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SYNTHESIS AND PROCESSING OF POLYMERIC COMPOSITES

THE STUDY OF CHEMICAL ASSEMBLY OF MACROMOLECULES IN POLYCONDENSATION OF DIFUNCTIONAL DIMETHYLSILANES

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The article describes the results of research on polycondensation «in situ» in the process of partial hydrolysis dimethyldimetoxysilane and dimethyldiacetoxysilane in compared with similar data for the dimethyldichlorosilane and homofunctional condensation of dimethylsilandiol. The effect of the molar ratio components on composition products by partial hydrolysis of the functional dimethylsilanes and dependence of the degree monomer conversion (X_m) vs. conversion of functional groups (X_f) are presented. It is shown that as the conversion of functional groups in composition products increases the share dimethylcyclosiloxanes and (when $X_f \rightarrow 1$) reaches more than 99%. It is found that among the monomers $(CH_3)_2Si(OH)_2 < (CH_3)_2Si(OCH_3)_2 < (CH_3)_2Si(OCOCH_3)_2 \approx (CH_3)_2SiCl_2$ the proportion unit-to-unit assembling oligomeric molecules, which are created by heterofunctional condensation hydrolysis of products and formation organocyclosiloxanes are increasing. It is assumed that the heterophase process which is responsible for the lack of hydrolyzing agent due to its slow diffusion is the cause of the unit-to-unit assembling.

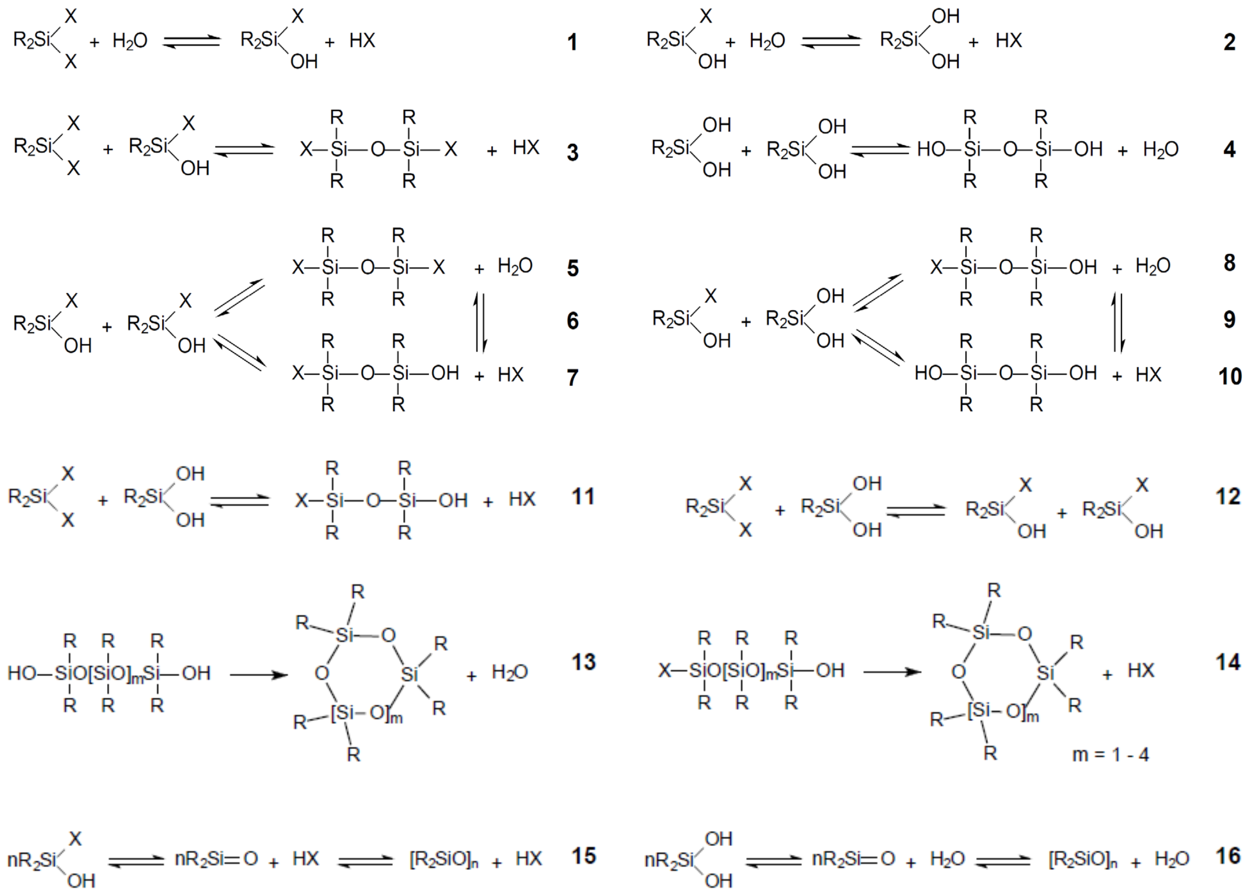
Keywords: *partial hydrolysis, polycondensation, chemical assembly, organosilanols, organochlorosilanes, organoalkoxysilanes, organoacetoxysilane, organocyclosiloxanes.*

Introduction

At the first stages of developing organosilicon compound chemistry special attention was paid to studying the regularities of the partial hydrolysis (PH) of organochloro- and organoalkoxysilanes. A common feature of the first works by Andrianov K.A. and subsequent works by Soviet and foreign scientists during the period from 1937 to 1980 on partial hydrolysis is the use of a narrow range of water and chloro- or alkoxysilanes molar ratios – m (m = 0.37 [1]; 0.5 [2]; 0.55 – 0.66 [3]; 0.75 – 0.9 [4]; 0.1 – 0.9 [5]; 0.75 – 1 [6]; 0.5 – 1.5 [7]), the order of mixing the reagents (dosing water to the monomer) and a long time of carrying out hydrolysis: usually from several tens of minutes to several hours [1–12]. The data of these studies showed that the main PH reaction products are only low-molecular linear oligomers (n = 1÷10) and a small amount of cyclic compounds. For this reason the interest in studying of PH organochloro- and organoalkoxysilanes gradually decreased from 1960s. Nowadays this process is practically not studied.

The hydrolysis of such monomers as organoalkoxysilanes and organoacetoxysilanes, as well as the hydrolysis of organochlorosilanes is a process of the polycondensation type, in which reaction centers are formed "in situ". It is known that both classes of the studied substances are monomers with a hidden functionality [13], the hydrolysis (**1**) of which results in the formation of molecules having two types of reaction centers: X (–Cl; –OR'; –OCOR') and OH. Further formation of the siloxane bond is possible in two directions: homofunctional condensation (HMFC) (**4, 5, 8**) and heterofunctional condensation (HTFC) (**3, 7, 10, 11**) of hydrolysis products $R_nSiX_{4-n-m}(OH)_m$. Besides, exchange reactions (**12**) between chlorine- (alkoxyl-, acetoxyl-) and hydroxyl-containing compounds, reactions of intramolecular homo- and heterofunctional condensation (cyclization) are possible (**13, 14**). Some authors allow also the formation and polymerization of organosilanones (**15, 16**) [14–16].

Besides, a general characteristic of organoalkoxysilanes, organoacetoxysilanes and organochlorosilanes is their limited mutual compatibility with water causing the heterophase nature of the hydrolysis process. Research on the macrokinetics of the heterophase hydrolysis of diorganodichlorosilanes [17] showed that due to the lack of water in the reaction zone the main reaction of oligoorganosiloxane formation is a heterofunctional condensation of hydrolysis products (reactions **4, 6**) rather than a homofunctional condensation (reactions **3, 5**) in contrast to what was supposed for many years. The lack of water in the organic phase is the main reason of HTFC in the hydrolytic polycondensation (HPC) of R_nSiX_{4-n}. This lack is caused by the following macroscopic factors: limited mutual solubility of water and R_nSiX_{4-n}, ratio of rates of the chemical reaction and interphase transfer. As a result, the chain is formed by the "attach met" of monomeric intermediate R_nSiX_{4-n-m}(OH)m to the growing chain. The high rates of HTFC reactions (≡SiOH + ≡SiCl) as compared to HMFC (≡SiOH + ≡SiOH) are caused also by kinetic reasons: Cl group is more electronegative and polarizable than OH, which leads to a higher rate of nucleophilic substitution in HTFC.



Since the hydrolysis organoalcoxy- and organoacetoxysilanes is also a heterophase process [18, 19], it was of interest to study the reactions of partial hydrolysis of these compounds that reactions occur in the organic phase of system and to compare the obtained results to the known regularities of dimethyldichlorosilane partial hydrolysis [20] and dimethylsilanediol HMPC [21].

Experimental

The starting reagents were synthesized and characterized by standard techniques [22, 23]. The partial hydrolysis of dimethyldiacetoxysilane $(CH_3)_2Si(OCOCH_3)_2$ and dimethyldimethoxysilane $(CH3)_2Si(OCH_3)_2$ was carried out with a 0.6N HCl solution at dioxane concentration in the mixture [A] = 60 mol % in a 10 ml batch-operated flat-bottomed perfect mixing microreactor supplied with a stirrer (2500 rpm) and reflective ribs. The process was carried out by instant input of the reagents into the reactor at $H_2O/(CH_3)_2SiX_2$ molar ratio from 0 to 1. After 1 min in case of $(CH_3)_2Si(OCOCH_3)_2$ hydrolysis and after 30 min in case of $(CH_3)_2Si(OCH_3)_2$ hydrolysis samples of the reaction mixtures were taken, and the composition of the products was determined by gas-liquid chromatography.

The chromatographic analysis was carried out with the use of a Kristall 2000M device equipped with a heat conductivity detector, a packed column of 2 m length and 3 mm diameter filled with stationary phase SE-30 on Cromaton N-AW-DMCS carrier. Helium was used as a carrier gas. The compounds were identified by means of reference samples of $(CH_3)_2SiY_2$, $Y\text{-}(Si(CH_3)_2O)_{n-1}\text{-}Si(CH_3)_2\text{-}Y$ (where Y = OH, X; n = 2–10) and $[(CH_3)_2SiO]p$ (where p = 3–6). Identification of the hydrolysis products was carried out with the use of a graph of the dependence of retention time on the number of the homological series member. The content of the reaction mixture components was calculated by the internal normalization method on the basis of peak areas with the use of correction coefficients taking into account the detector sensitivity.

Results and Discussion

The main analysis tool and main criterion of the oligomer chain formation in our work is the dependence of the monomer conversion (X_m) on the functional groups conversion (X_f) suggested for the first time in the work by Sokolov L.B. for taking into account the change (reduction or increase) in the oligomers reactivity with increasing extent of their polymerization [24]. This effect is taken into account in the modified Carothers equation [24, 25]:

$$n = 1/(1 - \lambda X_f) \tag{1}$$

where λ is a coefficient taking into account the change in the functional groups activity in the process. The oligomers activity as compared to the monomer increases at $\lambda > 1$ and decreases at $\lambda < 1$.

It was suggested for the first time in work [24] to distinguish polycondensation from polymerization by comparing the dependences of the monomer conversion (X_m) on the functional groups conversion (X_f). In the limiting case polycondensation is assembly by doubling, in which full conversion of the monomer into a dimer occurs at $X_f = 0.5$. The polymerization is a process of unit-by-unit assembly, at which the full conversion of functional groups corresponds to the full conversion of the monomer.

The invalidity of equation (1) and the invariancy of Carothers equation with respect to condensation conditions are shown in work [26]. The authors of the work note that Carothers equation reflects the block mode of the polymer formation, when the monomer disappears completely at the first step of the polycondensation. In this regard they considered the general case taking into account the existence of unreacted monomer in the reaction mixture, for which the polymer polymerization degree np is

$$n_p = (M_0 - M_t)/P_t \tag{2}$$

where M_0, M_t are the quantities of the monomer molecules at the beginning and in the end of the process; P_t is the quantity of the polymer molecules. Solving this equation enables finding the correlation of n_p with the functional groups conversion X_f and the monomer conversion X_m [26, 27] as follows:

$$n_p = \frac{1}{1 - \frac{f}{2}\frac{X_f}{X_m}} \tag{3}$$

When $X_m = 1$, equation (3) becomes Carothers equation. Unlike Carothers equation (1) equation (3) is general for the whole polymerization process: from the initial stages (that is, at $X_m > 0$) to late ones ($X_f \rightarrow 1$). It is important to note that equation (3) contains information about the influence of the process conditions on the polymer molecular mass. This information is indirectly contained in X_f/X_m ratio, in which the denominator can be expressed as a function of X_f. So, in case of statistical assembly of a macromolecule from monomers with independent functional groups ($\lambda = 1$) it is easy to obtain dependence $X_m = f(X_f)$ from Flory equation $Ni = (1 - X_f)^2 X_f^{(n-1)}$: $X_m = 2X_f - X_f^2$. Combining the obtained equation with equation (3) gives the required dependence as [26]:

$$n_p = (2 - X_f)/(1 - X_f) \tag{4}$$

A similar equation has been obtained before by the method of generating functions [28]. Since it is not always possible to estimate the value of X_m experimentally, it is possible to determine the type of polymeric assembly in coordinates $1/n = f(X_f)$ with the use of HPC or viscometry data having determined np indirectly [26].

Coordinate space $X_m - X_f$ serves as a tool for estimating kinetic and thermodynamic, as well as structural factors. Experimental data placed in these coordinates can reflect:

1. the ratio of block and unit-by-unit assembly caused by:
   - kinetic factors (change in the oligomer reactivity);
   - macrokinetic factors (ratio of the rates of mass transfer and the chemical reaction);
2. cyclization processes;
3. polymerization and depolymerization processes;
4. interchain exchange processes.

The monomer conversion X_m and the functional groups conversion X_f were calculated according to the following formulas:

$$X_m = \frac{C_0 - C_t}{C_0}$$

$$X_f = \frac{2(C_0 - C_t - \sum C_{nL})}{2C_0}; \; \mathrm{n} = \frac{C_0}{\sum C_n}$$

$$X_{fpr} = \frac{2(C_0 - C_t - \sum C_{nL} - \sum C_{nD})}{2C_0}$$

where n is polymerization degree; X_{fpr} is “reduced” conversion of the functional groups (that is, the consumption of the functional groups in the linear molecule cyclization is not taken into account); C_0 and C_t are the initial and final concentrations of the monomer; C_{nL} and C_{nD} are concentrations of the linear and cyclic products by the time of the reaction completion.

The current concentrations of the condensation products (C_i, mol/l) were calculated on the basis of the initial monomer concentration C_0, material balance ratios and the normalization condition:

$$C_0 - C_t = 2C_2 + 3C_3 + \ldots + nC_n$$

$\sum (C_n / \sum C_n) = 1$, where $C_n / \sum C_n = S_n$ determined from gas-liquid chromatography data:

$$S_n = \frac{A_n / M_n}{\sum_1^n (A_n / M_n)}$$

where *A* are instrument readings (peak area corrected taking into account the correction coefficient).

Dependences $X_m = f(X_f)$ (Fig. 1) are interpreted as follows: OA line corresponds to extreme block assembly in the polycondensation. From the viewpoint of kinetics it means that the monomer + monomer (L_1+L_1) interaction rate constant is much larger than the monomer + oligomer (L_1+L_n) interaction rate constant. Therefore, the monomer is consumed almost instantly. This postulate is the basis of Carothers equation. As the oligomer reactivity increases, the lines of $X_m = f(X_f)$ dependences gradually come nearer to OB line. Thus, OFB line ($X_m = 2X_f - X_f^2$) corresponds to Flory's case when the process participants have identical reactivities. Straight line OB characterizes another extreme option: the unit-by-unit assembly of the macromolecule. Besides, OB line corresponds in the HPC of R_2SiX_2 to complete cyclization of the oligomers and to polymerization processes, for example, of organocyclosiloxanes or an organosilanone.

And, at last, as it will be shown further, macrokinetic conditions of the reaction, particularly, the process heterogeneity causing a lack of the hydrolyzing agent in the reaction zone due to its slow diffusion, can be the cause of unit-by-unit assembly of the oligomer molecule.

Fig. 2 presents dependences of the structure of products of PH of $(CH_3)_2SiX_2$ and of HMPC of dimethylsilanediol $(CH_3)_2Si(OH)_2$ on the functional groups conversion (X_f). It can be seen from the presented dependences that the main reactions products are linear oligomers of formula Ln ≡ Y-$(Si(CH_3)_2O)_{n-1}$-$Si(CH_3)_2$-Y and cyclic organosiloxanes of general formula Dp ≡ $[(CH_3)_2SiO]_p$.

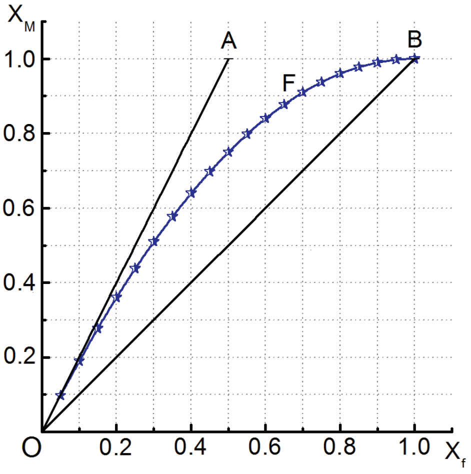
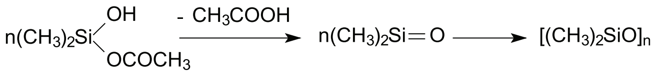


Fig. 1. Dependence of monomer conversion (X_m) on functional groups conversion (X_f) for processes: OA – block assembly, OB – unit-by-unit assembly, OFB – statistic polycondensation (according to Flory).

It can be seen from the dependence of the composition of products of homofunctional $(CH_3)_2Si(OH)_2$ condensation presented in Figure 2 (a) that the main products are linear dimethylsiloxanedioles. 1,1,3,3,5,5,7,7,9,9-Decamethylpentasiloxane-1,9-diol was found in relatively small amounts (3–5%), and cyclic products are practically absent in contrast to PH of $(CH_3)_2SiX_2$ (Fig. 2 b–d). It follows from this that ring formation from a linear chain occurs upon interaction of terminal ≡Si-X and ≡Si-ON groups more readily, and oligomers with two terminal OH groups practically do not form cyclic products (in the experimental conditions).

A common feature for all the obtained $S = f(X_f)$ dependences (Fig. 2 b–d) in the partial hydrolysis of organosilanes of formula $(CH_3)_2SiX_2$ is that the dependences of linear oligomers content in PH products Ln on the functional groups conversion are of an extreme nature, which indicates the formation of oligomers according to the HTFC mechanism. A fundamental difference of the composition of products of the partial hydrolysis of $(CH_3)_2Si(OCH_3)_2$, $(CH_3)_2Si(OCOCH_3)_2$ and $(CH_3)_2SiCl_2$ from statistical and literature data is the high content of organocyclosiloxanes at m > 0.7. It can be seen from the graphs that increasing molar ratio H_2O/ R_2SiX_2 leads to the emergence of organocyclosiloxanes in the composition of the reaction products. Their content reaches a maximum (> 95%) at $X_f \to 1$. This experimental fact cannot be explained on the basis of the mechanism of diorganosiloxanediols (**13**) intramolecular condensation, because an excess of water (m > 2) is required for the formation of these compounds. It is obvious that the formation of organocyclosiloxanes takes place due to $Si(CH_3)_2O[Si(CH_3)_2O]mSi(CH_3)_2$-OH intramolecular heterofunctional condensation (where m = 1, 2, 3, etc.) (**14**).

The formation of cycles with no linear oligomers in the composition of the products of dimethyldiacetoxysilane PH even at low conversions of the functional groups was unexpected. This fact allows to assume the possibility of organocyclosiloxanes formation with the participation of dimethylsilanone (**17**) according to the following scheme:



$$n(CH_3)_2Si(OH)(OCOCH_3) \xrightarrow{-\,CH_3COOH} n(CH_3)_2Si{=}O \longrightarrow [(CH_3)_2SiO]_n \qquad 17$$

However, we have not so far succeeded in obtaining an experimental confirmation of such mechanism [14]. Differences between the mechanism of the oligomeric molecules formation in homofunctional condensation and in partial hydrolysis distinctly show themselves when comparing the dependences of the monomer conversion (X_m) on the functional groups conversion (X_f) (Fig. 3).

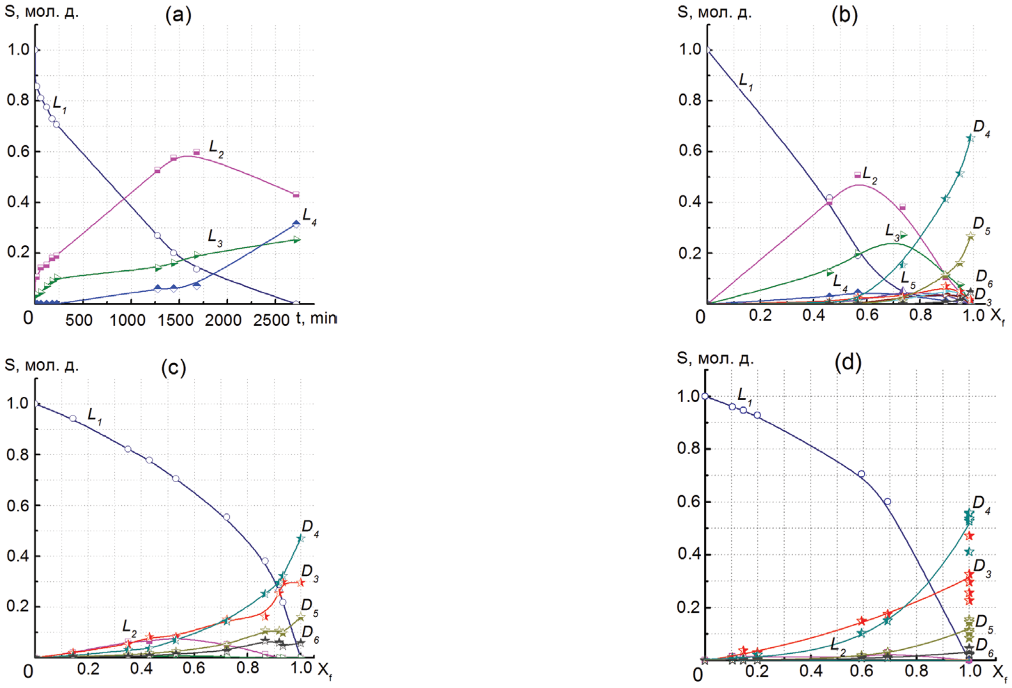


Fig. 2. Dependences of the composition (S) of products of dimethylsilanediol homofunctional condensation (pH=3, CM=0.9) [21] on experiment duration (a), partial hydrolysis of dimethyldimethoxysilane (b), dimethyldichlorosilane [20] (c) and dimethyldiacetoxysilane (d) on the degree of functional groups transformation (X_f) at dioxane concentration of 60 mol %.

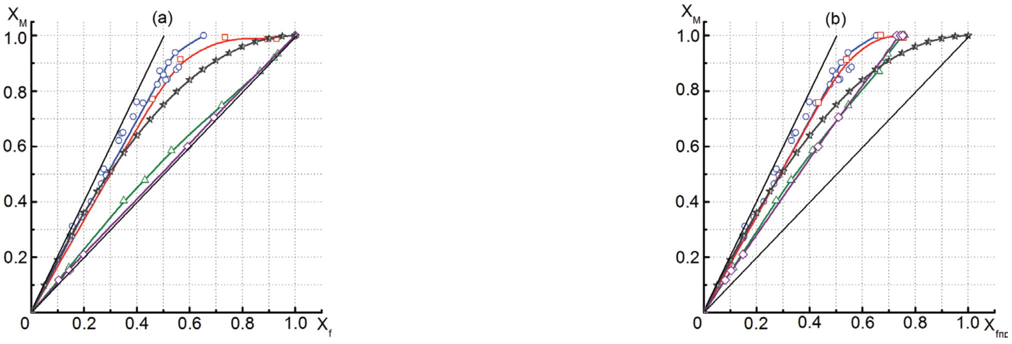
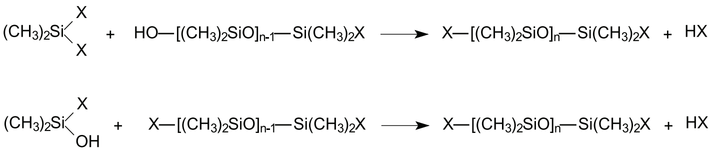


Fig. 3. Dependences of monomer conversion (X_m) on functional groups conversion (X_f) (a) and of monomer conversion (X_m) on the “reduced” conversion of functional groups (X_{fpr}) (b) for (★) statistical assembly according to Flory, (○) – $(CH_3)_2Si(OH)_2$ HMFC, partial hydrolysis (□) – $(CH_3)_2Si(OCH_3)_2$, (△) – $(CH_3)_2SiCl_2$ and (◇) – $(CH_3)_2Si(OCOCH_3)_2$.

Studies on the HMFC of a number of organosilanols including dimethylsilanediol showed that dependence $X_m = f(X_f)$ characterizes HMFC as a process of typical block assembly (Fig. 3 (a), (b)) [20] irrespective of the silanol initial concentration, medium pH, temperature, the nature of substituents at the silicon atom of and the solvent nature. This dependence combines the data with various types of kinetic curves [21] including concentration self-oscillations [14].

In contrast, in case of partial hydrolysis of R_2SiX_2 it can be seen from figures 3a, b that the fraction of unit-by-unit assembly of molecules in the oligomer formation considerably increases. The difference in the regularities of oligomeric molecules formation in HMFC and PH indicates that HMFC is not the main mode of assembly of molecules in the conditions of partial hydrolysis. The unit-by-unit assembly in PH is due to the deficiency of the hydrolyzing agent in the reaction zone. As a result, the polymeric chain assembly takes place by the "addition" of monomeric molecules (CH3)$_2$SiX$_2$ (**18**) and intermediate $(CH_3)_2SiXOH$ (**19**) to the growing chain.



$$(CH_3)_2Si\begin{smallmatrix}X\\ X\end{smallmatrix} + HO—[(CH_3)_2SiO]_{n-1}—Si(CH_3)_2X \longrightarrow X—[(CH_3)_2SiO]_n—Si(CH_3)_2X + HX \qquad 18$$

$$(CH_3)_2Si\begin{smallmatrix}X\\ OH\end{smallmatrix} + X—[(CH_3)_2SiO]_{n-1}—Si(CH_3)_2X \longrightarrow X—[(CH_3)_2SiO]_n—Si(CH_3)_2X + HX \qquad 19$$

The fraction of unit-by-unit assembly of oligomeric molecules according to the HTFC mechanism increases in the series of monomers $(CH_3)_2Si(OH)_2 < (CH_3)_2Si(OR)_2 < (CH_3)_2SiCl_2 \approx (CH_3)_2Si(OCOCH_3)_2$. The shift of $X_m = f(X_f)$ dependencies to the right is usually associated with the increase in the oligomer reactivity [26]. We assume that such a series of dependences can be a consequence of the processes heterogeneity causing the deficiency of the hydrolyzing agent in the reaction zone due to its slow diffusion.

Conclusions

Regularities of partial dimethyldimethoxy-and diacetoxysilane hydrolysis in dioxane were studied at various water/monomer molar ratios. It was shown that, while the conversion of functional groups increases, the fraction of dimethylcyclosiloxanes in the products increases and reaches a value higher than 99% at $X_f \rightarrow 1$.

Analysis of chemical assembly of oligodimethylsiloxanes was carried out on the basis of comparison of dependences of the monomer conversion on the functional groups conversion in the homocondensation of dimethylsilanediol and in the partial hydrolysis of dimethyldimethoxy-, dimethyldiacetoxy- and a dimethyldichlorosilane. It was established that the fraction of unit-by-unit assembly of oligomeric molecules by heterofunctional condensation of hydrolysis products increases in the series of monomers $(CH_3)_2Si(OH)_2 < (CH_3)_2Si(OR)_2 < (CH_3)_2Si(OCOCH_3)_2 \approx (CH_3)_2SiCl_2$, and the formation of organocyclosiloxanes increases. The unit-by-unit mode of assembly is caused by the deficiency of the hydrolyzing agent in the reaction zone of heterophase processes due to the low solubility of the reagents and slow diffusion of water into the reaction zone.

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