexes decompose in mixed systems to give free PhCOCl and a Lewis acid (Eq. (1)). However, it remains obscure why benzoyl adducts (rather than acetyl ones) tend to enter into the composition of a counterion. In addition, the structures and mechanism of formation of such counterions are still unclear.

It is known[6] that, in the formation of complexes of acyl halides RCOX with Lewis acids, the equilibrium between donor-acceptor and salt forms depends strongly on the nature of radical R. If R is an aryl radical, a donor-acceptor complex is usually a dominant form. With compounds having an alkyl R, the equilibrium shifts toward the acylium salt. This conclusion correlates with our data on the initiating efficiency of various cationogenic acyl complexes in the polymerization of IB. For example, as can be seen from Table 2, E_{in} for Ac-2 is nearly twice as high as that for Bn-2. A calorimetric study of complexation between acid bromides and $AlBr_3$ in dibromoethane showed[15] that the enthalpy of complexation of propionyl bromide is lower by ~5 kcal mol^{-1} than that of benzoyl bromide (22.4 and 27.6 kcal mol^{-1}, respectively). An enhanced strength of donor-acceptor aroyl complexes may be explained by the presence of a highly developed system of conjugation between the aromatic ring and the carbonyl group as well as of a dative π-bond between the halogen and metal atoms in the Lewis acid. For instance, it was shown[16] that even the most electronegative F atoms in the molecule of BF_3 can participate in such additional π-bonding; the B—F bond length in this compound is equal to 1.33 Å.[16] Although the extent of variation in the π-donating ability of halogens in the series F, Cl, Br, and I is quite controversial,[18,19] there is no doubt that π-donation significantly affects the properties of Lewis acids and some isoelectron cations. In complexes with aliphatic acyl halides, the conjugation chain is much shorter, which is why the transformation of these complexes from the donor-acceptor form into a salt one should occur much more easily.

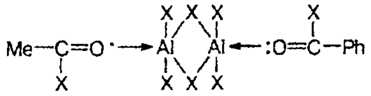
An important role of the developed conjugation chain in complexes of aroyl halides can also be seen in their capability for association (dimerization). For example, the association of the 1 : 1 complex (Bn-1) will yield dimers $(PhCOCl \cdot AlBr_3)_2$. The possibility of such complexation between ethers and aluminum-containing Lewis acids is long known.[19—21] The authors[22] believe that these complexes are essential and even decisive in some catalytic processes. Actually, there are no unambiguous concepts on the structure of 2 : 2 complexes. However, the advanced[22] scheme of equilibrium for 2 : 2 complexes

$$2\ AlX_3 \cdot D \rightleftharpoons [AlX_2D_2]^+[AlX_4]^-, \qquad (2)$$

$$[AlX_2D_2]^+[AlX_4]^- \rightleftharpoons AlX_2D_2^+ + AlX_4^- \qquad (3)$$

does not explain a large difference in the viability of centers with various compositions. In addition, we showed[23] for various mesitoyl complexes that the $AlBr_4^-$ anion is a strong nucleophile, which completely precludes the polymerization of IB on the carbocationic centers with such counterions. That is why the observed differences can be best explained by a change in the composition of a counteranion when varying the composition of an initiating acyl halide system.

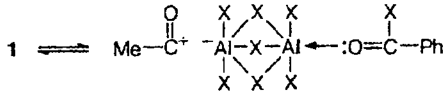
With the AcBn-1 system as an example, several ways in which initiating centers form can be proposed. According to the first mechanism, aluminum fragments are first associated through halogen bridge(s) to give a nonionized 2 : 2 molecular complex (**1**)



1

It can be expected that a close approach of the reagents during reactions can be hindered by electrostatic repulsion of the negatively charged ends of dipoles, which, however, can not be so strong because of a high polarizability of the benzoyl complex. An interaction between two molecules of the benzoyl complex should occur in a similar way. However, if both reacting particles are acetyl complexes, the electrostatic repulsion will significantly hinder the formation of associates of type **1**.

In the first step, such a dimer can undergo intramolecular isomerization to give ionic structure (**2**). The compositions of the cationic and anionic fragments of such a structure are dictated by a tendency of aliphatic acyl halides to form cationic fragments of acylium salts:



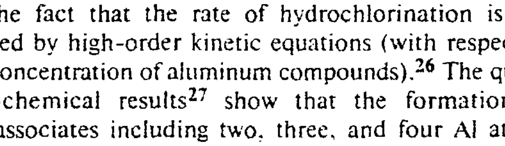
2

The formation of an ionic structure from the $(PhCOCl \cdot AlBr_3)_2$ dimer in this stage is hindered by the nonionic character of complexes of aromatic acyl halides. That is why the Bn-1 complex does not exhibit an initiating ability.[5]

To transform, at least in part, the benzoyl complex into an ionic acylium salt, an excess of a Lewis acid is required to reduces the nucleophilicity of a counterion. Such reduction of the nucleophilicity occurs in passing from Bn-1 to Bn-2. The resulting counterion contains up to four $AlBr_3$ molecules. The existence of polyassociates of aluminum chlorides was demonstrated earlier.[24,25] Their important role in catalysis is confirmed by the fact that the rate of hydrochlorination is described by high-order kinetic equations (with respect to the concentration of aluminum compounds).[26] The quantum-chemical results[27] show that the formation of polyassociates including two, three, and four Al atoms are beneficial both *in vacuo* and in solution. Such thermodynamically stable associated structures can contain tricoordinated Cl atoms and pentacoordinated Al atoms.

Let us consider the formation of initiating particles in an AcBn-2 mixture. The composition of the counterion, as in the case of Bn-2, should be $Al_4Br_{13} \cdot PhCOCl$ (or, taking account of rapid halogen exchange, $Al_4Br_{12}Cl \cdot PhCOBr$). The head group in macromolecules, important in the control of processes limiting the chain size,[2,27] is an acetyl group. Differences between the compositions of the counterions and the head groups seem to be responsible for the difference in the polymerization processes involving these complexes.

According to the second, alternative mechanism, the dipolar complexes Ac-1 and Bn-1 are arranged in the first stage so that their oppositely charged ends are directed toward each other:



$$\overset{\delta^+}{\text{MeCOBr}}\cdot\overset{\delta^-}{\text{AlBr}_3} + \overset{\delta^+}{\text{PhCOCl}}\cdot\overset{\delta^-}{\text{AlBr}_3} \longrightarrow$$

$$\longrightarrow \overset{\delta^+}{\text{MeCOBr}}\cdot\overset{\delta^-}{\text{AlBr}_3} \rightarrow \overset{\delta^+}{\text{PhCOCl}}\cdot\overset{\delta^-}{\text{AlBr}_3}$$

3

In such a nonionic structure (**3**), the benzoyl structure functions as an electron acceptor, and the electron density in this case should be transferred through the bromine atoms of $AlBr_3$ in the acetyl fragment and the aromatic ring in the benzoyl fragment. Although the developed conjugation chain in the benzoyl complex should also favor such an interaction, even strong electron acceptors such as chloranil cannot activate the donor-acceptor nonionic complex.[23] That is why the second pathway of formation of active centers seems to be less preferable.

Thus, in mixtures of complexes of Lewis acids with acyl halides RCOX containing aliphatic and aromatic radicals R, their components enter into an additional interaction affecting the structure, activity, and efficiency of centers that initiate the polymerization of olefins. This offers new possibilities for regulating the degree of the "closeness to the living state" of polymerization and the structure of the resulting polymer.

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