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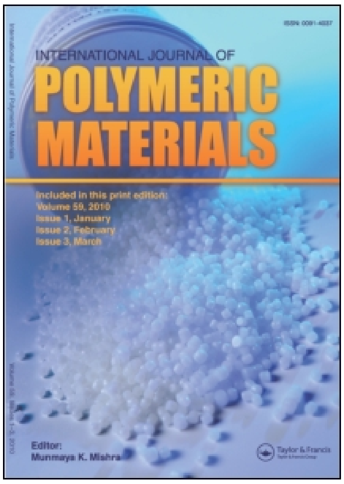

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Peculiarities of Alumoxanes Formation

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Peculiarities of Alumoxanes Formation

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Available experimental data on the processes of alkylalumoxanes formation have been analyzed. During a purposeful study the peculiarities of alkylalumoxanes formation via water hydrolysis of AlR_3 were revealed. On the basis of data obtained a simplified kinetic model and a mathematical description of the process under consideration are proposed and presented here.

Keywords: Alkylalumoxanes; formation; trialkylaluminium hydrolysis

INTRODUCTION

The alkylalumoxanes (AAO) are the linear, cyclic and three-dimensional oligomeric and polymeric aluminiumorganic compounds (AOC), containing $—O—Al(R)—$ fragments. The simplest examples of AAO are the AOC of general formula $R_2Al(OAlR)_nOAlR_2$, where R is an alkyl group and $n \geq 0$.

The fields of application of AAO become wider year by year. At present the AAO are used in the compositions of complex metalloorganic and metallocene catalysts intended for the polymerization and copolymerization of ethylene, propylene, butene-1, hexene-1, cycloolefins, dienes, acetylenes, styrene and other vinyl monomers.

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[*] Corresponding author.

They are used as a carrier for various catalysts and as a raw material for production of alumoxide fibres and films, ceramics and composite materials. They are also used as a bond for thermostable covers, as components of quik-drying varnishes, additives for fuels, alkyde and epoxy resins *etc.* [1–4]. Due to the great theoretical and practical importance of the research in the field of AAO synthesis more and more attention is paid to these compounds.

This work was aimed at the analysis of available experimental data on AAO formation, determination of peculiarities of their formation by water hydrolysis of AlR_3 and creation of a simplified kinetic model and mathematical description of the process under consideration.

PECULIARITIES OF AAO FORMATION

For the first time the AAO were mentioned in report by K. Ziegler [5] devoted to the investigation of interaction of triethylaluminium and carbon dioxide. Formation of AAO as side products was assumed during the investigation of some other reactions.

First the AAO were separated and characterized in an inert atmosphere by incomplete water hydrolysis of AOC in accordance with the following empirical Scheme:

$$2AlR_3 + H_2O \rightarrow R_2Al - O - AlR_2 + 2RH \qquad (1)$$

Numerous methods to prepare AAO are known by now [1–12]. Most widespread and available ones are grounded on the interaction of AOC and water.

AOC possess an extra high reactivity related to water. That is why the controllable interaction of AOC and water is accompanied by the serious difficulties.

In order to make the controllable selective water hydrolysis of AOC possible, it is necessary to realize the reaction at low temperatures, use dilute solution of AOC (about 0.1 mol/l), decrease the AOC reactivity to water by complexing ACO and water with Lewis bases. It is also necessary to ensure the uniform distribution of water in the whole reaction volume and high local molar relation AlR/H_2O during interaction of AOC and water *etc.*

The opportunity to realize all these requirements in synchronism depends on the technique how to feed water into its reaction with the AOC [1–4, 8, 13]. It has been proposed to feed it into the reaction zone in the form of: ice, vapor together with inert gases; water solutions in hydrocarbons or Lewis bases; crystal hydrates (*e.g.*, $CuSO_4{\cdot}5H_2O$; $Na_2SO_4{\cdot}10H_2O$; $ZnSO_4{\cdot}2H_2$) or as a part of some other compounds, containing combined (crystallized, constitution) water (*e.g.*, $LiOH{\cdot}xH_2O$; $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) [1–4, 6–18].

The controllable hydrolysis of AOC by water was revealed by purposeful studies to include the following stages [7–16]:

1. formation of a donor-acceptor complex of AOC with water:

$$R_3Al + H_2O \rightarrow [H_2O \cdot AlR_3] \tag{2}$$

2. intracomplex polarization of the complex formed and its reconstruction to form R_2AlOH and alkane:

$$[H_2O \cdot AlR_3] \rightarrow R_2AlOH + RH \tag{3}$$

3. condensation of R_2AlOH with AlR_3:

$$R_2AlOH + AlR_3 \rightarrow R_2Al - O - AlR_2 + RH \tag{4}$$

Apparently, this reaction also proceeds *via* the stage of formation of corresponding intermediate complex. Both hydrogen atoms in water molecule were shown to be active in reactions of AOC protolysis.

In further numerous studies all initial stages of AOC hydrolysis were testified by various physicochemical techniques.

More complete hydrolysis of AOC leads to the formation of oligomeric and then linear, cyclic and three-dimensional polymeric AAO [1–4, 11, 12, 19, 20]:

$$\begin{aligned} R_2Al{-}O - AlR_2 + HOH + R_3Al \rightarrow R_2Al - O \\ - AlR - O - AlR_2 + 2RH \end{aligned} \tag{5}$$

$$\begin{aligned}R_2Al - O - AlR_2 + H_2O \rightarrow R_2Al - O - AlR - O - AlR \\ -O - AlR_2 + 2RH\end{aligned} \quad (6)$$

etc.

An empirical equation of AlR_3 hydrolysis to form linear AAO is:

$$\begin{aligned}(n+2)AlR_3 + (n+1)H_2O \rightarrow R_2Al(-O - AlR-)_nOAlR_2 \\ + 2(n+1)RH\end{aligned} \quad (7)$$

where $n = 0-30$.

Hydrolysis of AOC is a typical multistage polycondensation process. It is characterized by the all principle regularities of polycondensation: stage and statistic character, great effect of medium nature and additions of Lewis acids and bases, dependence of the process rate and route on the reactivity of initial AOC, dynamic postpolycondensational transformations of AAO (association, auto- and thermo-polycondensation), formation of cyclic and three-dimensional structures [1, 6, 10, 13, 16, 21–23].

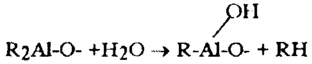
To choose the optimal conditions for synthesis of AAO of a definite structure it is necessary to know how various factors affect on the consumption kinetics of initial reagents, on the kinetics of accumulation and consumption of the intermediate products (*e.g.*, > Al —OH and — OAlR — fragments of AAO), and also on the kinetics of AAO accumulation and their molar mass distribution in the course of the reaction and after its completion. Such information may be obtained by developing and analyzing the kinetic model of the process under investigation.

KINETIC MODEL OF AAO FORMATION

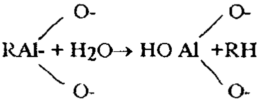
In order to explain the formation of AAO during interaction of AOC and water and analize the kinetics of this process we have taken into consideration the all available data on the mechanism of the process stages and adopted the following simplified kinetic model of the process:

1. Interactions of initial and intermediate AOC with water:

$$R_3Al + H_2O \rightarrow R_2AlOH + RH \qquad (8)$$



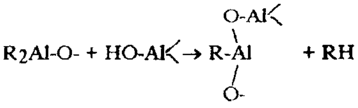
$$R_2Al\text{-}O\text{-} + H_2O \rightarrow R\text{-}\overset{OH}{Al}\text{-}O\text{-} + RH \qquad (9)$$



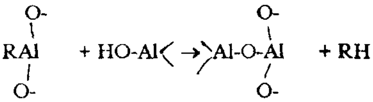
$$R\overset{O-}{\underset{O-}{Al}} + H_2O \rightarrow HO\overset{O-}{\underset{O-}{Al}} + RH \qquad (10)$$

2. Reactions of initial and intermediate AOC with hydroxylaluminium organic compounds:

$$R_3Al + HO\text{-}Al< \rightarrow R_2Al\text{-}O\text{-}Al< + RH \qquad (11)$$



$$R_2Al\text{-}O\text{-} + HO\text{-}Al< \rightarrow R\text{-}\overset{O\text{-}Al<}{\underset{O-}{Al}} + RH \qquad (12)$$



$$R\overset{O-}{\underset{O-}{Al}} + HO\text{-}Al< \rightarrow >Al\text{-}O\text{-}\overset{O-}{\underset{O-}{Al}} + RH \qquad (13)$$

3. Intra- and intermolecular reactions of AAO:

$$\begin{aligned} &R_2Al(OAlR)_m - (OAlR)_nOAlR_2 \\ &+ R_2Al - (OAlR)_x - (OAlR)_yOAlR_2 \\ &\rightarrow [R_2Al(OAlR)_m - (OAlR)_y - OAlR_2 \\ &+ R_2Al(OAlR)_x(OAlR)_n - OAlR_2 \end{aligned} \qquad (14)$$

or

$$\begin{aligned} &\rightarrow R_2Al(OAlR)_m(OAlR)_n - OAlR- \\ &(OAlR)_x - (OAlR)_y - OAlR_2 + AlR_3 \end{aligned} \qquad (15)$$

The main peculiarity of the process under consideration is that the kinetic constants of all types of the reactions, proceeding in system, significantly differ in their value [7, 24]. According to the experimental data obtained $K_8 \gg K_9 > K_{10}$; $K_{11} \gg K_{12} > K_{13}$; $K_8 > K_{11}$ *etc.*

As usual such polycondensation processes are given by Smolukhovsky's equation [25–27]:

$$dx_i/dt = -x_i \cdot \Sigma k(i,j) \cdot x_j + 1/2 \cdot \Sigma k(i-j,i) \cdot x_{i-j} \cdot x_j \qquad (16)$$

where x_i is the concentration of macromolecules containing i links in a chain.

The solution of Eq. (16) is accompanied by certain difficulties. The dependence of $k(i,j)$ related to i and j is very complicated and therefore the analytical methods are not acceptable here. Numerical solution of infinite system of equations finds difficult because the system is incomplete. The main disadvantage of this method is the impossibility to calculate the structural characteristics of crosslinked polymer-gel fraction of AAO.

In any case the structural characteristics of AAO may be calculated by statistical methods, however, the application of this approach is limited [27]. Nevertheless, it is often used to solve practically all polycondensation problems including substitution and cyclization. In that case the statistical approach was shown to be unacceptable on principle [25, 27].

The approach to analyze the kinetics of polycondensation based on an idea of bond blocks eliminates the above mentioned disadvantages [27]. The method to describe the kinetics of polycondensation and the structure of polycondensation polymers using bond blocks was proposed more than 15 years ago [28, 29]. Later on [30–35], various polycondensation systems have been analyzed using this approach and the advantages of its usage have been shown.

It is important that, the kinetic equations may be written for the bond blocks and, in any case the system of equations is complete: concentration of blocks of any length and complication depends only on those blocks whose length and complication are not over than that of required. It makes possible the usage of numerical method of precise calculation of concentration for the blocks of any length, that is to obtain exact concentrations of bonds.

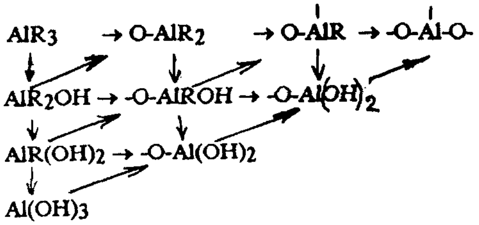
It was revealed [28, 31] that the system of kinetic equations, describing the accumulation of bond blocks, may be divided into some groups of equations so that the concentrations of structures describing by these equations must be calculated directly by their solution.

Concentrations of larger structures are calculated by the method of probability computation. If such a minimal block size is given as one link, the statistic methods are absolutely used. These structures of minimal size may be isolated practically always. On their basis as much as is desired large and complicated structures may be composed.

The idea of bond blocks will simplify to a high degree the solution of kinetic problems because in that case no differential equations for any sized blocks are needed: it is sufficient to solve these problems for an elementary block and use statistical calculations for larger formations.

A criterion of "elementariness" as it was revealed in [28, 29, 31] consists of the absence of substitution effects in the reactivity of functional groups. These effects take place inside of "elementary" block.

The "elementary" bond blocks in polycondensation system under consideration are:



(17)

The pointers represent the interactions between AlR groups and hydroxyl-containing agents: vertical pointers correspond to the interaction of AlR group of corresponding block with water, horizontal ones- with a hydroxyl group, inclined pointers reflect the interaction of hydroxyl group of corresponding block with the AlR bond.

THE RESULTS OF NUMERICAL ANALYSIS OF KINETIC MODEL OF AAO FORMATION AND THEIR DISCUSSION

The method under consideration has also been effectively used for the kinetic analysis of AAO formation in accordance with the Scheme (17) is:

$$
\begin{aligned}
dy(1)/dt &= -3 \cdot y(1) \cdot (k(1) \cdot y(11) \\
&\quad + k(4) \cdot y(12)); \\
dy(2)/dt &= 3 \cdot y(1) \cdot y(11) \cdot k(1) \\
&\quad - y(2) \cdot (x + 2 \cdot y(11) \cdot k(2) + 2 \cdot y(12) \cdot k(5)); \\
dy(3)/dt &= 2 \cdot y(2) \cdot y(11) \cdot k(2) \\
&\quad - y(3) \cdot (2 \cdot x + y(11) \cdot k(3) + y(12) \cdot k(6)); \\
dy(4)/dt &= y(3) \cdot y(11) \cdot k(3) - 3 \cdot y(4) \cdot x; \\
dy(5)/dt &= 3 \cdot y(1) \cdot y(12) \cdot k(4) \\
&\quad + y(2) \cdot x - 2 \cdot y(5) \cdot (y(11) \cdot k(2) + k(5) \cdot y(12)); \\
dy(6)/dt &= 2 \cdot y(5) \cdot y(11) \cdot k(2) \\
&\quad + 2 \cdot y(2) \cdot y(12) \cdot k(5) + 2 \cdot y(3) \cdot x \\
&\quad - y(6) \cdot (x + y(11) \cdot k(3) + y(12) \cdot k(6)); \\
dy(7)/dt &= y(6) \cdot y(11) \cdot k(3) + y(3) \cdot y(12) \cdot k(6) \qquad (18) \\
&\quad + 3 \cdot y(4) \cdot x - 2.y(7) \cdot x; \\
dy(8)/dt &= 2 \cdot y(5) \cdot y(12) \cdot k(5) \\
&\quad + y(6) \cdot x - y(8) \cdot (y(11) \cdot k(3) + k(6) \cdot y(12)); \\
dy(9)/dt &= y(8) \cdot y(11) \cdot k(3) + k(6) \cdot y(12) \cdot y(6) - y(9) \cdot x; \\
dy(10)/dt &= y(8) \cdot y(12) \cdot k(6) + y(9) \cdot x; \\
dy(11)/dt &= V - y(11) \cdot (3 \cdot k(1) \cdot y(1) + 2 \cdot k(2) \cdot (y(2) + y(5)) \\
&\quad + k(3) \cdot (y(3) + y(6) + y(8))); \\
dy(12)/dt &= y(12) \cdot x + y(11) \cdot (3 \cdot k(1) \cdot y(1) \\
&\quad + 2 \cdot k(2) \cdot (y(2) + y(5)) \\
&\quad + k(3) \cdot (y(3) + y(6) + y(8))); \\
x &= 3 \cdot k(4) \cdot y(1) + 2 \cdot k(5) \cdot (y(2) + y(5)) \\
&\quad + k(6) \cdot (y(3) + y(6) + y(8));
\end{aligned}
$$

where $y(i)$ are the concentrations of bond blocks, moreover, the numerals correspond to the blocks according to the following Scheme:

$$
\begin{array}{llll}
1 & 5 & 8 & 10 \\
2 & 6 & 9 & \\
3 & 7 & & \\
4 & & &
\end{array}
$$

Numeral 11 corresponds to water, numeral 12- to hydroxyl group. V is the rate of water feeding into the reaction system. Kinetic constants

$k(1)$, $k(2)$, $k(3)$ are rerred to the hydrolysis of AOC with three, two and one alkyl groups (reactions 8–10). Kinetic constants $k(4)$, $k(5)$, $k(6)$ are referred to the interactions of AlR and hydroxyl group (reactions 11–13). X characterizes the interaction of hydroxyl group given with all possible Al—C bonds.

All constants being equal the solution of system (18) is:

$$\begin{aligned} y(1) &= y(1)_0 \cdot (1-p)^3 \\ y(5) &= y(1)_0 \cdot 3p(1-p)^2 \\ y(8) &= y(1)_0 \cdot 3p^2(1-p) \\ y(10) &= y(1)_0 \cdot p^3 \end{aligned} \tag{19}$$

where $y(1)_0 = [AlR_3]_0$, $p = 2[H_2O]_0/3[AlR_3]_0$, and the reagents ratio q is connected with p by the following equation: $q = [H_2O]_0/[Al]_0 = 3p/2$.

Concentrations of the other groups are zero if $p < 1$.

The structure of polymer formed may be calculated by probability manner, for example, using the routine of the branching processes theory [36]. If $p < 1$ the relative concentrations of bond blocks will correspond to the probabilities of the theory:

$$p_0 = y(1)/y(1)_0,\ p_1 = y(5)/y(1)_0,\ p_2 = y(8)/y(1)_0,\ p_3 = y(10)/y(1)_0 \tag{20}$$

and the corresponding producing functions will be in the form:

$$\begin{aligned} F_0(s) &= \Sigma p_i s^i \\ F_1(s) &= \frac{1}{F_0(1)} \cdot \frac{\partial F_0(s)}{\partial s} \end{aligned} \tag{21}$$

For the medium-mass degree of polymerization:

$$P_w = 1 + dF_0(u)/ds \text{ for } s = 1 \text{ and } u = sF_1(u), \tag{22}$$

and a number of chains (average degree of polymerization, respectively) is identified by formula:

$$N = \int_0^1 F_0(s) \cdot ds \tag{23}$$

In that case it means that:

$$\overline{P}_w = 1 + \frac{(p_1 + 2p_2 + p_3)^2}{p_1 - 3p_3} \tag{24}$$

$$\overline{P}_n = \frac{1}{(p_1 + 2p_2 + 3p_3) \cdot \int_0^1 \frac{(p_0+p_1x+p_2x^2+p_3x^3)(p_1-3p_3x^2)}{(p_1+2p_2x+3p_3x^2)^2} dx} \tag{25}$$

The calculation of P_n and P_w was realized as follows. The system of kinetic equations at certain value of V was solving until q reached its given value. Then, at $V = 0$ the solution was continuing until OH groups exhausted. Then P_n and P_w were calculating by formulae (24) and (25).

Shown in Tables I and II are the results of calculations for various sets of the kinetic constants and compositions (9) of the system.

TABLE I Composition of alumoxane (relative parts of bond blocks) as a function of kinetic condition of polycondensation. $q = 0.75$

$k(1)$	100	100	100	100	100
$k(2)$	100	50	50	50	10
$k(3)$	100	10	10	10	10
$k(4)$	100	50	5	1	1
$k(5)$	100	25	2,5	0,5	0,5
$k(6)$	100	5	0,5	0,1	0,1
p_0	0,125	0,0383	0,0382	0,0382	0,0135
p_1	0,375	0,4481	0,4480	0,4480	0,4921
p_2	0,375	0,4891	0,4891	0,4887	0,4757
p_3	0,125	0,0244	0,0230	0,0215	0,0184
$\overline{P}_n$	4,0	4,0	4,0	4,0	4,1
$\overline{P}_w$	∞	7,0	6,9	6,8	6,1

TABLE II Composition of alumoxane as a function of the initial composition of system. Kinetic constants: 100(1); 10(2); 1(3); 1(4); 0,5(5); 0,1(6)

q	1	0,75	0,6	0,5	0,3
p_0	0,000	0,0135	0,0877	0,1819	0,4556
p_1	0,1146	0,4921	0,6306	0,6389	0,4893
p_2	0,7698	0,4757	0,2760	0,1768	0,0547
p_3	0,1054	0,0184	0,0057	0,0024	0,0003
$\overline{P}_n$	218,3	4,1	2,5	2,0	1,4
$\overline{P}_w$	∞	6,1	3,3	2,6	1,7
$\overline{P}_n(eq)$	∞	4,0	2,5	2,0	1,4
$\overline{P}_w(eq)$	∞	∞	7,0	4,0	2,0

As it can be seen, the statistical distribution of the fragments (blocks) takes place only when the kinetic constants are similar (Tab. I, column 1). In other cases the distribution is deflected from the statistical one.

In system under consideration (17) the reactions of interchain exchange [37] proceed between not only Al —O bonds but most likely also between Al —O and Al —R bonds as it was shown in [38, 39]. All things considered, it leads to the equilibrium molecular distribution, *e.g.*, the values of molecular masses will be given by the formulae:

$$\begin{aligned} \overline{P}_n &= \frac{1}{1-q} = \frac{1}{1-3p/2} = \frac{2}{r-1} \\ \overline{P}_w &= \frac{1+p}{1-2p} \end{aligned} \tag{26}$$

where $q = [H_2O]_0/[Al]_0$, $r = [R]_\infty/[Al]_0$.

Respectively, a critical point (gelation) corresponds to the terms: $p = 0{,}5$ or $q = 0{,}75$.

Naturally, these formulae do not take into consideration the cyclization process which proceeds intensively in such systems [37–39].

With the regard to the cyclization it is obvious, that the critical condition will correspond to the higher relationship of reagents. Thus, the system formed as a result of direct interaction of aluminium and water is nonequilibrium. During its storage or exploitation it changes its molecular structure up to formation the unsoluble highly cross-linked gel fractions.

CONCLUSIONS

The analysis of AAO formation by interaction of AOC and water that has been done in this study revealed that in spite of its complexity there are the ways to regulate the structure of AAO formed. To do this it is necessary to identify the exact kinetic constants of all the stages of the process. On the other hand, the equilibrium structure which depends only on the relationship of reagents may be obtained ultimately on expiry of a long time. It would be very interesting to study its catalytic activity and estimate the time of its formation.

The attempts to clear up by what means and which cyclic structures may be formed during the hydrolysis of AOC are failed now. Their role in catalytic polymerization of olefins also has not been studied. However, possibly just these structural elements may play an important role in formation of the active centres of polymerization.

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