The effect of the counterion composition on the chain restriction in the cationic polymerization of isobutylene

A. V. Orlinkov,[a] *T. V. Chulochnikova,*[b] *A. I. Nesmelov,*[b] *V. B. Murachev,*[b]* *E. A. Ezhova,*[b] *and A. M. Evtushenko*[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085
[b]*M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,*
86 prosp. Vernadskogo, 117571 Moscow, Russian Federation.
Fax: +7 (095) 430 7983

The effects of the nature of halogens in the initiating *tert*-butyl halide—aluminum-containing Lewis acid system on the number average molecular weight $\bar{M}_n$ and the structure of end groups of polyisobutylene macromolecules obtained in the cationic polymerization of isobutylene in hexane at −78 °C were studied. An increase in $\bar{M}_n$ is observed in the transition from chlorine to bromine and iodine, accompanied by a decrease in the fraction of end C=C groups and an increase in the relative content of C—Hal groups (Hal = Cl, Br, and I). When atoms of different halogens are present in the counterion, more bulky atoms preferentially participate in the formation of the end groups. The results are interpreted within the framework of the principle of hard and soft acids and bases.

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

Polyisobutylene (PIB) and the copolymer of isobutylene (IB) with dienes (butyl resin) have long been produced on industrial scales,[1] but many aspects related to the control of molecular weights (*M*) of these polymers are still unclear. In particular, the effect of the nature of the counterion on chain restriction reactions is poorly studied, although the existence of this effect is doubtless.[2] In this work, we attempted to estimate the effect of the counterion composition on both the molecular weight of PIB and individual reactions that determine this value. For the initiation of the polymerization of IB in hexane at −78 °C, the known[3,4] catalytic *tert*-butyl halide—Lewis acid systems ($Bu^tX—MY_n$) were used.

Experimental

Hexane was shaken with H_2SO_4, washed with a solution of NaOH and water, and dried over $CaCl_2$, molecular sieves 4 Å, and a potassium—sodium melt. Isobutylene was kept over alkali and additionally dried over CaH_2, butyllithium, and trialkylaluminum. Lewis acids were dried by distillation ($EtAlCl_2$, Bu^iAlCl_2) or sublimation ($AlBr_3$) *in vacuo*.

tert-Butyl chloride was dried over $CaCl_2$ and molecular sieves and distilled. *Tert*-Butyl bromide and *tert*-butyl iodide were obtained by shaking a solution of IB in hexane with aqueous solutions of the corresponding acids. After drying over $CaCl_2$ and molecular sieves, the organic layer was fractionally distilled to yield *tert*-butyl halide, which was finally dried *in vacuo* as Bu^tCl.

Solutions of components of initiating systems in hexane were dosed, using thin-wall glass balls.

Polymerization was studied in a high-vacuum all-sealed setup at the residual pressure of 10^{-3}—10^{-4} Torr. In the experiments, the results of which are presented in Table 1, solutions of components of the initiating system were preliminarily mixed in a separate branch, and then a solution of the monomer was immediately admitted. In the other series of experiments (Table 2), balls with solutions of Bu^iAlCl_2 and Bu^tCl were broken directly in a solution of the monomer, and the change in conversion was registered dilatometrically. Polymers were precipitated with methanol and dried *in vacuo*, and their yields were determined. Before the analysis of the content of functional groups, samples were additionally reprecipitated with methanol from solutions in hydrocarbons or CCl_4.

Number average molecular weights ($\bar{M}_n$) of PIB were determined by gel permeation chromatography, using a Waters-200 chromatograph equipped with a standard set of columns with Styrogel with different sizes of pores (toluene as the solvent, a refractometer as the detector). Calibration was performed by standard polystyrene samples. Viscosity of solutions of PIB in chloroform was determined at 30 °C on an Ubbelohde viscosimeter. The viscousity average molecular weight ($\bar{M}_v$) was calculated by the equation

$$[\eta] = 1.2 \cdot 10^{-3} \cdot \bar{M}_v^{0.53}$$

The content of halogen in polymers was determined by X-ray fluorescent analysis on a VRA-2 spectrometer. The amount of C=C groups was determined by the ozonization method on an ADS-4 instrument.

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Table 1. Results of the study of polymerization of isobutylene under the action of the initiating *tert*-butyl halide—Lewis acid ($AlBr_3$ or $EtAlCl_2$) system in hexane at −78 °C ($[IB]_0 = 1.15$ mol L^{-1}, $[Bu^tX] = [MY_n] = 0.8$ mmol L^{-1}, 30 min)

Parameter	$AlBr_3$			$EtAlCl_2$		
	Bu^tCl	Bu^tBr	Bu^tI	Bu^tCl	Bu^tBr	Bu^tI
Q (%)	99	98	98	99	99	98
$\bar{M}_n \cdot 10^{-3}$	39.2	52.0	66.9	19.0	41.7	54.0
Y/X [a]	Br/Cl = 3.0	—	Br/I = 3.0	—	Cl/Br = 2.0	Cl/I = 2.0
$f_{C=C}$ [b]	0.54	0.35	0.14	0.77	0.36	0.17
f_{C-Cl} [b]	0.11	—	—	0.22	0.12	0.07
f_{C-Br} [b]	0.41	0.64	0.27	—	0.52	—
f_{C-I} [b]	—	—	0.52	—	—	0.65
$(Y/X)_P$ [c]	Br/Cl = 3.7	—	Br/I = 0.5	—	Cl/Br = 0.2	Cl/I = 0.1
E_{in}	2.06	1.55	1.20	4.23	1.93	1.49
$E_{in} \cdot f_{C-Hal}$	1.13	0.99	0.95	0.93	1.24	1.07

[a] The ratio of amounts of halogen atoms in Lewis acid and Bu^tX.

[b] The amount of the corresponding end group per macromolecule.

[c] The ratio of amounts of halogen atoms in the polymer.

Results and Discussion

The polymerization of IB in hexane at −78 °C under the action of the initiating systems involving Bu^tX and $AlBr_3$ or $EtAlCl_2$ almost ceases for 30 min under the conditions indicated in Table 1. Information on chain termination reactions can be obtained from the results of the analysis of polymers on the content of end C=C and C—Hal groups. The data presented in Table 1 make it possible to draw several conclusions.

1. An increase in $\bar{M}_n$ and a decrease in the concentration of C=C groups in PIB are always observed in the transition from Bu^tCl to Bu^tBr and then to Bu^tI (when MY_n is constant).

2. When Bu^tX and MY_n contain atoms of different halogens (X ≠ Y), PIB molecules with the end C—Hal groups in which the halogen has the higher atomic weight are preferentially formed.

3. The overall functionalization of macromolecules by end C=C and C—Hal groups is close to unity. A somewhat lower sum is obtained for PIB synthesized under the action of iodine-containing systems, which can be explained by the partial alcoholysis of the $\sim CH_2CMe_2I$ groups under the conditions of isolation of polymer.[5] Apparently, the fraction of end groups that fail to reach unity can be assigned to the primarily formed C—I groups.

Table 2. Effect of concentrations (mmol L^{-1}) of Bu^iAlCl_2 and Bu^tCl on $\bar{M}_v$ of PIB (hexane, −78 °C, $[IB]_0 = 1.45$ mol L^{-1}, yields of PIB >95 %)

$[Bu^iAlCl_2]$	$[Bu^tCl]$	$\bar{M}_v \cdot 10^{-3}$
1.6	0.2	14.8
0.8	0.2	14.2
1.6	0.4	12.5
0.4	1.6	10.9
0.2	1.6	10.3

Nevertheless, only experimental data on the content of end groups were used in our further calculations.

4. The transfer of the ethyl group from the counterion $EtAlCl_2X^-$ to the growing carbocation, if any under the given conditions, occurs sufficiently slowly. In the opposite case, it should be expected that the overall functionalization by the end C=C and C—Hal groups is considerably lower than unity upon the polymerization in the presence of $EtAlCl_2$.

On the whole, the polymerization process can be presented as follows (reactions (1)—(6))[6]:

— initiation under the action of the cationogen—Lewis acid system

$$\mathrm{Me_3C{-}X + CH_2{=}CMe_2 + MY_n \longrightarrow Me_3CCH_2CMe_2^+,\ MY_nX^-}\ ; \qquad (1)$$

— chain propagation

$$\mathrm{Me_3CCH_2CMe_2^+,\ MY_nX^- +}\ m\ \mathrm{CH_2{=}CMe_2 \longrightarrow Me_3C(CH_2CMe_2)_{\mathit{m}}CH_2CMe_2^+,\ MY_nX^-}\ ; \qquad (2)$$

— chain restriction that can be caused by several reactions.

The "termination on the counterion" (reaction (3)) is a reversible process, because oligomeric *tert*-alkyl halide formed in this case can react with Lewis acid to generate the ternary carbocation again.

$$\mathrm{{\sim}CH_2CMe_2^+,\ MY_nX^- \rightleftharpoons {\sim}CH_2CMe_2{-}X + MY_n \ \text{or}\ {\sim}CH_2CMe_2{-}Y + MY_{n-1}X} \qquad (3)$$

This termination results in the formation of PIB molecules with end C—Hal groups. The direct chain transfer to the monomer (reaction (4)) and indirect chain transfer to form superacid as the intermediate product (reaction (5)) result in the appearance of macromolecules with end *exo*- or *endo*-C=C groups.

$$\begin{aligned}&\sim\mathrm{CH_2CMe_2^+,\ MY_nX^-} + \mathrm{CH_2{=}CMe_2} \longrightarrow\\ &\longrightarrow \sim\mathrm{CH_2CMe{=}CH_2} + \mathrm{Me_3C^+,\ MY_nX^-}\\ &\text{or} \sim\mathrm{CH{=}CMe_2} + \mathrm{Me_3C^+,\ MY_nX^-}\end{aligned} \qquad (4)$$

$$\begin{aligned}&\sim\mathrm{CH_2CMe_2^+,\ MY_nX^-} \xrightarrow{a}\\ &\longrightarrow \sim\mathrm{CH_2CMe{=}CH_2}\ (\text{or} \sim\mathrm{CH{=}CMe_2}) + \mathrm{HMY_nX}\\ &\qquad\qquad\qquad\qquad \mathrm{CH_2{=}CMe_2}\Big\downarrow b\\ &\qquad\qquad\qquad\qquad \mathrm{Me_3C^+,\ MY_nX^-}\end{aligned} \qquad (5)$$

The chain transfer to this reagent can take place in the presence of free butyl halide.[2]

$$\begin{aligned}&\sim\mathrm{CH_2CMe_2^+,\ MY_nX^-} + \mathrm{Me_3C{-}X} \rightleftharpoons\\ &\rightleftharpoons \sim\mathrm{CH_2CMe_2{-}X} + \mathrm{Me_3C^+,\ MY_nX}\end{aligned} \qquad (6)$$

Macromolecules with end C—Hal groups should also be formed due to reaction (6).

According to the analysis of PIB to the content of various end groups (see Table 1), the amounts of C=C and C—Hal groups in the samples are comparable. Let us try to estimate the contribution of each of the chain restriction reactions.

It has been established previously[7] that under similar conditions (hexane, −78 °C) the direct chain transfer to the monomer (see reaction (4)) does not occur upon the polymerization of IB under the action of the acyl complex $\mathrm{MeC(O)Br \cdot 2AlBr_3}$, while the indirect chain transfer is limited by the formation of superacid (see reaction (5, *a*)). This conclusion was made on the basis of the fact that almost all macromolecules obtained contained head MeCO groups, although C=C groups comprised a considerable fraction of the end groups. It is reasonable to assume that the direct chain transfer to the monomer is also improbable for the systems considered in this work. To estimate the possibility of the second stage of the indirect transfer (see reaction (5, *b*)), let us calculate the apparent efficiency of the initiator (E_{in}) determined by the ratio of molar concentrations of PIB obtained and initiator:

$$E_{\mathrm{in}} = \frac{[\mathrm{P}]}{[\mathrm{Bu^tX}]} = \frac{[\mathrm{M}]_0 \cdot Q \cdot 56}{\bar{M}_n \cdot [\mathrm{Bu^tX}]},$$

where $[\mathrm{M}]_0$ is the initial concentration of the monomer, 56 is its molecular weight, [P] is the concentration of the polymer, and Q is the degree of conversion. When $E_{\mathrm{in}} > 1$, it is evident that a portion of macromolecules is formed due to the chain transfer. It follows from the data presented in Table 1 that this is valid for all samples of PIB obtained.

If it is assumed that reaction (5) proceeds to completeness, the degree of the participation of the initiator in the polymerization can be estimated from the product $E_{\mathrm{in}} \cdot f_{\mathrm{C-Hal}}$, where $f_{\mathrm{C-Hal}}$ is the fraction of macromolecules containing end C—Hal groups. At $E_{\mathrm{in}} \cdot f_{\mathrm{C-Hal}} \ll 1$, only a slight portion of $\mathrm{Bu^tX}$ molecules reacts. On the contrary, if the product mentioned is close to unity, which is observed for the samples synthesized (see Table 1), then almost all of the initiator participated in the polymerization, and the chain transfer reaction (5) was complete.

Now let us estimate the possible contribution of the chain transfer to $\mathrm{Bu^tX}$ (see reaction (6)). When this reaction predominates in the formation of the end C—Hal bonds, it should be expected that the atoms of the halogen that is part of the $\mathrm{Bu^tX}$ molecule are mainly the terminal Hal atoms in PIB macromolecules. However, the analysis of the polymer obtained, for example, in the presence of the $\mathrm{Bu^tCl{-}AlBr_3}$ system, shows that Br (not Cl) atoms are the main fraction of the terminal Hal atoms. As shown in Table 2, using the $\mathrm{Bu^iAlCl_2{-}Bu^tCl}$ system (hexane, −78 °C) as an example, the eightfold increase in the concentration of ternary alkyl halide decreases $\bar{M}_{\mathrm{v}}$ of the polymer only by 30 %. Therefore, $\mathrm{Bu^tCl}$ is low active as a chain transfer agent under these conditions, and the mentioned decrease in $\bar{M}_{\mathrm{v}}$ at relatively low values of E_{in} can be caused, at least partially, by a decrease in the monomer/initiator ratio. Since even higher-molecular polymers are formed in the presence of $\mathrm{Bu^tBr}$ and $\mathrm{Bu^tI}$ (see Table 1), the alkyl halides mentioned also cannot be active transfer agents. All these data make it possible to consider that reaction (6) under the chosen conditions can be only of secondary significance, and hence will not be taken into account in further analysis.

Thus, the most probable chain restriction processes are reactions (3) and (5) resulting in the formation of macromolecules with end C—Hal and C=C groups, respectively. The observed dependences of $\bar{M}_n$ and the structure of end groups in PIB on the type of halogen in the counterion can be interpreted in terms of the principle of hard and soft acids and bases (HSAB),[8] which has been used previously to explain the relative activities of monomers in addition reactions of nucleophilic species.[9] In this work, the application of the HSAB principles to reactions (3) and (5) makes it possible to suppose that the exchange of small weakly polarizable halogen atoms X and Y in the counterion for more bulky and easily polarizable ones, *i.e.*, the transition from Cl to Br and especially to I, "softens" the anion, decreasing its tendency to the reaction with a hard proton (see reaction (5, *a*)) and resulting in a decrease in the fraction of end C=C groups, which is observed in fact (see Table 1). A decrease in the probability of reaction (5) favors an increase in the molecular weight. At the same time, the end of the growing chain can be considered a sufficiently soft, easily polarizable cation. As a consequence, in the reaction of reversible termination on the counterion, the addition of the most easily polarizable halogen atom, which is present in the MY_nX^- counterion, to the cation should predominate, *i.e.*, the preferableness of the participation of halogen in the formation of the end C—Hal group increases in the series Cl < Br < I.

According to the HSAB principle, the situation concerning the redistribution of halide ions between Lewis acid and the compound with the active C—Hal bond can change, when softer Lewis acids are used. In fact, as shown previously,[10] the exchange of halogen atoms occurs even at negative temperatures (the data of ^{1}H NMR spectroscopy) in mixtures of zinc-containing rather soft[11] Lewis acids ZnY_2 with adducts of the $MeCH(OBu^i)X$ type used for the initiation of the "living" cationic polymerization of isobutyl vinyl ether. As a result, atoms of more polarizable halogens preferably move to zinc, and those of less polarizable halogens move to carbon.

The data presented in this work make it possible to indicate the directions for the selection of counterions that provide required values of molecular weights upon the IB polymerization in hydrocarbon solvents. Counterions with bulky, easily polarizable atoms (or groups) are recommended to be used to increase M_n. It is likely that heterogeneous systems of the type of the Wichterle catalyst,[12] in which counterions enter the crystalline lattice of the solid phase, are one of the extreme cases in this approach. In addition, the analysis of the results obtained allows one to predict the most probable composition of end groups in PIB macromolecules. Finally, the most important, in our opinion, conclusion is that the systems of the $Bu^tX—MY_n$ type can possess a very high efficiency, which provides for the almost complete inclusion of the initiator in the composition of macromolecules formed. It is evident that in this case the ratio of concentrations of the monomer and initiator should be taken into account (as for the "living" cationic polymerization[13]) upon the selection of conditions for preparation of high-molecular polymer.

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