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Catalytic degradation of polyolefins—a promising method for the regeneration of monomers

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ABSTRACT. **The catalytic degradation of polyolefins, which in contrast to the purely thermal process takes place selectively, can help solve the problem of the regeneration of monomers.**

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I. Introduction

The kinetics of the catalytic degradation of polyolefins in the presence of electrophilic reagents differ considerably from the kinetics of their thermal degradation.[1,2] This is due primarily to differences in the initiation of decomposition reactions of the polymer products. In general, in both thermal[3–5] and catalytic[6,9] reactions of polyolefins two mechanisms of initiation can be distinguished: a) initiation of depolymerisation of the macromolecules on the terminal groups; b) initiation of decomposition of macromolecules randomly. To date it has not been possible to determine the contribution of each of these mechanisms using the existing theoretical and experimental approach to a study of the kinetic reaction parameters.[10] A new method of determining the apparent constants of initiation and length of the kinetic chain of competing processes[11] has made it possible to bring closer the development of a general theory concerning the processes of selective catalytic degradation of polyolefins.

II. Thermal degradation of polyolefins

The thermal degradation of polyolefins as an independent process became a topic of interest for research workers at the end of the 1940's, primarily in order to achieve the selective extraction of valuable gaseous hydrocarbons from a polymer feedstock.[12–14] However, with rare exceptions [poly(α-methylstyrene), poly(methylmethacrylate)] very low selectivity with respect to the yield of monomer has been recorded in the thermal degradation of polyolefins. For the majority of polyolefins the formation of a wide range of low-molecular weight products—gaseous, liquid, and waxy—during degradation was typical.[15] The experimental data, in particular the change in molecular weight of the polymer as a function of the temperature and degree of degradation, the observed composition of volatile and nonvolatile degradation products, and the rate of the process, showed that reactions involving chain scission with hydrogen transfer and depolymerisation of the macromolecules are the most probable.[4,15] The degradation of polyolefins can in a number of cases be accompanied by side reactions, such as cross-linking of macromolecules. Moreover in some cases, particularly in the degradation of polyethylene, an active site is formed at a point of branching followed by detachment of a side-chain residue.

The combination of successive parallel reactions that form the basis of the complex chemical process of thermal degradation of polyolefins predetermines the complex task of studying and defining the process. Nevertheless, in relation to the decomposition of polyolefins the main reactions that determine the chemical nature of the overall process are: chain depolymerisation to form the corresponding monomer and its isomerisation and hydrogenation products and random decomposition of the macromolecules with the formation of sequences of polymer molecules of different length (degradation) resulting in a decrease in the molecular weight of the polymer.

As a rule initiation of decomposition of macromolecules is related to the occurrence of various kinds of defects in the polymer chain (structural irregularities) that are formed, for example, during polymerisation. Groups that are formed by addition of a monomer according to the "tail-to-tail" principle, and when there are side-chain substituents, internal double bonds of various types,[15] etc. can become labile. The resulting primary macroradicals decompose in chain propagation reactions, undergoing β-cleavage (Rice's rule) to form lower olefins, and also decompose in chain transfer and chain termination reactions leading to the formation of heavier hydrocarbons. Typically, during the thermal decomposition of polymer products the role of chain transfer to the polymer is very important,[10] which is a determining factor in the formation of a series of reaction products of variable composition.

Of the reactions that occur during the thermal degradation of polyolefins, the three most typical reactions that govern the yield and distribution of products can be distinguished: 1) radical decomposition (degradation) of macromolecules; 2) reactions that occur with hydrogen transfer; 3) radical substitution reactions (chain transfer to the polymer). The role of these reactions can vary according to the chemical structure of the polyolefins. Thus, for

Table 1. Yield and composition of gaseous products from thermal and catalytic degradation of polyolefins.

Catalyst	Polyolefin	T, K	Yield of gas, wt.%	Composition of gaseous products*, wt.%							
				C_1-C_3	iso-C_4H_{10}	n-C_4H_{10}	α-C_4H_8	iso-C_4H_8	β-C_4H_8	$C_4H_8+C_4H_{10}$	C_5 and higher
No catalyst	PE	673	40.8	52.9	18.7	7.5	–	1.1	19.8	47.1	–
	PIB	653	75.9	1.9	2.1	–	0.1	16.0	0.9	19.1	79.0
	BR	653	50.4	2.7	w	0.5	3.0	2.9	30.3	36.7	60.6
$AlCl_3$	PE	643	47.6	5.7	22.4	–	0.1	15.7	2.7	40.9	53.4
	PIB	643	62.7	1.5	2.1	–	w	19.1	1.0	22.2	76.3
	BR	643	85.0	14.3	59.0	–	0.1	0.6	0.2	59.9	25.8
$NaAlCl_4$	PE	643	84.8	24.8	54.9	0.8	–	19.7	0.3	75.5	–
	PIB	583	47.9	1.1	7.8	w	0.3	88.8	2.0	98.9	–
	BR	573	38.8	16.4	23.6	0.4	0.5	39.0	12.4	62.6	7.7
$MgCl_2 \cdot AlCl_3$	PE	643	88.2	15.0	42.5	6.7	–	21.8	14.0	85.0	–
	PIB	573	93.8	1.4	24.9	0.1	0.1	73.4	0.1	98.6	–
	BR	573	75.4	1.7	2.1	0.2	0.5	93.8	0.6	95.9	1.1

*Traces of hydrogen were identified in the gaseous products.

example, for polyethylene (PE) all three types of reaction are equally probable, while for polyisobutylene (PIB), which has two methyl substituents on every second carbon atom, only reactions 1) and 3) are typical. This has the result that in the degradation of PE formation of the monomer in appreciable quantities is improbable and, moreover, is thermodynamically unfavourable, while in the degradation of PIB up to 20% monomer is formed (Table 1). When internal double bonds occur in the polyolefin, such as in butyl rubber (BR), the role of hydrogen transfer reactions once again increases (Table 1). As a consequence the yield of monomer is very small.

Chain transfer reactions with removal of a hydrogen atom from the main chain and a substituent (for PE, branching, which in the vast majority of cases consists of ethyl or *n*-butyl groups, should be regarded as a substituent) during the thermal degradation of PE and BR are of equal probability. For PIB, on the other hand, chain transfer reactions with removal of a hydrogen atom from the internal hydrocarbon atoms are typical, with the result that hydrocarbons of an isomeric structure are mainly formed (Table 1).

On the whole it can be seen that the thermal decomposition of PE, PIB, and BR, as for the majority of other polyolefins, leads equally to the formation of such a wide range of reaction products that the concept of selectivity in relation to the thermal degradation of polyolefins loses its meaning. Nevertheless, from a practical viewpoint, the derivation of hydrocarbon fractions by thermal degradation may be of interest not only as a method of processing various polymer waste products in order to destroy them but also as one of the methods of obtaining liquid hydrocarbons for use as solvents, additives, or fuel.[16] Catalytic methods of treating polyolefins to obtain gaseous and liquid fuels are also possible.[17,18]

III. Catalytic degradation of polyolefins

The electrophilic catalytic degradation of polyolefins that occurs by a cationic mechanism[8] is very interesting from the theoretical viewpoint as an example of the decomposition of polymer products by terminal group or random mechanisms.

Compared to a purely thermal process, the electrophilic catalytic degradation of polyolefins in the presence of $AlCl_3$ takes place with a higher yield of low-molecular weight products (Table 1) at considerably lower temperatures, but it is insufficiently selective with respect to the yield of monomer. In the presence of strongly acidic systems there is an intensification not only of the decomposition processes of the macromolecules but also of secondary processes, in particular isomerisation and cross-linking. The formation of primary polymer carbocations on treatment with aluminium chloride (probably in the form of $H^+(AlCl_3 \cdot OH^-)$),[19] occurs in the degradation of PE with the random removal of a hydride ion:

$$R{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}R' + H^+[AlCl_3 \cdot OH]^- \rightarrow$$

$$\rightarrow R{-}CH_2{-}\overset{+}{C}(CH_3){-}CH_2{-}R'[AlCl_3 \cdot OH]^- + H_2,$$

$$R{-}CH_2{-}CH(CH_3){-}CH_2{-}R' + H^+[AlCl_3 \cdot OH]^- \xrightarrow[-H_2]{}$$

$$\rightarrow R{-}CH_2{-}CH(\overset{+}{C}H_2){-}CH_2{-}R'[AlCl_3 \cdot OH]^- \rightarrow$$

$$\rightarrow R{-}\overset{+}{C}H_2 \cdot [AlCl_3 \cdot OH]^- + CH_2{=}CH{-}CH_2{-}R'.$$

Initiation of degradation of polyolefins is also probable on the defect groups of macromolecules, for example, on vinylidene double bonds:

$$RR'C{=}CH_2 + H^+[AlCl_3 \cdot OH]^- \rightarrow RR'CH{-}\overset{+}{C}H_2[AlCl_3 \cdot OH]^-.$$

The primary ion isomerises to give a more stable tertiary carbocation:

$$RR'CH-\overset{+}{C}H_2[AlCl_3\cdot OH]^- \rightleftharpoons R-\overset{R'}{\underset{CH_3}{\overset{|}{\underset{|}{C^+}}}}[AlCl_3\cdot OH]^-.$$

In the decomposition of polymer carbocations a wide range of products is formed: gaseous products from CH_4 (detachment of methyl branches) to C_4H_8 (skeletal isomerisation of a macroion followed by β-cleavage) and liquid and waxy products from C_5 hydrocarbons and above (Table 1). A typical feature is that in the degradation of PE the yield of just the monomer (ethylene) is low.

Terminal double bonds play a considerable role in chain initiation reactions. However, the proportion of reactions that occur on the terminal groups is small in the case of PE degradation because of the high content of internal defect groups. An increase in the content of the terminal double bonds in PIB and BR macromolecules increases the probability of initiation of the process by a terminal group mechanism, although the expected increse in selectivity of the process also does not occur (Table 1). It is evident that successive chain-transfer reactions to the polymer by the random mechanism play a fairly large part in degradation processes of polyolefins in the presence of strongly acidic catalysts.

Side reactions are usually suppressed in electrophilic processes when the acidity of the catalyst is reduced. This phenomenon together with a high activity and selectivity has been established in the catalytic degradation of polyolefins in the presence of complexes of the type $MCl_n\cdot AlCl_3$ (M = Li, Na, K, Mg, Ca, Ba, n = 1–2).[20–22] Fused $MCl\cdot AlCl_3$ salts, which are familiar as ionic media,[23,24] exhibit properties of weakly acidic catalysts. The decrease in the ionic strength of the outer-sphere cation of an $MCl\cdot AlCl_3$ complex on going from Li^+ to Na^+ is consistent with the order of change in rate of conversion of the polymer (Table 1). A decrease in acidity of the catalysts relative to $AlCl_3$ has a favourable effect on the ratio of chain propagation to chain transfer by considerably reducing the contribution of chain transfer reactions. This in turn results in a considerbale increase in selectivity of the process with respect to the yield of C_4 hydrocarbons. The gaseous reaction products contain up to 90–95% hydrocarbons (Table 1).

Amongst individual salts—metal chlorides of Groups I and II of the Mendeleev Periodic Table—$MgCl_2$ has high activity and selectivity with respect to the yield of monomer during catalytic degradation of PIB and BR (Table 2). The water of crystallisation plays an important role in the formation of catalytically active magnesium chlorides.[25] The aqua complexes $MgCl_2\cdot H_2O$ and $MgCl_2\cdot 2H_2O$ proved to be the most effective. Quantum-chemical calculations confirmed the possibility of the water of crystallisation having an activating effect (Table 3). The catalytic activity of the aqua complexes $MCl\cdot AlCl_3\cdot H_2O$ and $MgCl_2\cdot H_2O$ is caused by the fairly large positive charges on the hydrogen atoms. The stability of the $MAlCl_4\cdot H_2O$ aqua complex, determined from the energy of complexation with water, is somewhat less than for aqua complexes of magnesium chlorides. Therefore, despite the higher charges on the hydrogen atoms, the activity of $MAlCl_4\cdot H_2O$ during the degradation of polyolefins is somewhat lower than that of $MgCl_2\cdot H_2O$ (Table 3). It should also be noted that the quantum-chemical calculations are in agreement with the experimentally determined series of activity of $MAlCl_4$ catlaysts: $LiAlCl_4$ > $NaAlCl_4$ > $KAlCl_4$, namely, the acidity $P_{k\alpha}$ and charges q_{H^+} on the hydrogen atoms of the aqua complexes diminish with an increase in ionic radius of the cation.

Thus, weakly acidic complex catalysts of the type $MCl_n\cdot AlCl_3\cdot H_2O$ and $MgCl_2\cdot H_2O$ are fairly active and selective during the electrophilic catalytic degradation of polyolefins.

Table 2. Catalytic degradation of polyolefins in the presence of some aqua complexes of metal chlorides.

Catalyst	T, K	Yield of gas, wt.%			Yield of monomer, wt.%		
		PIB	BR	PE	PIB	BR	PE*
$MgCl_2\cdot nH_2O$	583	12.4	27.4	8.7	96.2	96.0	76.5
n=1–2	603	81.9	92.0	24.5	99.5	96.4	77.1
	623	100.0	100.0	33.9	99.5	97.0	78.3
$MgCl_2\cdot 4H_2O$	583	11.4	19.7	–	90.1	93.1	–
	603	36.2	31.6	21.4	92.4	92.0	73.0
	623	62.0	35.9	–	98.6	97.0	–
$BaCl_2\cdot 2H_2O$	583	3.8	4.0	2.2	23.5	19.0	53.2

*Total yield of C_4 hydrocarbons given.

Table 3. Quantum-chemical calculations of polyolefin degradation catalysts (LCAO MO method with CNDO/2 approximation).

Catalyst	$P_{k\alpha}$	q_{H^+}	Energy of complexation, kJ mol^{-1}	Yield of gas, wt.% (603 K)		
				PIB	BR	PE
$LiCl\cdot H_2O$	10.5	0.182 0.182	131	9.1	21.2	–
MgOHCl	23.0	0.070	–	8.5	23.4	–
$MgCl_2\cdot H_2O$	12.7 15.4	0.166 0.185	265	100.0	100.0	49.5
$MgCl_2\cdot 2H_2O$	15.4 10.0	0.146 0.185	260 260	100.0 100.0	100.0 100.0	45.0 45.0
$MgCl_2\cdot 4H_2O$	13.7 12.5	0.158 0.165	216	59.5	45.2	21.4
$LiAlCl_4$	5.6	0.253 0.217	88	61.1	96.5	57.4
$NaAlCl_4$	4.5	0.226 0.229	249	55.0	46.7	55.9
$KAlCl_4$	–	–	–	6.3	18.0	12.3

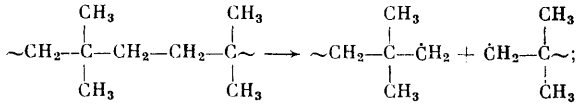
IV. Mechanism of catalytic degradation

The mechanisms of the thermal and thermocatalytic degradation of polyolefins differ. The purely thermal decomposition of polymer products takes place by a radical mechanism,[5] while for the degradation of polyolefins in the presence of electrophilic catalysts an ionic mechanism occurs.[26,27]

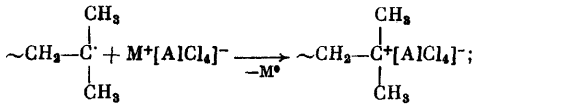
In early studies on the catalytic degradation of polyolefins in the presence of $MAlCl_4$ complexes, a cationic process mechanism was interpreted on the basis of a possible single-electron oxidation of primary radicals formed by the action of heat on the polymer:[1,2]

a) thermal decomposition by the random mechanism, preferentially on the defect groups ("head-to-head" addition of

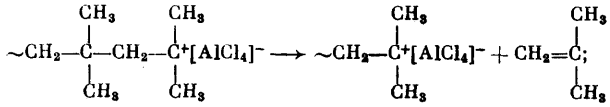
monomer) contained in the macromolecules, for example



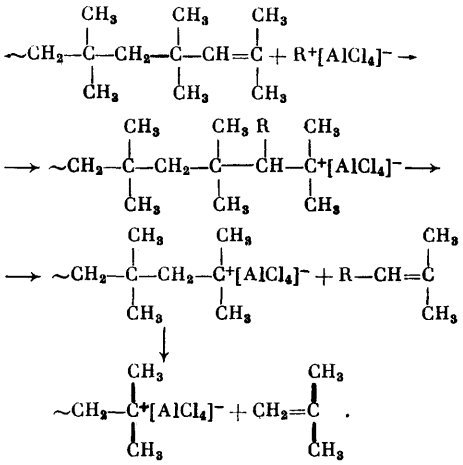
b) a redox reaction with the formation of a polymer carbocation



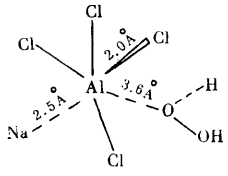
c) depolymerisation of macroions to form the monomer



d) chain transfer to the polymer followed by depolymerisation of the macroions by the terminal group mechanism

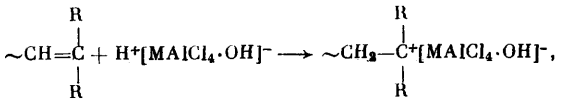


When $MAlCl_4 \cdot H_2O$ aqua complexes are used, initiation of degradation of polyolefins takes place on $H^+(MAlCl_4 \cdot OH)^-$, which has the structure



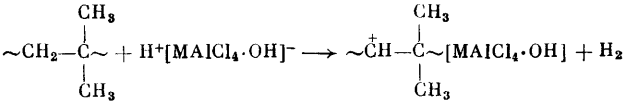
An aqua complex can initiate decomposition both randomly and on the terminal groups. Interaction of the catalyst with the weak bonds of the polymer chain by the random mechanism is governed by the structure of the polyolefin. In PE, degradation of macromolecules is initiated mainly on vinylidene and *trans*-vinylene internal double bonds, while for BR it occurs on the sites where the isobutyl residues are connected to an isoprenyl unit. Initiation by the terminal group mechanism occurs on the terminal double bonds.

a) Terminal group mechanism

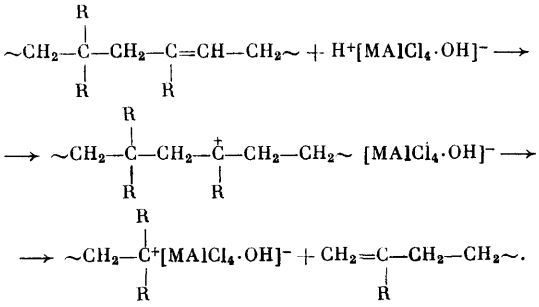


where R = CH_3 PIB, BR) or H (PE).

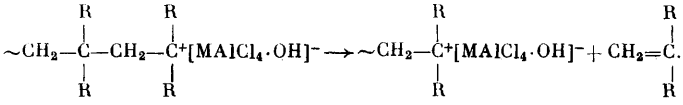
b) Random mechanism



or (what is more probable for BR and PE)

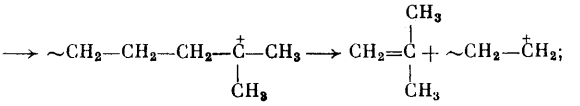


Chain propagation reactions of macrocations can differ considerably according to the chemical nature of the polymer used. For example, for PIB and BR the resulting carbocations mainly undergo β-cleavage with elimination of an isobutylene monomer (Table 1):

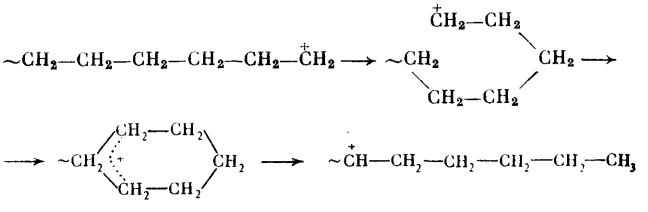


A linear carbocation $R-\overset{+}{C}H_2$ formed during the degradation of PE undergoes conversions by two main routes:

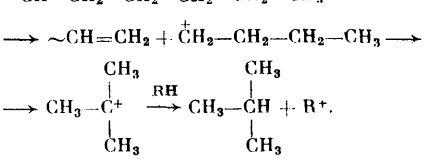
1) skeletal isomerisation with the formation of a tertiary carbocation that subsequently undergoes β-cleavage to give isobutylene



2) isomerisation of a macroion with transfer of excess positive charge to the sixth carbon atom via an intermediate cyclisation reaction of "flexible" methylene sequences

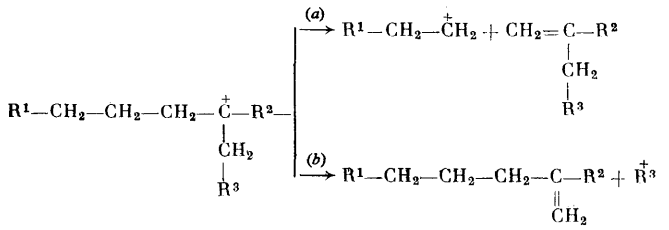


β-Cleavage of the resulting carbocation followed by isomerisation and removal of a hydrogen atom from a neutral molecule gives isobutane:



This reaction does not correspond to the classical route for depolymerisation and can be defined as an associated reaction of degradation and chain transfer.

In the case of the thermocatalytic degradation of PE, which always contains branching, the formation of carbocations can occur on a tertiary carbon atom. The subsequent decomposition of the macrocation occurs by two routes: decomposition of the main chain (*a*) and elimination of the side chain (*b*).



In both cases a new carbocation which undergoes further decomposition and an "inert" polymer with a vinylidene double bond are formed.

Thus, initiation of thermocatalytic destruction of polyolefins with different chemical structures in the presence of $MAlCl_4 \cdot H_2O$ and $MCl_n \cdot H_2O$ aqua complexes has the general characteristics: formation of an active site on the terminal double bonds of the macromolecule (terminal group mechanism) and random scission of the macrochains on defect groups and weak bonds. The mechanism of the chain propagation reaction is determined by the structure of the polyolefin; the presence of bulky substituents results either in depolymerisation reactions mainly occurring (PIB, BR) or depolymerisation (in parallel) with initial isomerisation of the carbocation. The absence of such groups in a linear polymer (PE) results in degradation with chain transfer to the polymer.

V. Kinetic features of the catalytic degradation of polyolefins

The chemical nature of the catalyst determines the sequence of degradation reactions of polyolefins and hence also the characteristics of the kinetic scheme of the process. When weakly acidic ionic catalysts of the type $MAlCl_4$, $MAlCl_4 \cdot H_2O$, and $MCl_n \cdot H_2O$ are used, the kinetics of the process are given by the following scheme:

$$\left.\begin{array}{l} \mathrm{P} \xrightarrow{W_r} 2\mathrm{R}^{\cdot} \\ \mathrm{P}+\mathrm{cat} \xrightarrow{k} 2\mathrm{R}^{\cdot} \\ \mathrm{R}^{\cdot}+\mathrm{cat} \xrightarrow{k_{in}} \mathrm{R}^{+} \end{array}\right\} \text{(random mechanism)}$$

$$\mathrm{P}+\mathrm{cat} \xrightarrow{k_{in}} \mathrm{R}^{+} \text{ (terminal group mechanism)}$$

$$\mathrm{R}_n^{+} \xrightarrow{k'_{dep}} \mathrm{R}^{+}_{n-z} + z\mathrm{M}; \quad \mathrm{R}_n \xrightarrow{k_{dep}} \mathrm{R}^{\cdot}_{n-z} + z\mathrm{M}$$

$$\mathrm{R}^{\cdot} \xrightarrow{k_{deg}} \mathrm{R}_n^{\cdot} + \mathrm{R}_m; \quad \mathrm{R}^{+} \xrightarrow{k'_{deg}} \mathrm{R}_n^{+} + \mathrm{R}_m$$

$$\mathrm{R}^{\cdot}+\mathrm{P} \xrightarrow{k_{ct}} \mathrm{RH}+\mathrm{P}^{\cdot}; \quad \mathrm{R}^{+}+\mathrm{P} \xrightarrow{k'_{ct}} \mathrm{RH}+\mathrm{P}^{+} + \Pi^{+}$$

$$\mathrm{R}^{+} \xrightarrow{k_t} \mathrm{P}.$$

In this case k'_{in}, k_{in}, k'_{dep}, k_{dep}, k'_{deg}, k_{deg}, k'_{ct}, k_{ct} and k_t are the rate constants of initiation, depolymerisation, and degradation by ionic and radical sites, chain transfer of ionic and radical sites, and chain termination respectively.

For degradation of the polymer by the random mechanism, the change in concentration of macrocations $[R^+]$ is given by the equation

$$d[R^+]/dt = k_{in}[cat][R^{\cdot}] - k_t[R^+]. \quad (1)$$

For a steady state

$$[R^+] = k_{in}[cat][R^{\cdot}]/k_t,$$

where

$$[R^{\cdot}] = -\frac{k_{in}[cat]}{2k_1} + \sqrt{\left(\frac{k_{in}[cat]}{2k_1}\right)^2 + \frac{W_r}{k_1}} =$$

$$= \frac{k_{in}[cat]}{2k_1}\left[\sqrt{\frac{4k_1(W_t + k_1[cat])}{(k_{in}[cat])^2}} + 1 - 1\right]. \quad (2)$$

Here $W_r = W_t + k_1[cat]$ is the rate of formation of radicals as a result of thermal scission of the polymer chain and by catalytic action.

Let us consider two limiting cases:[1]

a) There is only a small quantity of catalyst, in other words, only a small proportion of the radicals that are formed is converted to polymer carbocations. This corresponds to the condition

$$4k_1(W_t + k_1[cat])/(k_{in}[cat])^2 \gg 1, \quad (3)$$

then

$$[R^{\cdot}] = \sqrt{(W_t + k_1[cat])/k_1},$$

and the expression for the rate of random decomposition of polyolefins takes the form

$$V_1 = (k'_{dep} + K'_{deg})\frac{k_{in}[cat]}{k_t}\sqrt{\frac{W_t + k_1[cat]}{k_1}} +$$

$$+ (k_{dep} + k_{deg})\sqrt{\frac{W_t + K_1[cat]}{k_1}}. \quad (4)$$

In this case the rate-limiting stage of the process is the interaction of catalyst with a radical;

b) there is a considerable quantity of catalyst in the system, in other words, all of the radicals formed are converted to carbocations

$$4k_1(W_t + k_1[cat])/(k_{in}[cat])^2 \ll 1.$$

In this case the concentration of macroradicals in the system is defined by the relationship

$$[R^{\cdot}] = (W_t + k_1[cat])/(k_{in}[cat]), \quad (5)$$

and the rate of process is in the form of

$$V_1 = (k'_{dep} + k'_{deg})(W_t + 2k_1[cat])/k_t. \quad (6)$$

In the initiation of depolymerisation of PIB by the terminal group mechanism, the concentration of active sites $[R^+]$ is defined by the relationship

$$d[R^+]/dt = k_{in}[cat]C_n - k_t[R^+],$$

where $C_n = A_0/\overline{P}_n$ is the concentration of double bonds in the polymer (A_0 is the concentration of polymer, $\overline{P}_n$ is the degree of polymerisation of the polymer).

The equation for the rate of depolymerisation of PIB by the terminal group mechanism has the form

$$V_2 = k_r[R^+] = \frac{(k'_{dep} + k'_{deg})k_{in}[cat]C_n}{k_t} = \frac{(k'_{dep} + k'_{deg})k'_{in}A_0[cat]}{k_t\overline{P}_n}. \quad (7)$$

Then the rate of depolymerisation in general form is given by the equation

$$V = V_1 + V_2 = (k'_{dep} + k'_{deg}) \frac{k_{in}[cat]}{k_t} \sqrt{\frac{W_t + k_l[cat]}{k_l}} +$$

$$+ (k_{dep} + k_{deg}) \sqrt{\frac{W_t + k_l[cat]}{k_l}} + \frac{(k'_{dep} + k'_{deg}) k'_{in} A_0[cat]}{k_t \overline{P}_n} \quad (8)$$

The equation obtained takes into account the concurrent reactions of degradation and depolymerisation on active ionic and radical sites but cannot elucidate the reasons for the difference in selectivity of the process with respect to the yield of monomer in the presence of catalysts. The selectivity of the catalyst can be determined quantitatively from the values of z (z is the length of the kinetic chain, representing the number of monomer units eliminated on average per macromolecular cleavage):

$$z = \frac{k'_{dep}[R^+] + k_{deg}[R^\cdot] + k'_{deg}[R^+] + k_{dep}[R^\cdot]}{W_t + k'[cat] + k_{ct}[R^\cdot] + k'_{ct}[R^+]}. \quad (9)$$

Table 4. Overall parameters of the catalytic degradation of polyolefins ($c_{cat} = 1 \times 10^{-3}$ mol g^{-1}; $\tau = 3.6 \times 10^3$ s).

Polyolefin	Catalyst	T, K	$z \pm 10\%$	$(k_{in} \times 10^7) \pm 5\%$, s^{-1}	E_a, kJ mol^{-1}
Polyisobutylene	$LiAlCl_4$	583	10	0.6	100
		603	8	1.7	
		623	6	4.3	
	$NaAlCl_4$	583	10	0.3	105
		603	7	0.8	
		623	6	2.4	
	$KAlCl_4$	583	4	0.4	140
		603	3	1.1	
		623	3	3.7	
Butyl rubber (copolymer of isobutylene with isoprene)	$NaAlCl_4$	573	40	0.7	54
	$MgCl_2 \cdot AlCl_3$	573	55	1.2	55
	$BaCl_2 \cdot AlCl_3$	573	62	2.0	48
Polyethylene	$LiAlCl_4$	573	8	0.4	118
		603	19	1.2	
		623	26	3.9	
		643	31	5.8	
	$NaAlCl_4$	573	10	0.4	124
		603	12	1.3	
		623	17	3.6	
		643	20	5.0	
	$KAlCl_4$	573	7	0.1	151
		603	9	0.5	
		623	12	1.2	
		643	19	2.7	

With an increase in activity of the catalyst in the series $LiAlCl_4$ > $NaAlCl_4$ > $KAlCl_4$, the value of z and the overall rate of degradation of polymer products increase (Table 4), while with an increase in temperature the length of the kinetic depolymerisation chain of PIB and BR on each of the selected catalysts decreases whereas the rate constant of depolymerisation increases. This is due to an increase in the contribution of the thermal component, which increases the probability of random degradation of the chain as well as chain transfer and termination. In the degradation of PE the yield of monomer is low and the concept of the length of the polymer chain should be applied to the elimination of C_4 hydrocarbons rather than monomer units. However, in contrast to PIB and BR, for PE the adopted value of z increases with an increase in temperature (Table 4), which is evidently due to the increased role of reactions involving decomposition with subsequent chain transfer which assist in increasing the yield of one of the main products of catalytic degradation of PE—isobutane. The overall energy of activation values of the catalytic degradation of polyolefins in all of the cases given are lower than for the thermal decomposition of polymers. This is attributed to a reduction in both the energy of initiation and the energy of decomposition of the polymer chain because of the cationic nature of the active site.

The kinetic scheme presented here represents the overall process of degradation of polyolefins that occurs in the presence of electrophilic catalysts. Therefore it can also be used to represent the overall kinetics of degradation of polyolefins in the presence of active and proton-donating forms of catalysts. However, at the same time it is necessary to take account of the fact that the rate constants of the interaction between catalyst and radical and the radical decomposition of polymer decrease considerably, and the rate of depolymerisation will be determined primarily by ionic processes involving initiation and chain continuation. In this case the kinetic scheme of catalytic thermal degradation of polyolefins can be represented as follows:

a) initiation (valid for initiation by both random and terminal group mechanisms)

$$P + cat \xrightarrow{k_{in}} R^+;$$

b) chain propagation

$$R_i^+ \xrightarrow{k_{dep}} R_{i-z}^+ + zM;$$

c) intermolecular chain transfer

$$R_i^+ + P_m \xrightarrow{k_{ct}} R_i + P_m^+;$$

d) destruction of active sites (chain termination)

$$R_i^+ \xrightarrow{k_t} P.$$

The rate of change in concentration of the polymer carbocations formed by the random mechanism can be given by the equation:

$$d[R^+]/dt = k'_{in}[cat][P] - k_t[R^+].$$

Assuming a steady-state concentration of active sites, we obtain

$$[R^+] = k'_{in}[P][cat]/k_t.$$

In the formation of active sites by the terminal group mechanism the expression for the rate of change in concentration of the active sites is given by the equation:

$$d[R^+]/dt = k''_{in}[cat]C_t - k_t[R^+],$$

where C_t is the concentration of terminal double bonds. Hence under steady-state conditions

$$[R^+] = k'_{in}[cat]C_t/k_t.$$

The equations for the rate of depolymerisation have the form

$$V_1 = k_{dep}[R^+] = k_{dep}k'_{in}[P][cat]/k_t \text{ (random mechanism)},$$

$$V_2 = k_{dep}[R^+] = k_{dep}k''_{in}[cat]C_t/k_t \text{ (terminal group mechanism)}.$$

Assuming that the random and terminal group processes are independent, we obtain an expression for the overall rate of degradation

$$V = k_{dep}[cat](k'_{in}P + k''_{in}C_t)/k_t.$$

Thus, the rate of the overall process of degradation of polyolefins is determined mainly by the initiation reactions, and in particular by the values of the apparent rate constants of initiation by the random and terminal group mechanisms. This makes it necessary to carry out a quantitative determination of the kinetic parameters of the initiation process.

VI. Determination of apparent kinetic parameters

Electrophilic catalytic degradation of polyolefins can be represented by a general equation that takes into account the contribution of both the random and terminal group reactions.

$$-dP/dt = z_t k_{ti} C_t + k_{ri} z_r P. \quad (10)$$

Here P is the decrease in polymer concentration (as a fraction of the original); k_{ri} and k_{ti} are the rate constants of initiation of degradation of polymer by the random and terminal group mechanisms respectively; z_r and z_t are the lengths of the kinetic chain during degradation by the random and terminal group mechanisms: C_t is the concentration of terminal double bonds. Assuming that the terminal groups which can initiate depolymerisation are consumed exponentially during degradation according to $C_t = C_{t0}\exp(-k_{ti}t)$ (C_{t0} is the initial content of terminal double bonds), which is especially typical for PIB, we obtain

$$P = \exp(-k_{ri}z_r t) + \frac{k_{ti}z_t C_{t0}}{k_{ti} - k_{ri}z_r}[\exp(-k_{ti}t) - \exp(-k_{ri}z_r t)]. \quad (11)$$

It is possible to determine the numerical values of k_{ti}, z_t, k_{ri}, and z_r at the initial stages of the process when $P \ll 1$, $t \ll 1/k_{ti}$ and $t \ll 1/k_{ri}z_r$ (experimentally this is possible when the process is carried out under low-temeprature conditions (200–300 °C) when the rates of "burning away" the chains are relatively small). Then

$$P = 1 - k_{ri}z_r t - k_{ti}z_t C_{t0} t. \quad (12)$$

The change in molecular weight of PIB can be determined from the total number of chain scissions. The number of macromolecules is given by $n = n_0 + k_{ri}t$ and their molecular weight is determined from the expression

$$\overline{M}_n = P/n \simeq \frac{1 - k_{ri}z_r t - k_{ti}z_t C_{t0} t}{n_0(1 + k_{ri}t/n_0)} \simeq \overline{M}_n^0(1 - k_{ri}z_r t - k_{ti}z_t C_{t0} t - k_{ri}t/n_0) \quad (13)$$

where $\overline{M}_n^0 = 1/n_0 = 1/C_{t0}$ (the presence of a single terminal double bond in each initial macromolecule of PIB is assumed). The relative degree of polymerisation during degradation will change in accordance with the equation

$$\overline{P}_n/\overline{P}_n^0 = 1 - k_{ri}z_r t - k_{ri}\overline{P}_n^0 t - k_{ti}z_t t/\overline{P}_n^0. \quad (14)$$

Hence it is possible to determine the change in relative degree of polymerisation in relation to the change in degree of conversion $d\alpha = \Delta P$. From Eqn. (12) we obtain

$$\Delta P = (k_{ri}z_r + k_{ti}z_t C_{t0})t.$$

As a result we obtain

$$\frac{d(\overline{P}_n/\overline{P}_n^0)}{d\alpha} = -\frac{k_{ri}z_r + k_{ri}\overline{P}_n^0 + k_{ti}z_t/\overline{P}_n^0}{k_{ri}z_r + k_{ti}z_t/\overline{P}_n^0}. \quad (15)$$

Provided that the length of the kinetic chain z_r is many times less than the degree of polymerisation $\overline{P}_n^0$, namely, $z_r \ll \overline{P}_n^0$, Eqn. (15) can be simplified.

$$\frac{d(\overline{P}_n/\overline{P}_n^0)}{d\alpha} = -\frac{k_{ri}\overline{P}_n^0 + k_{ti}z_t/\overline{P}_n^0}{k_{ri}z_r + k_{ti}z_t/\overline{P}_n^0}. \quad (16)$$

In order to simplify the calculations of the values of the kinetic parameters for each of the competing reactions we shall consider the following limiting cases:

a) when there is a small contribution from reacitons that occur on the terminal groups, i.e., when $k_{ti}z_t/\overline{P}_n^0 \ll k_{ri}z_r \ll k_{ri}\overline{P}_n^0$, the expression for the adjusted relative degree of polymerisation takes the form

$$d(\overline{P}_n/\overline{P}_n^0)/d\alpha = -\overline{P}_n^0/z_r; \quad (17)$$

b) when there is a small contribution from reactions that occur randomly, we obtain $d\alpha/dt \simeq k_{ti}z_t/\overline{P}_n^0$. The value of $\overline{P}_n^0$ in such a process for the most probable initial molecular weight distribution ($\overline{P}_w/\overline{P}_n \simeq 2$) is virtually unchanged, i.e., $d(\overline{P}_n/\overline{P}_n^0)/d\alpha \simeq 0$. This is consistent with the experimental data (Fig. 1, curves *1–3*). There is no point in using Eqn. (16) in this case since complete "burning away" of the macromolecules during depolymerisation of the polymer was not taken into account in its derivation;

c) when the main role in changing the number of chains is played by the random mechanism while the terminal group mechanism plays the main role in depolymerisation, namely when $k_{ri}\overline{P}_n^0 \gg k_{ti}z_t/\overline{P}_n^0 \gg k_{ri}z_r$, we obtain

$$d(\overline{P}_n/\overline{P}_n^0)/d\alpha = -k_{ri}(\overline{P}_n^0)^2/k_{ti}z_t. \quad (18)$$

The three variants a), b), and c) correspond to the three sections on the curve of the dependence of the calculated values of $d(\overline{P}_n/\overline{P}_n^0)/d\alpha$ on $\overline{P}_n^0$ obtained from the gradients of the corresponding experimental curves (Fig. 1). With an increase in the degree of polymerisation each of the three possible variants b), c) and a) occurs successively (Fig. 2).

It is possible to determine z_r and $k_{ri}/k_{ti}z_t$ respectively from the gradients for sections a) and c) of the curve of $d(\overline{P}_n/\overline{P}_n^0)/d\alpha$ against $\overline{P}_n^0$ (Fig. 2). The value of k_{ri} can be calculated by taking into account the fact that the random mechanism provides the main contribution to the decrease in molecular weight of the polymer. This corresponds to the relationship $d(\overline{P}_n/\overline{P}_n^0)/d\alpha = -k_{ri}\overline{P}_n^0$, from which the value of k_{ri} can be determined.

The values of z_r and k_{ri} that are obtained by treatment of the experimental data can be used to determine the numerical values of k_{ti} and z_t from Eqn. (11). The values of the kinetic parameters obtained—the rate constants of initiation and the lengths of the kinetic chain of polymer depolymerisation (given in Table 5 for the degradation of PIB in the presence of $NaAlCl_4$)—suggest that initiation of catalytic degradation by the terminal group mechanism has a predominant role under low-temperature conditions. As the temperature of degradation of the polyolefins is increased, the ratio of k_{ti} to k_{ri} decreases and at 260 °C their values become comparable.

The effect of catalysts on the degradation of polyolefins has been studied using the salts $NaCl{\cdot}AlCl_3$ and $MgCl_2{\cdot}AlCl_3$. The complex salt $MgCl_2{\cdot}AlCl_3$ has a slightly higher acidity than $NaCl{\cdot}AlCl_3$. This gives rise to an increase in activity of the $MgCl_2{\cdot}AlCl_3$ catalyst

during degradation of the polymer. It was shown in the case of the thermocatalytic destruction of PIB that in the presence of $MgCl_2 \cdot AlCl_3$ the total yield of gaseous products and the yield of just isobutylene increase considerably compared to when $NaCl \cdot AlCl_3$ is used. The change in acidity of the catalyst also has an effect on the selectivity of the process with respect to the yield of monomer. The kinetic studies on a determination of the ratio of initiation of degradation of macrochains by the random mechanism to initiation of depolymerisation by the terminal group mechanism suggest that the increase in selectivity of the process is due to an increase in the role of depolymerisation by the terminal group mechanism (Table 5). The ratio of the rate constants of random initiation to that on terminal groups during degradation in the presence of $MgCl_2 \cdot AlCl_3$ is higher than in the presence of $NaCl \cdot AlCl_3$ (Table 5), although the tendency for this ratio to decrease with an increase in temperature also remains.

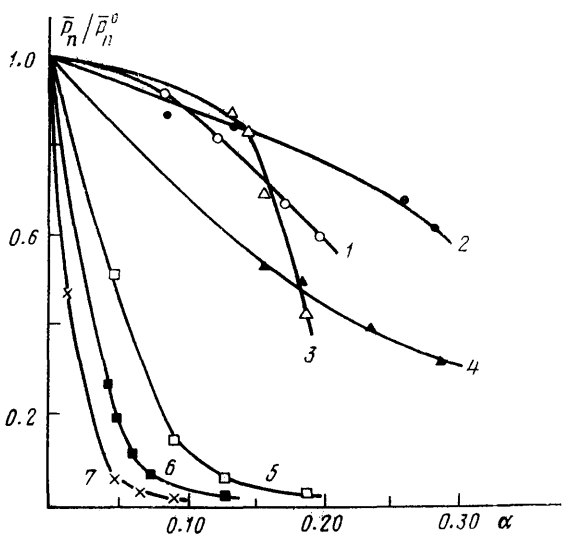


Figure 1. Dependence of relative degree of polymerisation during degradation of polyisobutylene on degree of conversion of samples of polyisobutylene. Initial degree of polymerisation: *1*, 15; *2*, 17; *3*, 20; *4*, 49; *5*, 360; *6*, 1790; *7*, 3570. Catalyst—$NaAlCl_4$, temperature—473 K.

Qualitative proof of the prevailing role of initiaiton by the random mechanism is provided by the nature of the variation in the curves of the dependence of the relative degree of polymerisation on the degree of conversion of the polymer, in particular the marked fall in $\bar{P}_n/\bar{P}_n^0$ at only small degrees of conversion of PE (Fig. 3) and the experimentally determined lack of dependence of the rate of the process on $\bar{P}_n^0$. At the same time similar results obtained using PIB suggest that there is a clearly defined dependence of the degree of conversion of the polymer on the molecular weight of the samples being degraded. Low-molecular weight polyisobutylenes (M = 800–2000) with a high content of terminal double bonds mainly undergo depolymerisation by the terminal group mechanism and the relative degree of polymerisation changes only slowly (Fig. 1, curves *1–3*). An increase in the molecular weight of PIB (Fig. 1, curve *4*) and hence a decrease in the content of C=C double bonds results in a marked increase in the proportion of initiation reactions by the random mechanism and with a very considerable increase in the initial degree of polymerisation ($\overline{M}$ = 1800–16000) (Fig. 1, curves *5–7*), when the content of terminal double bond is small, initiation by the random mechanism plays a decisive role.

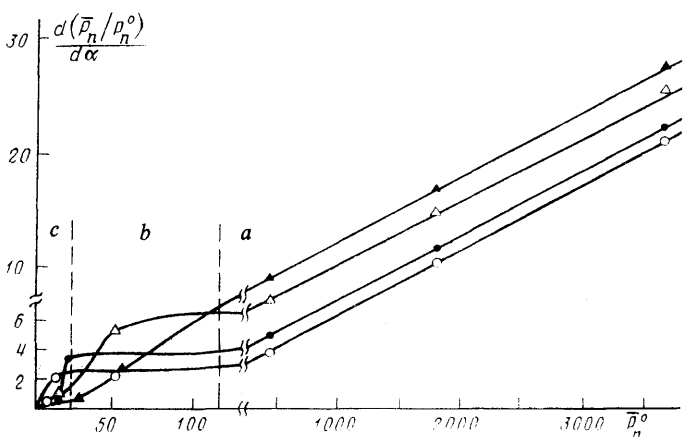


Figure 2. Change in $d(\bar{P}_n/\bar{P}_n^0)/d\alpha$ during degradation of polyisobutylene on an $NaAlCl_4$ catalyst at different temperatures: *1*, 473 K; *2*, 493 K; *3*, 513 K; *4*, 533 K.

VII. Effect of chemical structure of the polymer

For polyolefins that contain internal double bonds as well as terminal double bonds and possibly other defect groups as occurs in PE and BR, the ratio of initiation by the random mechanism to that on terminal groups varies during decomposition of the polymer.

Calculation of the kinetic parameters of catalytic degradation of PE in the presence of $NaCl \cdot AlCl_3$ shows that the values of the rate constants of initiation by the random mechanism are comparable to the rate constants of the overall process of polymer degradation (Table 6). This provides an indication of the predominance of random initiation of PE degradation and the small contribution of reactions that occur by the terminal group mechanism.

Hence, it can be maintained in general that the ratio of the number of internal labile groups (including C=C bonds) to terminal double bonds determines the nature of initiation of catalytic degradation of polyolefins and as a result has a considerable effect on the numerical values of the apparent rate constants of initiation.

VIII. Conclusion

Analysis of the currently available data on the catalytic degradation of polyolefins in the presence of different types of catalysts is able to demonstrate that acidity is one of the deciding factors in the variation in efficiency and selectivity of catalytic

degradation of polymers. However, up to the present time there has been no clear interpretation of the relationship between the acidity of the degradation catalyst and its activity and selectivity values for the majority of catalysts of polyolefin degradation (zeolites, aluminosilicates, superacids).

Table 5. Parameters of the initiation of catalytic degradation of polyisobutylene by random and terminal group mechanisms on different catalysts.

Catalyst	T, K	$k_{ti} \times 10^6$	z_t	$k_{ri} \times 10^6$	z_r	k_{ti}/k_{ri}	E_{ri}, kJ mol^{-1}	E_{ti}, kJ mol^{-1}
$NaAlCl_4$	473	1.6	–	0.2	8.1	8.1	69	47
	493	1.7	–	0.3	6.2	5.7		
	513	1.9	1.3	0.4	4.7	4.8		
	533	2.7	5.7	0.7	3.7	3.8		
$MgCl_2 \cdot AlCl_3$	473	3.35	–	0.3	8.4	10.8	70.7	45.8
	493	3.4	–	0.5	7.1	7.6		
	513	3.8	1.4	0.6	4.9	6.4		
	533	5.4	5.9	1.1	3.7	5.1		

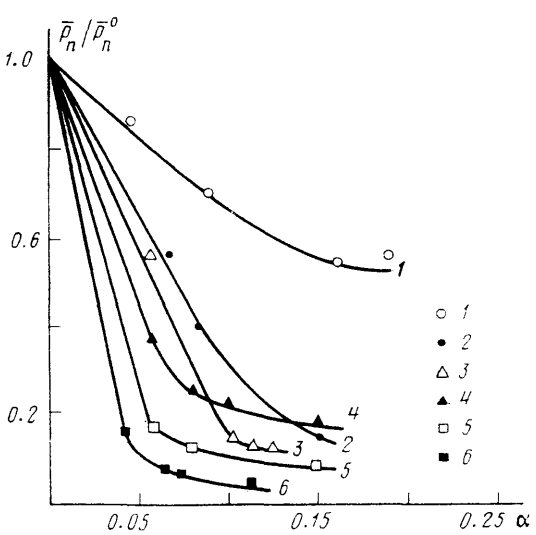


Figure 3. Dependence of change in relative degree of polymerisation on degree of conversion of samples of polyethylene with different initial molecular weights: *1*, 2 × 10^3; *2*, 2 × 10^4; *3*, 6 × 10^4; *4*, 1.45 × 10^5; *5*, 2.5 × 10^5; *6*, 2.7 × 10^5. Catalyst—$NaAlCl_4$; temperature—633 K.

It has been established that by using complex electrophilic catalysts of moderate acidity (considerably lower than the acidity of $AlCl_3$ and $HF{\cdot}SbF_5$) it is possible to increase the selectivity of the process.

The mechanism of the catalytic decomposition of polyolefins on electrophilic catalysts is based on reactions involving the formation of a polymer carbocation and its subsequent selective decomposition to form monomeric and other valuable low-molecular weight products. Initiation of the process is determined by the nature of the catalyst and the chemical structure of the macromolecules and occurs both randomly and on the terminal groups. From kinetic analysis it is possible to determine the ratio of these processes for polyolefins with different macrochain structures.

Table 6. Overall rate constants and rate constants of initiation of catalytic degradation of polyethylene by the random mechanism ($NaAlCl_4$).

T, K	$k_{ri} \times 10^7$, s^{-1}	$k_{rate} \times 10^7$, s^{-1}
573	0.25	0.93
593	0.21	1.56
613	0.95	2.80
633	1.31	6.90
653	1.71	8.70

Note: E_{ri} = 79 kJ mol^{-1}; E_a (overall reaction) = 92 kJ mol^{-1}.

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