¹H NMR spectroscopic study of the *tert*-butyl chloride—aluminum bromide cationic initiating system

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The interaction of *tert*-butyl chloride with aluminum bromide in methylene dibromide at -30 °C leads to the formation of two types of adducts, which give signals with δ 2.4 and 3.2 in the ¹H NMR spectra in addition to that of free alkyl halide. These signals are attributed to a polarized complex (PC) and ion pair (IP), respectively. An excess of AlBr₃ shifts the equilibria toward IP. The latter contains more AlBr₃ than the polarized complex. Based on the spectral data, we calculated the limiting values of some equilibrium constants. The ability of AlBr₃ to solvate counterions is consistent with the results of isobutylene polymerization under the action of the initiating Bu¹Cl—AlBr₃ system at different ratios of the starting concentrations [AlBr₃]₀/[Bu¹Cl]₀. An increase in this ratio results in both the acceleration of polymerization and an increase in the relative role of chain transfer reactions.

Key words: *tert*-butyl chloride, aluminum bromide, complexes, ¹H NMR spectroscopy, isobutylene, cationic polymerization.

tert-Butyl halide-Lewis acid systems are considered to be most suitable for studying isobutylene (IB) polymerization, since the tert-butyl cation formed during their interaction is close in structure and activity to the growing polyisobutenyl (PIB) cation.¹ Due to this, the rate constants of the reaction of the monomer with the primary Me₃C⁺ cation and polymeric $+CH_2-CMe_2$, $CH_2Me_2C^+$ cation should be sufficiently close, which simplifies significantly the interpretation of the results obtained. Moreover, the tert-butyl cation provides, most likely, the highest "cationic activity" as compared to other carbocations during initiation of IB polymerization.² The effect of the concentration of the cationogen and the tert-butyl halide/Lewis acid ratio in these systems on the polymerization kinetics was studied in detail by several authors.³⁻⁵ However, no direct data on the effect of the Lewis acid/cationogen ratio on the composition and structure of products of their interaction were published. Meanwhile, this ratio affects significantly both the rate of IB polymerization and parameters of the polymer obtained.

The purpose of this work is to study the Bu^tCl— AlBr₃ system by ¹H NMR spectroscopy and compare the data obtained with the results of IB polymerization under the action of this system.

Experimental

Starting reagents and solvents were thoroughly purified and dried. Experiments on polymerization were carried out in a

completely-sealed glass vacuum installation. These procedures as well as the methods of isolation of polymers and determination of molecular weights by gel permeation chromatography and terminal groups in macromolecules are described in Ref. 6. The polymerization kinetics was studied by dilatometry.

¹H NMR spectra were recorded on a Tesla 60 spectrometer with a working frequency of 60 MHz. Chemical shifts were determined relative to signals of protons of the solvent (methylene dibromide) and then recalculated with respect to tetramethylsilane.

Results and Discussion

The ¹H NMR spectrum (Table 1) of Bu^tCl (sample 1) contains a single singlet with δ 1.6. Mixing of Bu^tCl with an equimolar (sample 2) or double (sample 3) amount of AlBr3 results in the appearance of two new signals with δ 2.4 and 3.2. Signals of protons of free alkyl halide appear as two peaks, and the more intense signal is shifted downfield by 0.2 ppm relative to the signal of the starting Bu^tCl, which is retained as a shoulder. The peaks were broadened considerably upon heating to room temperature, but repeated cooling returned them to the starting state. This fact shows that mixing of Bu^tCl and AlBr₃ results in the formation of at least two types of complexes, which were in equilibrium with each other and with the starting components. At -30 °C, equilibrium is achieved in the time necessary for mixing of the components, placing the ampoule in the NMR cell, and thermostatting, which requires ~5 min. However, exchange of molecules between free and bound in

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Table 1. Chemical shifts, relative intensities, and assignment of signals in ${}^{1}H$ NMR spectra of solutions of Bu^tCl and its mixtures with aluminum bromide in methylene dibromide at -30 °C

Sample $(C/\text{mol } L^{-1})^{b}$				
		δ	Assignment	I _{rel}
1:	Bu ¹ Cl (-3)	1.6	Me ₃ CCI	
2:	Bu ^t Cl (2.0)+ +AlBr ₃ (2.0)	1.6 1.8 2.4 3.2	$ \begin{array}{c} Me_{3}CCI \\ Me_{3}CBr \\ Me_{3}CX \cdot 2AIX_{3} \\ Me_{3}C^{+}Al_{2}X_{7}^{-} \end{array} $	8 4 1
3:	Bu ¹ Cl (1.0)+ +AlBr ₃ (2.6)	1.6 1.8 2.4 3.2	$\left.\begin{array}{c} Me_{3}CCI\\ Me_{3}CBr\\ Me_{3}CX\cdot 2AIX_{3}\\ Me_{3}C^{+}AI_{2}X_{7}^{-}\end{array}\right\}$	1 2 1

^{*a*} All spectra contained the signal of CH_2Br_2 (-5.0 ppm), which was not taken into account in calculation of relative intensities.

^b Concentration in solution.

a complex *tert*-butyl halides occurs sufficiently slowly in the NMR scale at this temperature. Heating accelerates the exchange, which is the reason for broadening of resonance lines at temperatures of $\sim 20-25$ °C.

Splitting of the peak at 1.6 ppm is probably related to the exchange of halogen between Bu'Cl and AlBr₃. The component with δ 1.8 is attributed to free tert-butyl bromide (Bu^tBr). The higher intensity of this signal relative to that at 1.6 ppm agrees well with the tendency (which we have mentioned previously) to add more bulky halogen atoms to the end of the chain of PIB molecules in . the presence of tert-butyl halides and Lewis acids with different halogen atoms.⁶ This exchange is important to determine the preferableness of these or other atoms to enter into the terminal groups of PIB macromolecules, but most likely this is not essential for the mechanism of formation of active centers or their precursors. Therefore, hereinafter we do not take into account this exchange, and the system studied is designated as ButX- $AIX_3(AI_2X_6)$, where X = CI and Br are in a ratio determined by the starting molar [AlBr₃]₀/[Bu^tCl]₀ ratio.

The presence of peaks with δ 2.4 and 3.2 indicates that protons of methyl groups of tert-butyl halide molecules entering the complexes formed are less screened than those in unbound Bu^tX molecules. This fact allowed us to assign the adducts obtained to polarized complex (PC) 1 (δ 2.4) and ion pair (IP, δ 3.2), respectively. (The signal with δ 4.15 shifted strongly to the weak field, which was observed in Ref. 7 for a solution of Me_3CF in SbF_5 , is probably related to the free carbocation.) A similar shift of signals of protons of acyl halides during the formation of donor-acceptor complexes and acyl salts has been observed previously.8,9 Alkyl halides Bu^tCl and Bu^tBr are weak electron-donors, and the main contribution to the formation of their complexes with a Lewis acid is made by polarization interactions rather than charge transfer forces. Therefore, the adducts with chemical shifts 2.4 ppm can reasonably be assigned precisely to polarized molecular complexes.

The position of the signals in the ¹H NMR spectrum is independent of the $[AlBr_3]_0/[Bu^tCl]_0$ ratio, but the relative integral intensities of these signals change significantly when this ratio changes (see Table 1). In our opinion, it is most important that as the $[AlBr_3]_0/[Bu^tCl]_0$ ratio increases, the [IP]/[1] ratio of concentrations increases as well. This indicates that the concentration of AlX_3 in the ion pair observed in the spectra is higher than the content of the Lewis acid in compound 1.

Based on our observations and taking into account the data in Ref. 10, we can try to estimate the most probable composition of complexes 1 that formed. The authors of this work mixed equimolar amounts of ButCl and AlCl₃ in CH₃Cl or CH₂Cl₂ at -78 °C, the suspension formed was filtered off, and the liquid phase was slowly concentrated at a reduced pressure to obtain white or light-yellow needle-like crystals in 25-70% yield depending on the method of introduction of AICl₁. The assumed 1 : 1 composition of the complex is consistent with the data of elemental analysis and cryoscopy. However, this complex is very unstable toward temperature increase: already at -30 °C the crystals decomposed to yield HCl and a reddish liquid with an unknown composition. Since complex 1 formed under our experimental conditions exhibited no noticeable tendency to decomposition even at ~ 20 °C, it is reasonable to assume that its composition differs from the equimolar one.

In fact, due to the same reason, we can rule out the assumption that complex 1 has the $AlX_3 \cdot 2Bu^tX$ composition. In this case, it should be expected that AlX_3 , which is additionally introduced and favors the formation of structures with an increased content of Lewis acids, gives the same thermolabile 1 : 1 (2) complexes according to the equation

 $AIX_3 \cdot 2Bu^tX + AIX_3 \implies 2 Bu^tX \cdot AIX_3.$

Let us emphasize once more that, in fact, colored liquid products were observed in none of the experiments, and the ¹H NMR spectra obtained at -30 °C were reproduced after heating at room temperature and repeated cooling.

Thus, it is most probable that complex 1 contains an excess of AIX_3 with respect to Bu^tX and has the $Bu^tX \cdot 2AIX_3$ composition. If it is accepted that aluminum halides in alkyl halides used as solvents exist predominantly in the monomeric form,¹¹ the formation of 1 can be presented as two sequential reactions:

$$Bu^{t}X + AIX_{3} \xrightarrow{K_{1}} 2, \qquad (1)$$

$$\mathbf{2} + \mathsf{AIX}_3 \xrightarrow{K_2} \mathbf{1}, \qquad (2)$$

$$Bu^{t}X + 2AIX_{3} \xrightarrow{K_{1}} 1, \qquad (3)$$

where K_1 and K_2 are the equilibrium constant of stages (1) and (2), respectively; and $K_3 = K_1 \cdot K_2$ is the effective constant of complex formation:

$$K_{3} = \frac{[1]}{[Bu^{t}X]_{free}[AlX_{3}]_{free}^{2}} .$$
 (4)

where $[Bu^tX]_{free}$ and $[AIX_3]_{free}$ are the concentrations of free (unbound in complexes) components.

Most likely, under our conditions, the concentration of the intermediately formed thermolabile 1 : 1 complex 2 should be very low, *i.e.*, this complex reacts with the second AlX₃ molecule more rapidly that its thermodecomposition occurs. Therefore, we observed no formation of the decomposition products mentioned in Ref. 10. It can be assumed that the preferred formation of the 1 : 1 complex described¹⁰ is due to the specific character of the procedure used, which is directed toward the isolation of the product (complex) in the crystalline state and/or to the special state of aluminum trichloride molecules at concentrations close to the limiting solubility.¹²

For the determination of effective constant K_3 , the [1], $[Bu^tX]_{free}$, and $[AlX_3]_{free}$ values should be known. The two first values (or their ratio) can be calculated from integral intensities of the signals with chemical shifts 2.4 and 1.6-1.8 ppm taking into account the fact that complex 1 contains one Bu^tX molecule (the results of the calculation are presented in Table 2). The determination of the concentration of AIX₃ unbound in a complex is a considerably more difficult problem. For the calculation of this value from material balance, the amount of AlBr₃ in ion pairs should be known. The concentration of IP can be easily calculated from the ¹H NMR spectra (these data are also presented in Table 2), but the composition of these pairs is unknown and, as could be assumed, variable. The point is that, in fact, counter-anions in ion pairs are solvated by AlX₃

Table 2. Results of calculation of concentra-tions of complex 1, IP bound in these structures, and free components for samples 2 and3 (see Table 1)

Component	Concentration/mol L ⁻¹			
	Sample 2	Sample 3		
[1]	0.615	0.50		
[1P]	0.154	0.25		
[Bu ⁱ X] ₁	0.615	0.50		
[Bu ¹ X] _{1P}	0.154	0.25		
[Bu ^t X] free	1.23	0.25		
[AIX ₃]	1.23	1.00		
[AIX3]IP	>0.31	>0.68		
[AIX ₃]free	<0.46	<0.92		

Note. Limiting values of some equilibrium constants calculated from the data presented in Table 2: $K_3 \ge 2.36$ L mol⁻¹, $K_4 \le 0.25$, $K_5 \cdot K_6 \ge 2.37$ L² mol⁻².

molecules. Solvation of this type occurs efficiently even at low concentrations of Lewis acid in both nonpolar hexane and more polar methylene dichloride.¹³ Processes of ion solvation are described by equations of the Langmuir type¹⁴ or a system of successive equilibria. In our case, this system of equilibria is the following:

$$1 \xrightarrow{K_4} IP', \tag{5}$$

$$IP' + AIX_3 \xrightarrow{K_5} IP'', \tag{6}$$

$$IP'' + AIX_3 \xrightarrow{K_6} IP''', \qquad (7)$$
... etc.

The formation of the ion pair IP' due to the selfionization of 1 seems to be a rather real process, since the $Al_2X_7^-$ counterion appearing in the process is rather stable and low-nucleophilic even in the absence of additional specific solvation.^{13,15}

This mutual transition of polarized and ionic forms of adducts of Bu^tCl with AlBr₃ (Bu^tX with AlX₃) makes it possible to assign these adducts to the so-called "endosphere complexes" or "ion-transfer complexes" considered in detail, e.g., in the review.¹⁶ Such complexes are characterized by the possibility to exist in two forms, one of which is an intermediate state of the type of charge-transfer complex, and the other is the ion state. Two potential wells separated by the energy barrier correspond to these states in the energy diagram. In our case, these states appear in the ¹H NMR spectra at -30 °C as two separate signals with δ 2.4 and 3.2. The complexes of Bu^tX with AlX₃ have certain specific features: an excess of Lewis acid can participate in stabilization (solvation) of the ion state; in the non-ion state, the polarization interaction contributes mainly to binding rather than the charge transfer (this problem is discussed above). However, the polarization (Coulomb) interaction often plays an important (unless decisive) role in the formation of other molecular complexes, which are sometimes considered as charge-transfer or donor-acceptor complexes.17

Sequential equilibrium reactions (5), (6), (7),... result in the formation of a set of ion pairs with different degrees of solvation (IP', IP", IP''', and others). This conclusion does not contradict the fact that we observed only one signal (3.2 ppm) in the ¹H NMR spectrum, which was attributed to ion pairs. The virtually unchanged position of signals in ¹H and ¹³C NMR spectra for acetylium salts $CH_3CO^+SbF_6^-$ or $CH_3CO^+Sb_2F_{11}^$ and mesitoyl salts with counterions $AlBr_4^-$ or $Al_2Br_7^$ was demonstrated in Ref. 18. Thus, the relative intensity of the signal with δ 3.2 allows one to determine only the overall concentration of ion pairs ([IP]).

The presence of a set of ion pairs with different degrees of solvation of counterions determined by the concentrations or the ratio of components (Bu^tX and AlX₃) is confirmed by the results of experiments on IB polymerization in the presence of the Bu^tCl-AlBr₃

system at different ratios of the components, which are considered in detail below. As for the possibility of quantitative determination of the K_3 constant and other equilibria constants, we did not manage to perform this calculation because of an uncertain content of ion pairs with different compositions. In this case, ²⁷Al NMR spectroscopy can provide poor information, since the appearance of a large set of broad ($\Delta \approx 900$ Hz) signals corresponding to the Al₂X₇⁻ ions with different Br/Cl ratios^{18,19} should be expected, as well as signals from free, bound in 1, and entering in the solvate shell of IR of AlX₃ (Al₂X₆) molecules. If aluminum remains tetracoordinated, all signals from the structures indicated should be arranged in the narrow δ 80–110 range.²⁰

Nevertheless, some semi-empirical estimations were successful. For example, the ratio of concentrations of AlX_3 ($[AlX_3]_{free}$) for samples 2 and 3 (the number of the sample is shown by the subscript) can be determined from Eq. (4) and concentrations calculated from the spectra (see Table 2):

$$\frac{[A|X_3]_{free,3}^2}{[A|X_3]_{free,2}^2} = \frac{[1]_3}{[Bu^T X]_{free,3}} \cdot \frac{[Bu^T X]_{free,2}}{[1]_2} .$$
(8)

This ratio is equal to 2. Based on the data obtained, we also calculated the maximum concentrations of free halide AlX₃ for both samples. The [AlX₃]_{free,2,max} concentration was calculated from the material balance with account of the fact that each particle of complex 1 contains two AIX₃ molecules and each ion pair includes at least two AlX₃ molecules (i.e., the system of equilibria (5)-(7) was restricted only by reaction (5)). As a result, we obtained the value $[AIX_3]_{free,2,max} = 0.46 \text{ mol } L^{-1}$. Therefore, $[AIX_3]_{free,3,max} = 2 \cdot 0.46 = 0.92 \text{ mol } L^{-1}$. It follows from the material balance for sample 3 that the consumption of AIX_3 in the formation of IP in this sample is not lower than 0.68 mol L^{-1} ([AIX₃]₀ - 2 [1] - [AIX₃]_{free,3,max}), *i.e.*, at least 2.7 AIX₃ molecules fall, on the average, on one ion pair IP, and due to the solvation of one ion pair IP', at least 0.7 AIX₃ molecules are bound additionally in this sample.

Inserting the $[AIX_3]_{\text{free,max}}$ values in Eq. (4), we obtain that $K_3 \ge 2.36$ L mol⁻¹. It follows from Eq. (5) and the [1] and [1P] values presented in Table 2 that $K_4 \le 0.25$, *i.e.*, equilibrium (5) is noticeably shifted to the left. When we restrict our consideration of the equilibrium solvation of $AI_2X_7^-$ counter-anions (in the first approximation) by only three stages (5)–(7) (which seems reasonable taking into account the restricted capacity of the solvate shell of the counterion in the ion pair and comparable sizes of the counterion and solvating agent), the calculation gives the following inequality: $K_5 \cdot K_6 \ge 2.37$ L² mol⁻².

Note that similar results are obtained when aluminum bromide is assumed to exist in methylene dibromide mainly as a dimer.

As follows from the ¹H NMR spectral results presented above, the specific solvation of anions of IP by

additional AIX₃ molecules even in relatively polar methylene dibromide evidently plays an important role in the stabilization of the ionized state. We mentioned¹³ the significance of this solvation for the polymerization process in the study of the initiating capability of mesitoyl salts $Me_3C_6H_2C(O)^+AlBr_4^-$ (Mst-1) and $Me_3C_6H_2C(O)^+Al_2Br_7^-$ (Mst-2). Despite the ionic character, Mst-1 did not initiate IB polymerization in hexane or methylene dichloride. However, this salt could be activated by small additives of Lewis acids or even organic electron-acceptors (for example, chloranil). The Mst-2 salt itself initiated the IB polymerization in hexane and CH₂Cl₂, but the polymerization rate increases even more when the additives indicated above were introduced in amounts comparable with the amount of the salt, i.e., at concentrations of an order of several mmol L⁻¹.

Based on these data, we can assume that the specific solvation of counter-anions by an excess of Lewis acid or organic electron-acceptors plays the main role in the determination of activity of cationic initiators, which, of course, does not rule out the influence of the solvent polarity on the rates of particular elementary reactions. The increase in the fraction of IP (established from the spectra) with an increase in the $[AlBr_3]_0/[Bu^tCl]_0$ ratio should result in an increase in the content of active centers in the polymerization system and, hence, the polymerization rate. To confirm this conclusion, we compared the NMR spectral data obtained with the IB polymerization in hexane under the action of the initiating Bu'Cl-AlBr₃ system. This comparison of the data obtained in different but low-polar solvents is quite reasonable in this case taking into account the aforementioned (for acyl salts) considerably higher sensitivity of carbocationic initiators precisely toward the content of specifically solvating additives rather than to the polarity of the medium.13

The experimental results of IB polymerization (Table 3) agree, as a whole, with the expected results: the initial polymerization rate (W_0) increases by approximately two orders of magnitude as the molar [AlBr₃]₀/[Bu¹Cl]₀ ratio increases from 1 to 8. Moreover, such a sharp increase in the polymerization rate can be considered as an indication that the activity of carbocations in acts of polymer chain growth increases as well.

Table 3. Results of polymerization of IB by the Bu^tCl-AlBr₃ system (hexane; -78 °C; [IB] = 1.08 mol L⁻¹; [Bu^tCl]₀ = 1 mmol L⁻¹; 20 min; conversion ~100%, except for entry 1)

Entry			$\overline{M}_{n} \cdot 10^{-1}$	$^{3} f_{C=C} C_{(C=C),rel}$		
	/mol_mol_1	/mol L 's '			(%)	
1	0.5	No polymer is formed				
2	1.0	$2.1 \cdot 10^{-3}$	126.5	27	$8.2 \cdot 10^{-3}$	
3	2.0	$1.4 \cdot 10^{-2}$	110.6	71	$4.2 \cdot 10^{-2}$	
4	4.0	~1.0 · 10-1	68.2	97	8.8 · 10 ⁻²	
5	8.0	-2.8 • 10-1	52.8	127	$1.6 \cdot 10^{-1}$	

The absence of polymerization at the ratio $[AlBr_3]_0/[Bu^tCl]_0 = 0.5$ (see Table 3, sample 1) was rather unexpected. To explain the latter result, we can assume that an excess of Bu¹Cl decreases the probability of IP formation (i.e., decreases the [IP]/[1] ratio as mentioned above), but also solvates the carbocations formed, thus decreasing their activity. This assumption is based on mass spectrometric data²¹ of processes occurring during laser evaporation/ionization of aluminum in the gas flow of the IB-ButCl-He mixture. The authors observed a set of clusters containing oligoisobutenyl cations and Bu¹Cl molecules. The study of gas-phase equilibria for similar systems showed²² that the energy of binding of the carbocation and Bu'Cl should decrease as the size of the oligomeric cation increases. In other words, an excess of Bu^tCl prevents the addition of the monomer to, first of all, small carbocations, including the initial IP.

In the analysis of the results obtained on polymerization, it is reasonable to assume that an increase in the initial $[AlBr_3]_0/[Bu^tCl]_0$ ratio results in a change in the composition of active centers rather than in an increase in the concentration of IP and, correspondingly, the concentration of active centers. The aforementioned very sharp increase in the polymerization rate as the ratio indicated increases only 8 times agrees, most likely, with this assumption.

Then, assuming that changes in the composition (structure) of active centers should be reflected in their relative activities in acts of chain growth and restriction, i.e., selectivity of these centers, we analyzed the parameters of the polymers (see Table 3). For cationic systems, we have suggested previously²³ the so-called criteria of "approach to viability," which allow one to estimate the relative disposition of carbocationic centers to side chain transfer or termination reactions. In the same work,²³ we showed that the proton elimination from the carbocation is usually the only possible chain restriction reaction for the IB polymerization under specified conditions (hexane, -78 °C) under the action of acyl RCOX · 2AIBr₃ complexes. In this case, the use of the second criterion of those suggested by us can be recommended: the ratio of rate constants of proton elimination (k_{el}) to chain growth (k_{er}) .

However, the experimental results presented in Table 3 cannot be analyzed using this criterion, since the polymers formed at higher $[AlBr_3]_0/[Bu^{t}Cl]_0$ ratios have a degree of functionalization $f_{C=C}$ exceeding 100% (more than one double bond C=C per macromolecule). This increase can be explained only in part by errors in determination of the numerical-mean molecular weight \overline{M}_n and content of C=C bonds. We believe that an increase in the $[AlBr_3]_0/[Bu^{t}Cl]_0$ ratio leads to a decrease in the selectivity of the growing carbocation, which results in an increase in the role of the reaction of proton elimination and also (at the highest $[AlBr_3]_0/[Bu^{t}Cl]_0$ ratios) in another side reaction, hydride shift (here A⁻ is the counter-anion):
$$\begin{split} \mathsf{Me_3C(CH_2CMe_2)_nCH_2CMe_2^+A^-} + \mathsf{CH_2=CMe_2} &\longrightarrow \\ &\longrightarrow \mathsf{Me_3C(CH_2CMe_2)_nCH_2CMe_2H} + \mathsf{CH_2=C(Me)CH_2^+A^-}, \end{split}$$

 $CH_2=C(Me)CH_2^+A^- + n CH_2=CMe_2$ ---- chain growth.

The contribution of this reaction should be noticeable only in the case where the reaction involves oligomeric carbocations with small n values or even the starting *lert*-butyl cation, since the low-molecular isoparaffins that formed contain no terminal double C=C bonds and can be removed during isolation of the polymer. The nonisothermic character of the process, which most probably takes place due to very high polymerization rates at a considerable excess of AlBr₃, can be an additional prerequisite for the hydride shift reaction. The temperature increase is known^{2,24} to favor an increase in the relative role of processes associated with hydride ion transfer; in some cases (see, e.g., Ref. 25), these processes can become determining with respect to the structure of the polymeric product. However, further studies are necessary for a deeper understanding of the specific features of the hydride shift reaction.

For the estimation of "viability" of polymerization processes involving various reactions of chain restriction, which result in the appearance of double bonds in macromolecules, we suggested²³ another criterion:

$$C_{(C=C),rel} = f_{C=C}/DP_n ,$$

where $C_{(C=C),rel}$ is the relative content of double bonds in the polymer; $\overline{DP_n}$ is the numerical-mean degree of polymerization (in this case, $\overline{DP_n} = \overline{M_n}/56$). The decrease in $C_{(C=C),rel}$ indicates a decrease in the relative role of side restriction reactions. The application of this criterion for the comparison of "viability" of systems is possible at close conversions and initial concentrations of the monomer, which corresponds to the conditions of experiments, the results of which are presented in Table 3. The calculated $C_{(C=C),rel}$ values demonstrate rather clearly an increase in the role of chain restriction reactions with an increase in the [AlBr₃]₀/[Bu^tCl]₀ ratio. It is important that the increase in the criterion indicated is sufficiently great (almost 7 times) even for an increase in [AlBr₃]₀/[Bu^tCl]₀ ratio from 1 to 2 only, *i.e.*, under conditions of moderate rates that provide a regime at least close to the isothermic one.

Thus, an increase in the $[AlBr_3]_0/[Bu^4Cl]_0$ ratio changes the concentration of active centers and their composition (structure) as well. Evidently, an excess of Lewis acid in this system is capable, in fact, of additional solvation of counter-anions to decrease their nucleophilicity, which, in turn, increases the activity but decreases the selectivity of carbocations. This conclusion agrees well with the previous observations²⁶ of the very important role of nucleophilicity of the counterion for providing the "viable" character of cationic polymerization of vinyl monomers: a decrease in nucleophilicity of the counter-anion results, as a rule, in an increase in the role of side chain restriction (for example, chain transfer) reactions.

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