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On the Microstructure of Copolymer Chains Obtained by the Linear Heterocopolycondensation Process

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ABSTRACT

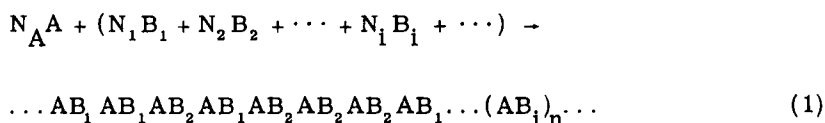
During the statistical analysis of copolymers obtained by the heteropolycondensation method, simulating the difference in the reactivity of the original comonomers by varying the preset reactive conditions, it is shown that the microstructure of the condensation copolymer chains should not depend on the relative reactivity of the comonomers. It is also shown that the microstructure of the chains can be influenced by choosing the copolycondensation conditions in such a way that the process would proceed from a insufficient quantity of the intermonomer in the reactive zone.

INTRODUCTION

Let heterocopolycondensation be a process in which one of the original reagents (A), which contains functional groups, does not react with the other, which is designated as the intermonomer, and which reacts with two or more of the other original reagents ($B_1, B_2, \dots, B_i, \dots$), which are designated as the comonomers and contain functional groups, and which react only with the intermonomer functional

groups and not with one another. (In a more general case, even two or more reagents may appear as the intermonomers, and this will result in the interaction of two groups of comonomers, each of which, in relation to other, will appear in the role of a multi-component intermonomer.) All the original reagents (intermonomer and comonomers) are bifunctional in the linear heterocopolycondensation. Sometimes during the heterocopolycondensation an interaction of the functional groups of the intermonomer or comonomers may take place, which in relation to the main process is a side reaction and shall not be dealt with in this article.

In a general form the synthesis of a polymer by heteropolycondensation process can be presented as



where N_A , N_1 , N_2 , ..., N_i are the quantities of the moles of the original intermonomer and comonomers, respectively. For our investigation it makes absolutely no difference whether a low-molecular by-product of the reaction is produced during the polycondensation or not.

The microstructure of the chains of such copolymers may be clearly defined by the average length and distribution of the sequences of the units of each species in the chain, i.e., sequences consisting of units AB_1 , AB_2 , ..., AB_i , If the molecules of one of the original reagents are asymmetrical and can be arranged in the chain in two ways, this may result in one more reagent taking part in the reaction.

The standard method of evaluating the microstructure of the copolymer chains according to the relative content of homo- and heterotriads [1-3] makes it possible to evaluate only the number-average lengths of sequences of the units of one species but does not allow evaluation of the distribution inside the sequences (i.e., a judgment of their intrinsic polydispersity), therefore the question of the microstructure of the condensation copolymer chains often becomes a question of their compositional heterogeneity, i.e., of the differences in the composition of various copolymer fractions [4]. However, in one of the previous works [5] an approach was outlined to evaluate the microstructure of the condensation copolymer chains. It was based on obtaining the distribution functions of the unit sequences of one species. If we can obtain such distribution functions for various concrete conditions, it will then be possible to calculate, if necessary, the content of the corresponding triads.

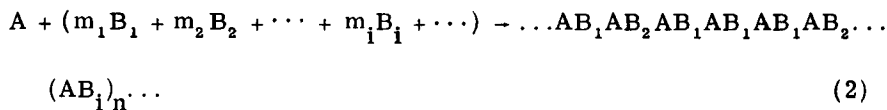
The question of the connection between the microstructure of the condensation copolymer chains and the conditions for obtaining them (relative reactivity of original reagents and their quantitative ratios, procedure of the synthesis, topochemistry of the process, etc.) remains controversial. According to one point of view, when the copolymer chains are formed with the participation of comonomers of different reactivities, at first the macromolecules of the block structure are formed, which later, as a result of the exchange reaction between chains, are turned into the macromolecules with a random distribution of units of various species [6-8]. On the other hand, it has recently been shown by direct experiments that under conditions of low-temperature polycondensation, when it is possible to exclude the effect of the exchange between chains, the copolymers are likewise formed with a "statistical" distribution of units of various species even when there are substantial differences in the reactivities of the comonomers [2].

In this connection it is expedient to examine theoretically the possible results of heterocopolycondensation under certain preset conditions and try to determine the factors that can affect the copolymer chain microstructure.

COMPLETED REACTION AT EQUIVALENT QUANTITIES OF THE FUNCTIONAL GROUPS OF ORIGINAL REAGENTS

For convenience the presentation will be made calculating per 1 mole of intermonomer.

Then Eq. (1) can be rewritten as



where $m_1, m_2, \dots, m_i, \dots$ are molar fractions of the comonomers in relation to their total quantity ($\sum_i m_i = 1$).

The distribution function of units of one species can be found in the simplest way when the formation of the copolymer occurs as a result of the reaction of the intermonomer with the comonomers at a simultaneous introduction of all the components into the reaction, and under condition of equality and invariability in the course of the reaction of relative reactivities of the functional groups of the comonomers in their reactions with the functional groups of the

intermonomer. Let us also assume that the reaction from beginning to end takes place under homogenous conditions in the kinetic region.

The probability that Unit AB, taken at random from the copolymer, will prove to be AB_i will be equal to m_i . Since it is provided that addition of A to AB_i does not change the subsequent relative rates of addition, the probability that the sequence chosen at random will contain n units of the i -th type is equal to the product of m_i^n and the probability that after these n units there will be found A connected with any other than the i -th Component B:

$$N_i(n) = m_i^n (1 - m_i) \quad (3)$$

where $N_i(n)$ = number-distribution function of sequences $(AB_i)_n$ according to the lengths. If the reaction for all the B comonomers is of the first order, then evidently, the value of the number distribution function is maintained over the entire period of the reaction owing to the proportionality of the change in the quantity of comonomers in time.

Summing up the distribution function (Eq. 3):

$$\sum_{n=1}^{\infty} N_i(n) = m_i (1 - m_i) \sum_{n=1}^{\infty} m_i^{n-1} = m_i \quad (4)$$

shows that the probabilities of the entry of each comonomer into all its possible sequences are equal to their molar fractions in the original mixture, which should be expected.

Evidently the molar fraction of sequences, consisting of n units of AB_i , among those similar to themselves is determined by

$$\mu_i(n) = \frac{N_i(n)}{\sum_{n=1}^{\infty} N_i(n)} = m_i^{n-1} (1 - m_i) \quad (5)$$

and the weight fraction

$$\omega_i(n) = \frac{nN_i(n)}{\sum_{n=1}^{\infty} nN_i(n)} = nm_i^{n-1} (1 - m_i)^2 \quad (6)$$

Proceeding from the number distribution function (Eq. 3), we can find expressions for the number-average, weight-average, and z-average lengths of sequences of Units AB_i , respectively [9]:

$$\bar{p}_{ni} = \frac{\sum_{n=1}^{\infty} nN_i(n)}{\sum_{n=1}^{\infty} N_i(n)} \tag{7}$$

$$\bar{p}_{wi} = \frac{\sum_{n=1}^{\infty} n^2 N_i(n)}{\sum_{n=1}^{\infty} nN_i(n)} \tag{8}$$

$$\bar{p}_{zi} = \frac{\sum_{n=1}^{\infty} n^3 N_i(n)}{\sum_{n=1}^{\infty} n^2 N_i(n)} \tag{9}$$

The solution of Eqs. (7)-(9) yields

$$\bar{p}_{ni} = 1/(1 - m_i) \tag{10}$$

$$\bar{p}_{wi} = (1 + m_i)/(1 - m_i) \tag{11}$$

$$\bar{p}_{zi} = (1 + 4m_i + m_i^2)/(1 - m_i^2) \tag{12}$$

Infinite sums $N_i(n)$ and $nN_i(n)$ are solved by a known method [10], and the others are solved by successive differentiation over m_i and multiplication of the sum of terms of the geometrical progression by m_i .

From Eqs. (10)-(12) it follows that the ratio $\bar{p}_{zi} : \bar{p}_{wi} : \bar{p}_{ni}$ is equal to

$$\frac{1 + 4m_i + m_i^2}{1 + m_i} : (1 + m_i) : 1$$

and is transformed at $m_1 = 1$ to 3:2:1, the known ratio obtained by Flory [9] as the most probable distribution in condensation polymers.

The fact is that distribution is according to the lengths of the sequences of units of one species, and the evaluation of the average lengths of these sequences shows that even in the so called "statistical" copolymers there is a probability of the formation of homogeneous sequences of such length and in such quantities (of course, at the corresponding molar ratios between the comonomers) at which they may be able to form individual structures. The behavior of a number of such "statistical" copolymers in some respects can turn out to be similar to the behavior of the block copolymers.

Let us examine further in which way and in what cases the microstructure of the polymer chains can be changed if the intermonomer does not react immediately with a mixture of comonomers but with each one of them in turn. For convenience let us take the case of obtaining a binary copolymer, i.e., the reaction of the intermonomer with two comonomers:



Since the intermonomer in relation to any of the comonomers taken separately is in excess, then, after the completion of the reaction with one of them in the first step, the end groups in the product obtained will be the functional groups of the intermonomer and in the second step, if it is carried out in such a way as to avoid an exchange between chains, it will be impossible to form continuous sequences of the units with the participation of the first comonomer with its different length and distribution compared to those obtained in the first step. Thus the problem here is to find the average lengths and distribution of the sequences of units in the product of the reaction in the first step.

Let us take comonomer B_1 to carry out the first step with the intermonomer and designate their mole ratio as

$$q_1 = 1/m_1 \quad (14)$$

The molar fractions of components in this mixture are

$$A = q_1/(q_1 + 1), \quad B_1 = 1/(q_1 + 1) \quad (15)$$

Let us consider the particles of the product of the reaction between A and B_1 as the particles consisting of a certain quantity of units AB_1 and end A unit, i.e., $AB_1AB_1AB_1 \dots AB_1AB_1A$ or $(AB_1)_n A$. Then the fraction of A equal to

$$1/q_1 \quad (16)$$

will be equal to the probability of finding A in unit AB_1 . The probability of finding A as the end unit is equal to

$$1 - 1/q_1 \quad (17)$$

The number distribution function or the probability that the particle chosen at random from the system will contain a sequence of n units of B_1 and $(n + 1)$ units of A can be written as

$$N_1(n) = (1/q_1)^n (1 - 1/q_1) \quad (18)$$

At $n = 0$ this function gives the probability of finding particles in the system that do not contain component B_1 , i.e., particles of free unreacted A. Summing up Eq. (18) we have

$$\sum_{n=0}^{\infty} N_1(n) = (1 - 1/q_1) \sum_{n=0}^{\infty} (1/q_1)^n = 1 \quad (19)$$

i.e., any particular value of the number-distribution function is simultaneously equal to the molar fraction of particles in the system containing a preset sequence of n units of AB_1 .

Thus, after the first step, the molar fraction of the unreacted A in the reaction product will be

$$N_1(0) = 1 - 1/q_1 \quad (20)$$

while the molar fraction of the product of the reaction of A with B_1 (polymer or oligomer) will be equal to

$$\sum_{n=1}^{\infty} N_1(n) = \frac{q_1 - 1}{q_1^2} \sum_{n=1}^{\infty} (1/q_1)^{n-1} = 1/q_1 \quad (21)$$

We can also arrive at these expressions using another method [11]. The weight fractions of the unit sequences, derived from the distribution function (18), correspond exactly to the weight fractions of $(2n + 1)$ -mers derived from the distribution function in the degrees of polycondensation [9], of which we can easily be convinced after an appropriate recalculation.

Using the same techniques used for deriving Eqs. (10)-(12) from Eq. (3), we have

$$p_{n1} = q_1 / (q_1 - 1) \quad (22)$$

$$\bar{p}_{w1} = (q_1 + 1)/(q_1 - 1) \quad (23)$$

$$\bar{p}_{z1} = (q_1^2 + 4q_1 + 1)/(q_1^2 - 1) \quad (24)$$

Then, if we conduct the reaction of the first-step product with B_2 , and if the molar fraction of the unreacted A in the first-step product is given by expression (20), the probability of finding A within unit AB_2 is $1 - 1/q_1$, which is equivalent to the finding of a two-unit sequence, including AB_2 , since unit AB_2 from the other end can be added to any particles of the first-step product only through B_2 . This means that the number distribution function for the unit sequences, including B_2 , can be written as

$$N(n) = (1 - 1/q_1)^{n-1} (1/q_1) \quad (25)$$

Again deriving Eqs. (10)-(12) from Eq. (3), we have

$$\bar{p}_{n2} = q_1 \quad (26)$$

$$\bar{p}_{w2} = 2q_1 - 1 \quad (27)$$

$$\bar{p}_{z2} = (6q_1^2 - 6q_1 + 1)/(2q_1 - 1) \quad (28)$$

In equations (22)-(24) and (26)-(28) the average lengths of the sequences of units of each species are expressed in terms of mole ratios of the components in the first synthesis step. Substituting Eq. (14) into them and taking into account that $m_1 + m_2 = 1$, we find

$$\bar{p}_{n1} = 1/(1 - m_1) \quad \bar{p}_{n2} = 1/(1 - m_2) \quad (29)$$

$$\bar{p}_{w1} = (1 + m_1)/(1 - m_1) \quad \bar{p}_{w2} = (1 + m_2)/(1 - m_2) \quad (30)$$

$$\bar{p}_{z1} = (1 + 4m_1 + m_1^2)/(1 - m_1^2) \quad \bar{p}_{z2} = (1 + 4m_2 + m_2^2)/(1 - m_2^2) \quad (31)$$

The similarity of Eqs. (29)-(31) with Eqs. (10)-(12) is evident.

Thus, irrespective of Reaction (13) being carried out in one step or in two steps, and irrespective of which of the comonomers is taken first for the reaction with the intermonomer in a two-step process, the average lengths and the distribution of the sequences of units AB_1

and AB_2 are determined only by the molar fractions of B_1 and B_2 in their mixture. Hence, if we examine the reaction in two steps as the simulation of an extremely large difference in the reactivity of the comonomers, another conclusion follows: At the completion of heterocopolycondensation between equimolar quantities of the intermonomer and the sum of the comonomers, irrespective of the exchange between chains taking place or not, the microstructure of the copolymer should not depend on the reactivity of the comonomers if this reactivity is invariable in the reaction time or even changes, but in the same manner.

However, a two-step process may also be carried out in a different way. It is possible, for example, to use in the first step not the whole quantity of the intermonomer but only a part of it, say X , when $1 > X > m_1$. Then the ratio of the components in the first step will be equal to X/m_1 and

$$q_1 = X/m_1 \quad (32)$$

Substituting Eq. (32) into Eqs. (22)-(24),

$$\bar{p}_{n1}' = X/(X - m_1) \quad (33)$$

$$\bar{p}_{w1}' = (X + m_1)/(X - m_1) \quad (34)$$

$$\bar{p}_{z1}' = (X^2 + 4Xm_1 + m_1^2)/(X^2 - m_1^2) \quad (35)$$

It is obvious that $\bar{p}_{n1}' > \bar{p}_{n1}$, $\bar{p}_{w1}' > \bar{p}_{w1}$, and $\bar{p}_{z1}' > \bar{p}_{z1}$.

If for the measure of the distribution breadth we take $r_1 = \bar{p}_{w1}'/\bar{p}_{n1}'$ and $r_1' = \bar{p}_{w1}'/\bar{p}_{n1}'$, then $r_1 = 1 + m_1$ and $r_1' = 1 + m_1/X$. Here it is also obvious that $r_1' > r_1$, i.e., in the first step with a reduction in the quantity of A we find both an increase in the average lengths of the sequences of units AB_1 and a broadening of their distribution.

Then, taking the reaction product after the first step and adding to it the quantity of moles of component A that are lacking $(1 - x)$, we can carry out the reaction of the B_2 mole with m_2 . Having carried out the recalculation of the molar fractions and the operations with a corresponding, analogous (Eq. 25) distribution function of units AB_2 ,

$$\bar{p}_{n2}' = \frac{Xm_2}{X(1 - m_2) - (1 - m_2)^2} \quad (36)$$

$$\bar{p}_{w2}' = \frac{2X}{1 - m_2} \frac{m_2}{X + m_2 - 1} - 1 \quad (37)$$

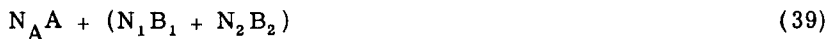
$$p_{z2}' = \frac{6X^2}{(1 - m_2)^2} \frac{\frac{m_2}{X + m_2 - 1} - \frac{2}{3} \frac{1 - m_2}{X}}{2 \frac{X}{1 - m_2} - \frac{X + m_2 - 1}{m_2}} - 1 \quad (38)$$

Here also, comparing Eqs. (36)-(38) with Eqs. (29)-(31), we can see that $\bar{p}_{n2}' > \bar{p}_{n2}$, $\bar{p}_{w2}' > \bar{p}_{w2}$, $\bar{p}_{z2}' > \bar{p}_{z2}$, and $r_2' > r_2$. Therefore, using such a procedure for carrying out a two-step synthesis, the absolute values of the average lengths of the sequences of units of each species depend on X, besides the ratio of the comonomers, as well as on their distribution breadth. The numerical calculation shows that at $m_1 = m_2 = 0.5$ the average lengths of the sequences of units AB_1 and AB_2 are equal over the entire range of the possible changes of X from 1 to 0.5. At $m_1 \neq m_2$ for the preset values of X, the average lengths of the sequences of units and their distribution will depend on which of the comonomers (B_1 or B_2) is the first to react with A. This is clear because in this case the X-th fraction of A in the first step will be in unequal ratios with B_1 or B_2 .

Again, assuming that the reaction in two steps simulates the extremely large difference in the reactivity of the comonomers, we can draw conclusions from the fact that because of the difference in the reactivity of the comonomers the microstructure of the copolymer chains will be affected by the gradual (continuous or in portions) introduction of the intermonomer into the reaction mixture with the progress of the reaction.

COMPLETED REACTION WITH AN EXCESS OF THE INTERMONOMER

Examining further the completed heterocopolycondensation



at $N_A > N_1 + N_2$ and introducing the designations

$$q = N_A / (N_1 + N_2); \quad q_1 = N_A / N_1; \quad q_2 = N_A / N_2 \quad (40)$$

it is easy to show that the number-distribution functions of the sequences of units of each species in a copolymer (co-oligomer), obtained both in one and in two steps, are expressed by

$$N_1(n) = (1/q_1)^n (1 - 1/q_1) \quad (41)$$

$$N_2(n) = (1/q_2)^n (1 - 1/q_2) \quad (42)$$

From Eqs. (41) and (42), after appropriate transformations, we may have

$$\bar{p}_{n1} = q/(q - m_1); \quad \bar{p}_{n2} = q/(q - m_2) \quad (43)$$

$$\bar{p}_{w1} = (q + m_1)/(q - m_1); \quad \bar{p}_{w2} = (q + m_2)/(q - m_2) \quad (44)$$

$$\bar{p}_{z1} = (q^2 + 4qm_1 + m_1^2)/(q^2 - m_1^2); \quad \bar{p}_{z2} = (q^2 + 4qm_2 + m_2^2)/(q^2 - m_2^2) \quad (45)$$

It is obvious that here we can also draw a conclusion about the independence of the microstructure of the copolymer chains from the relative reactivities of the comonomers.

COMPLETED REACTION WITH INSUFFICIENT QUANTITIES OF INTERMONOMER

Here, in contrast to the previous case, $N_A < N_1 + N_2$, and at different ratios of q_1 and q_2 we can show that in the one-step synthesis at equal reactivities of the comonomers the number-distribution functions of units AB_1 and AB_2 are respectively equal to

$$N_1(n) = (q_1 m_1^2)^n (1 - q_1 m_1^2) \quad (46)$$

$$N_2(n) = (q_2 m_2^2)^n (1 - q_2 m_2^2) \quad (47)$$

Also, in accordance with Eq. (2), a part of the unreacted comonomers, whose molar fraction in relation to the total product will be q , will be left in the system while its composition is determined by the original ratios between the comonomers.

If we carry out a two-step synthesis, then depending on the ratio between q_1 and q_2 and on the sequence in which it is carried out, quite different results can be obtained as illustrated in Table 1. Here we discover cases where, on the whole, it will be impossible to form a

TABLE 1. Results of the Two-Step Reaction with Insufficient Intermonomer and at Different Ratios of the Intermonomer and Each of the Comonomers with a Different Sequence of Carrying out the Synthesis

Ratios between q_1 and q_2	Sequence of synthesis ^a	Results of synthesis
$q_1 = 1, q_2 = 1$	1	Mixture of polymer $(AB_1)_n$ with unreacted B_2
	2	Mixture of polymer $(AB_2)_n$ with unreacted B_1
$q_1 < 1, q_2 < 1$	1	Mixture of $(B_1A)_n B_1$ with unreacted B_2 ; $n_{\min} = 0$
	2	Mixture of $(B_2A)_n B_2$ with unreacted B_1 ; $n_{\min} = 0$
$q_1 < 1, q_2 = 1$	1	Mixture of $(B_1A)_n B_1$ with unreacted B_2 ; $n_{\min} = 0$
	2	Mixture of polymer $(AB_2)_n$ with unreacted B_1
$q_1 = 1, q_2 < 1$	1	Mixture of polymer $(AB_1)_n$ with unreacted B_2
	2	Mixture of $(B_2A)_n B_2$ with unreacted B_1 ; $n_{\min} = 0$
$q_1 < 1, q_2 > 1$	1	Mixture of $(B_1A)_n B_1$ with unreacted B_2 ; $n_{\min} = 0$
	2	Mixture of $(B_1A)_n B_1$ with the residue of free B_1
$q_1 > 1, q_2 < 1$	1	Mixture of $(B_1A)_n B_1$ with the residue of free B_2
	2	Mixture of $(B_2A)_n B_2$ with unreacted B_1 ; $n_{\min} = 0$.
$q_1 > 1, q_2 > 1$	1	Mixture of $(B_1A)_n B_1$ with the residue of free B_2
	2	Mixture of $(B_1A)_n B_1$ with the residue of free B_1

^a1: A reacts first with B_1 . 2: A reacts first with B_2 .

coproduct; only a product of the polycondensation of the intermonomer with one of the comonomers will be formed while the other comonomer will remain in excess

The coproduct can be formed only in those cases where the intermonomer is in excess in relation to the comonomer used for carrying out the first step of the reaction.

Let us stipulate that in general, the products named in Table 1, such as $(B_1A)_n B_i$, are not identical to one another; such a designation is chosen only to show that a coproduct is formed. Naturally, for every case where the product includes both comonomers it is not difficult to find the distribution functions of sequences of the corresponding units.

Thus only in the range of the ratios of the reagents corresponding to a insufficient quantity of the intermonomer relative to the sum of the comonomers can we expect that, depending on whether it is a one-step or a two-step synthesis or on the procedure for carrying out the two-step synthesis, the microstructure of the chains of the products obtained will be different.

Hence there follows a direct conclusion that when carrying out a one-step synthesis with the participation of comonomers with different reactivities, the microstructure of the chains of the copolymers will depend on the relative reactivities of the comonomers only when conditions are created beforehand or occur in the course of the reaction, thus guaranteeing that the synthesis process is due to an insufficient quantity of the intermonomer in the reactive zone or volume. Such conditions can be created by gradually feeding the intermonomer in the homogeneous processes; in doing this it is clear that the average lengths of the sequences of units of each species and the distribution of these sequences will depend, to a large extent, on the rate of this gradual feeding. In the case of the interphase processes such conditions can be created by restricting the rate of the intermonomer diffusion toward the interface when there are no such restrictions for the comonomers. If, in this case, there are no restrictions for the diffusion of the intermonomer, then the differences in the rates of the diffusion of comonomers or the feeding procedure [12] may affect the microstructure of the copolymer chains. The spontaneous occurrence of such conditions in the course of the reaction can be connected with the development of microheterogeneity, and in these cases the appearance of differences in the copolymers obtained by the one-step and prepolymerization methods become quite probable.

ON THE POSSIBILITY OF INFLUENCE BY AN INCOMPLETE REACTION

At first glance it may appear that when using comonomers of different reactivities, in the case of an incomplete reaction, we can expect the

appearance of blocks formed by the more reactive comonomer in the reactive system, and as a result of this the formation of the blocks formed by the less reactive comonomer in the last steps of the reaction. However, as was convincingly shown earlier [5], in spite of the enrichment of the product in the first steps of the reaction by the more reactive monomer, the sequences of units of one species of greater length than those at the completion of the reaction (in this case their lengths and the distributions correspond to the "statistical" distribution) cannot be formed because in these steps the degrees of polycondensation of the product are not very high themselves, and the restriction of the lengths of the unit sequences is thus defined by the nature of the polycondensation process.

CONCLUSION

From the above it follows that when carrying out a statistical analysis of the processes of linear heterocopolycondensation at certain preset boundary conditions, it is possible, without using a kinetic approach which is complex in application to this situation, to draw rather interesting conclusions regarding the influence of the relative reactivities of the comonomers on the microstructure of the condensation copolymer chains and about the ways of utilizing the differences in the reactivities of the comonomers to affect this microstructure.

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