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

5.* Polymerization of isobutylene in the presence of the complexes of benzoyl chloride with aluminum bromide

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Polymerization of isobutylene in *n*-hexane at −78 °C in the presence of the complex of benzoyl chloride with $AlBr_3$ (1 : 2) was investigated. The results were compared to those obtained previously for the polymerization of this monomer induced by the complex of acetyl bromide with $AlBr_3$. Both complexes initiate the polymerization only by acyl cations. The number average molecular weight ($\bar{M}_n$) of the polymer linearly increases as the degree of isobutylene conversion increases. The polymerization restarts after repeated addition of the monomer, and $\bar{M}_n$ continues to increase linearly. The efficiency of the initiaton by the benzoyl chloride complex does not exceed 6.2 %; the reaction has the second order with respect to the initiator in the case of $PhCOCl \cdot Al_2Br_6$; and the chain-propagation rate constant is 13.9 L mol^{-1} s^{-1}. The use of $PhCOCl \cdot Al_2Br_6$ as the initator of the polymerization of isobutylene allows one to prepare macromolecules with very low contents of the terminal C=C double bonds and with narrow molecular weight distributions. Unlike the $MeCOBr \cdot AlBr_3$ complex, $PhCOCl \cdot AlBr_3$ does not initiate polymerization of isobutylene.

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

In the previous works of this series,[1–3] we have considered the cationic polymerization of isobutylene (IB) initiated by complexes of acetyl bromide MeCOBr with aluminum bromide of the composition 1 : 1 (Ac-1) and 1 : 2 (Ac-2). It was shown that in a nonpolar medium at a low temperature (*n*-hexane, −78 °C), the Ac-1 complex acts as a proton-producing initiator, while Ac-2 is a cation-producing species ensuring the formation of polyisobutylene (PIB) with 100 % content of head acyl groups. The proton-producing activity of Ac-1 was explained by the acidic character of the hydrogen atoms of the methyl groups in this complex.

In this work, we have studied polymerization of IB induced by complexes of benzoyl chloride with aluminum bromide. The results were compared to the results of the study of the polymerization of this monomer initiated by acetyl complexes.

Experimental

The purification of the initial reagents and of the solvent (*n*-hexane) and the procedures for conducting the polymerization and for the isolation and analysis of the polymers were described previously.[1]

Commercial PhCOCl was dried over PCl_5 and distilled under argon. Complexes of benzoyl chloride with aluminum bromide of the composition 1 : 1 (Bn-1) and 1 : 2 (Bn-2) were prepared similarly to the corresponding complexes of acetyl bromide.[1]

The efficiency of initiation over the period of time *t* $(E_{in})_t$ was determined from the equation given in one of the preceding papers:[3]

$$(E_{in})_t = \frac{[i\text{-}C_4H_8]_0 \cdot Q_t}{(\bar{M}_n/56)_t \cdot [\text{Bn-2}]} \cdot 100\ \%,$$

where $[i\text{-}C_4H_8]_0$ is the initial concentration of IB, Q_t is the degree of conversion of the monomer, $(\bar{M}_n/56)_t$ is the degree of polymerization at instant *t*, and [Bn-2] is the concentration of the initiator based on PhCOCl.

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The degree of functionalization of the polymers, *i.e.*, the fractions of macromolecules containing the corresponding functional groups ($f_{C=O}$, $f_{C=C}$ and f_{C-Hal}, where Hal = Cl, Br), were calculated from the results of the analysis of polymeric samples for the contents of these groups, carried out by IR spectroscopy, ozonization, and X-ray fluorescence analysis and from the $\bar{M}_n$ values of these polymers determined by gel-permeation chromatography.[1]

Results and Discussion

Unlike complex Ac-1, complex Bn-1 does not initiate polymerization of IB. This is a consequence of the absence of acidic β-protons in the donor-acceptor complex (DAC) $PhC(Cl){=}O{\rightarrow}AlBr_3$ (see Ref. 4). This structure of Bn-1 is consistent with the occurrence of the signal at δ 190.0 corresponding to the carbonyl group in its ^{13}C NMR spectrum.

The ^{13}C NMR spectrum of the complex Ac-1 exhibits a signal at δ 210.0, which can also be assigned to the $MeC(Br){=}O{\rightarrow}AlBr_3$ DAC. The addition of the second $AlBr_3$ molecule (giving Ac-2) results in the appearance of an additional signal at δ 152.0, which has been assigned to the ionic acylium salt.[4] No signal in the region of 150.0 ppm could be observed in the spectrum of the complex Bn-2 under similar conditions, which is probably due to the low concentration of the acylium salt and also to the fact that this signal is difficult to distinguish against the background of the intense resonances of the C atoms of the aromatic ring.[4] However, in the low-field region of the spectrum, two signals associated with DAC appear at 192.2 and 193.4 ppm, the ratio of their intensities being 3 : 1. The presence of two forms of DAC can be explained by the exchange of halogen atoms between PhCOCl and $AlBr_3$, occurring *via* the formation of acylium salt.

$$PhC(Cl){=}O{\rightarrow}Al_2Br_6 \rightleftharpoons PhCO^+,\ Al_2Br_6Cl^- \rightleftharpoons$$
$$\rightleftharpoons PhC(Cl){=}O{\rightarrow}Al_2Br_5Cl$$

Unlike Bn-1, complex Bn-2 is active in the polymerization of IB. Comparison of the results of the analysis of polymers formed in the presence of Bn-2 with their $\bar{M}_n$ values showed that virtually all the macromolecules contained head PhC=O groups ($f_{C=O} \approx 100$ %). In this respect, the situation is completely similar to the initiation by the complex Ac-2,[1] which is also accomplished by the acyl cations. The linear increase in $\bar{M}_n$ of PIB with the increase in the degree of conversion of the monomer during the process, the efficiency of initiation being invariable (within the accuracy of the measurements) (Table 1), also indicates that the behavior of Bn-2 is similar to that of Ac-2 (*cf.* Ref. 3).

On the basis of the results, we may assume that the previously proposed[3] schemes, describing the initiation involving acylium cations, chain propagation, chain termination, and the equilibrium between DAC and the acylium salt for Ac-2, are also applicable to Bn-2. In the latter case, the main role in the initiation is played by the $PhCO^+$ cations. It should be noted that both complexes ensure only low efficiency of initiation. In this respect, our initiators differ from systems of the tertiary alcohol—BCl_3 (excess)—an electron-donating compound type,[5] although in the case of some other initiating systems, even those providing "living" cationic polymerization, relatively low E_{in} values have also been observed.[6,7] These results indicate that the use of Bn-2 as the initiating complex ensures the quantitative involvement of the head benzoyl groups in the PIB molecules and that the initiation mechanisms for Ac-2 and Bn-2 are similar.

However, a more detailed investigation of the effects of concentrations of Ac-2 and Bn-2 on the kinetics of

Table 1. Study of the two-step polymerization of IB initiated by the complex Bn-2 ($[IB]_0 = 1.02$ mol L^{-1}, [PhCOCl] = $4.6 \cdot 10^{-3}$ mol L^{-1}, *n*-hexane, −78 °C)[a]

t /min	*Q* (%)	Polymer[b]				$(E_{in})_t$ (%)	$[n^*] \cdot 10^3$ /mol L^{-1}
		$\bar{M}_w \cdot 10^{-3}$	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$	f_{C-Hal} (%)		
			The first step				
2	14	109	71	1.54	102	2.45	0.113
8	52	354	225	1.62	—	2.87	0.132
16	76	531	318	1.67	—	2.97	0.137
20	84	621	337	1.84	97	3.09	0.142
			The second step				
28	23[c]	953	526	1.81	93	2.90	0.133
52	78[c]	1440	762	1.89	89	2.90	0.133

[a] In the first and in the second step, equal amounts of IB were introduced.

[b] For all the PIB samples obtained, $f_{C=O} \approx 100$ %.

[c] The degree of conversion *Q* in the second step was calculated with respect to the second portion of the monomer.

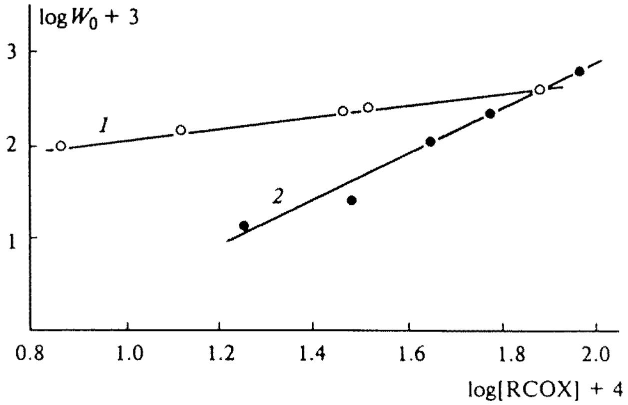

Fig. 1. Determination of the order of the initial rate of the polymerization (W_0) of IB in hexane at −78 °C with respect to the concentration of the initiating complexes Ac-2 (*1*) and Bn-2 (*2*); $[IB]_0$/mol L^{-1} = 1.64 (*1*) and 1.02 (*2*).

Table 2. Effect of the concentration of the initiating complex Bn-2 on the polymerization of IB and on the characteristics of the polymers ($[IB]_0$ = 1.02 mol L^{-1}, *n*-hexane, −78 °C)

$[PhCOCl] \cdot 10^3$ /mol L^{-1}	*t* /min	*Q* (%)	Polymer				E_{in} (%)	$[n^*] \cdot 10^3$ /mol L^{-1}
			$\bar{M}_w \cdot 10^{-3}$	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$	f_{C-Hal} (%)		
9.6	15	100	145	96	1.51	89	6.20	0.595
6.1	19	97	326	217	1.50	—	4.18	0.255
4.6	20	84	621	337	1.84	97	3.09	0.142
3.0	26	65	1248	640	1.95	97	2.05	0.062
1.8	45	31	1534	768	2.01	96	1.28	0.023

polymerization of IB and on the characteristics of the polymers formed points to a number of substantial differences between the behavior of these complexes. The results of this study are presented in Fig. 1 and in Table 2.

It can be seen from Fig. 1 that for relatively low concentrations of the initiators (up to 3—4 mmol L^{-1}), complex Ac-2 is markedly more active than Bn-2, but at higher concentrations of the acyl complexes their activities approach each other. Moreover, the orders of the initial polymerization rates (W_0) with respect to the initiator are substantially different: 0.5 for Ac-2 and 2 for Bn-2. Correspondingly, the efficiency of the initiation decreases with an increase in the content of Ac-2,[3] whereas an increase in the concentration of Bn-2 results in an increase in E_{in} (see Table 2). Attention is attracted by the considerably higher f_{C-Hal} values for polymers prepared in the presence of Bn-2 as the initiator (for the PIB samples obtained with Ac-2, this value can decrease to 52 %).[3] The high values of f_{C-Hal} indicate a low probability of the chain termination *via* elimination of a proton from the active center yielding a "superacid," which is inactive under the given conditions, and a polymeric molecule with terminal C=C bond ($f_{C-Hal} \geq 89$ % and $f_{C-Hal} + f_{C=C} = 100$ %).[1,3] For the same reason, the initiation with complex Bn-2 gives polymers with rather narrow molecular-weight distributions: $\bar{M}_w/\bar{M}_n \leq 2.01$ (when Ac-2 is used, the index of polydispersivity is 5.07),[3] and the concentration of the growing chains $[n^*]$ varies only slightly with an increase in the degree of conversion of IB (see Table 1).

The fact that the initial polymerization rate has the second order with respect to the initiator Bn-2 (see Fig. 1) suggests that two molecules of this complex participate in the formation of the active center. One of them is obviously a source of the initiating acyl cation $PhCO^+$. To explain the role of the second molecule at least, two versions can be suggested. According to one of them, PhCOCl, which is an organic donor of electrons, (most likely as the complex with the Lewis acid) stabilizes the growing carbocation.[8,9] Normally this stabilization leads to the suppression of reactions that limit the chain (chain transfer and chain termination), and the process approaches the "living" polymerization, which is accompanied as a rule by a substantial decrease in the activity of the propagation centers.[10,11] To determine the activity of the initiator Bn-2, we calculated the rate constant of the chain propagation (k_p), assuming that it is a first-order reaction with respect to the current concentration of the monomer and neglecting the slight variations of $[n^*]$ during the polymerization (see Table 1). In this case, the equation for the polymerization rate

$$-d[M]_t/dt = k_p[M]_t[n^*]$$

assumes the following form after integration

$$\ln([M]_0/[M]_t) = k_p[n^*]t,$$

where $[M]_0$ and $[M]_t$ are the initial and current concentrations of the monomer, respectively.

It can be seen from Fig. 2 that the kinetic curves are really rectifiable in semilogarithmic coordinates, which confirms the assumption that the reaction has the first

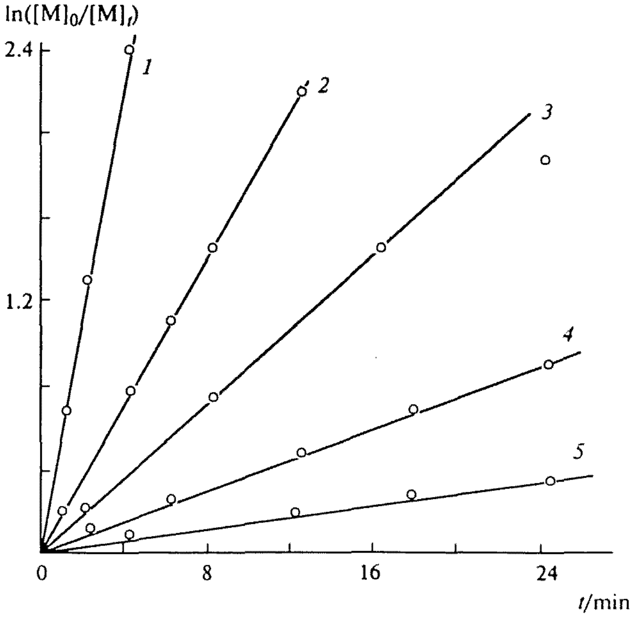

Fig. 2. Kinetics of the polymerization of IB in the presence of the complex Bn-2. The conditions are given in Table 2; $[Bn-2] \cdot 10^3$/mol L^{-1} = 9.6 (*1*), 6.1 (*2*), 4.6 (*3*), 3.0 (*4*), and 1.8 (*5*).

order with respect to the current monomer concentration. From the slopes of these plots and the $[n^*]$ values presented in Table 1, we calculated the values of k_p, which vary from 9.1 L mol^{-1} s^{-1} (see Fig. 2, *5*) to 26.6 L mol^{-1} s^{-1} (see Fig. 2, *4*). The certain noncoincidence of these values may be due both to the inaccuracy in the determination of $\bar{M}_n$ (gel-permeation chromatography in toluene), and, consequently, in the determination of $[n^*]$ and to the assumption that $[n^*]$ remains constant during polymerization. Apparently, the most accurate value k_p = 13.9 L mol^{-1} s^{-1} was obtained from the slope of the straight line *3* in Fig. 2 ([Bn-2] = $4.6 \cdot 10^{-3}$ mol L^{-1}); in this case, the arithmetic mean of the values listed in Table 1 was taken for $[n^*]$. The rate constant found is almost twice that determined in the case where Ac-2 was used as the initiator (6.2 L mol^{-1} s^{-1}),[12] the order of the initial polymerization rate with respect to Ac-2 being 0.5 (see Fig. 1). The latter value indicates a low probability of the participation of the adduct Ac-2 in the solvation of the growing center or of any of its constituents.

The alternative explanation of the second order of the polymerization rate with respect to the concentration of Bn-2 is the suggestion that the second molecule of the complex solvates the anion. Such a solvation decreases the basicity of the anion and, hence, it should decrease the probability of the proton elimination from the growing carbocation. In fact, as noted above, Bn-2 makes it possible to obtain PIB with a very low $f_{C=C}$ value compared to the products of polymerization initiated by Ac-2, which cannot be explained by the somewhat greater k_p value in the former case. Previously[13] it has been noted that the ratio of the chain transfer and chain propagation constants decreases 20-fold on going from the rather basic tosylate ion to the relatively non-basic $EtAlCl_2OH^-$ in the polymerization of styrene (benzene, 70 °C). In view of these data, the fact that in the presence of Bn-2, k_p is somewhat higher than in the case of the Ac-2-initiated process can be attributed either to a shift of the equilibrium between contact, space-separated, and solvent-separated ion pairs[14] (the formation of a substantial amount of free ions in nonpolar hexane seems unlikely) or to an increase in the time during which the active polymeric carbocationic centers are "awake". In our opinion, the latter explanation is preferable. One should take into account that, as has been stressed previously,[3] these centers exist most of the time in a "sleeping" nonionic state: $\sim CH_2-C(CH_3)_2-Br$ or $\sim CH_2-C(CH_3)_2-Cl$, and k_p is actually the apparent value, which is however accessible for measurements. Similar conclusions have been drawn by other researchers who analyzed cationic polymerization of styrene.[15]

Thus, it was shown that the polymerization of IB initiated by the complex $PhCOCl \cdot Al_2Cl_6$ makes it possible to obtain PIB with a very low content of terminal double bonds and a narrow molecular-weight distribution, the process having the second order with respect to the initiator.

The results of the comparison of the behaviors of the acetyl bromide and benzoyl chloride complexes with $AlBr_3$ (Al_2Br_6) during the polymerization of IB are summarized below.

1. In the presence of the complex Ac-1, proton initiation occurs. In the presence of Bn-1, polymerization does not proceed at all.

2. Polymerization in the presence of the complexes Ac-2 and Bn-2 has the following similar features:

(a) initiation with acyl cations, $f_{C=O} \approx 100$ %;

(b) linear increase in $\bar{M}_n$ with an increase in the degree of conversion of IB;

(c) low E_{in} values;

(d) resumption of the polymerization and the linear increase in the $\bar{M}_n$ of PIB upon repeated addition of the monomer;

(e) absence of the initiation activity of the "superacid" formed by the proton elimination;

3. The most significant differences between the behaviors of the Ac-2 and Bn-2 catalysts are the following:

(a) the order of the initial polymerization rate with respect to the concentration of the initiating complex is 0.5 in the case of Ac-2, and 2 in the case of Bn-2;

(b) in the case of Ac-2, the efficiency of initiation increases as the concentration of the initiator decreases, while in the case of Bn-2 the efficiency decreases;

(c) during the polymerization induced by Ac-2, f_{C-Hal} substantially decreases and $\bar{M}_w/\bar{M}_n$ increases; in the presence of Bn-2, f_{C-Hal} slightly decreases, and the molecular weight distribution is broadened;

(d) the k_p values for the polymerization initiated by Ac-2 and Bn-2 are 6.2 and 13.9 L mol^{-1} s^{-1}, respectively.

The results obtained by us are in better agreement with the assumption that the second molecule of the Bn-2 complex participates in the solvation of the anion, which accounts for the second order of the polymerization rate with respect to the initiator, for the high values of f_{C-Hal}, and for the increase in E_{in} on an increase in the concentration of Bn-2.

Although the reasons for some differences between the behaviors of the complexes Ac-2 and Bn-2 in the polymerization of IB have not been ultimately elucidated, one may assume that an important role in the solvation of the counterion is played by the fact that the solvating Bn-2 molecule contains a benzene ring, through which this species interacts with the anion.

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