

Simulation of the Composition and Proportions of Anions in Polymerized Silicate Melts

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Abstract—A new statistical model is proposed for describing an equilibrium structure of polymer complexes in a silicate melt. The model makes it possible to calculate the molecular-mass distributions of polyanions of the general formula $(\text{Si}_i\text{O}_{3i+1-j})^{2(i+1-j)-}$, where i is the number of silicon atoms and j is the number of intramolecular closures of bridging bonds. The proposed model is implemented as the STRUCTON computer program (version 1.1, 2006) intended for calculating the composition and proportions of polyanions at different degrees of polymerization of the system. The executable code is implemented on personal computers. The distributions of Q^n structons, which are obtained experimentally from Raman and NMR spectroscopic data or evaluated theoretically, are used as input parameters for the computer program. The testing calculations are performed with the STRUCTON program for three arbitrary distributions of Q^n particles corresponding to different degrees of polymerization $0.25 \leq \alpha \leq 0.49$ for the model system containing 10^4 initial structons. The results of the statistical simulation have demonstrated that a limited ensemble of polymer complexes is formed in the system, so that the mean number of different types of complexes varies from 46 to 141. This result correlates with an increase in the mean size of anions from 1.87 to 8.60 and with a decrease in the total number of polymer particles from 5320 to 1166 in the aforementioned range of degrees of polymerization α .

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INTRODUCTION

Thermodynamic models accounting for the formation of molecular complexes (associates) that are in a reversible chemical equilibrium with unreacted oxides in melts and obey the law of mass action have been widely used in the modern theory of glass-forming melts [1]. The methods used for simulating these systems have been developed within the theory of associated solutions [2] and used to describe the mixing properties of metallurgically important oxide systems [3], as well as a number of alkali silicate and silicoborate systems (see, for example, [4, 5]). However, one of the main problems associated with the practical use of the models under consideration is a correct choice of an optimum set of chemical compounds that can allow one to describe adequately the behavior of more complex systems involving different combinations of metal oxides and complex-forming components, in particular, SiO_2 and Al_2O_3 . This problem cannot be solved using only data on physical properties of glasses or characteristics of simple phase diagrams. It is necessary to invoke structural chemical models that are based on the results of spectroscopic investigations of the structure of silicate melts and take into account the possibility of forming various complexes, including those with high

molecular masses. This implies the necessity of developing and analyzing models of polymer equilibria, which occur in silicate melts and lead to the formation of silicon–oxygen groups that differ substantially in the composition, size, charge, structure, etc.

In the 1960s–1970s, several approaches were proposed for the construction of the model of silicate liquids with allowance made for the dissociation of metal oxides in a melt,

$$Me_nO = nMe^{(2/n)+} + O^{2-}, \quad (1)$$

and the polycondensation of silicon–oxygen tetrahedra with the formation of high-dimension chain–ring structures

$$i(\text{SiO}_4)^{4-} = (\text{Si}_i\text{O}_{3i+1-j})^{2(i+1-j)-} + (i-1+j)\text{O}^{2-}, \quad (2)$$

where i is the polyanion size (the number of silicon atoms) and j is the number of intramolecular closures of Si–O–Si silicon–oxygen bonds [6–9]. These reactions lead to the formation of chain ($j=0$) and various cyclic (or ring, $j \geq 1$) structures. Their common feature is the assumption that the final number of polymer species and low-molecular products, i.e., O^{2-} ions, are in equi-

librium. The concentration (activity) of free oxygen ions O^{2-} is considered a characteristic of the basicity of the silicate melt [10–12] and plays an important role in the evaluation of the degree of polymerization of the silicon–oxygen matrix and the size distribution of anionic complexes. The knowledge of the size distribution of anionic complexes, i.e., their molecular-mass distribution [13], is crucial for evaluating the thermodynamic properties of silicate melts according to the theory of associated solutions [8, 14, 15].

A large number of attempts to calculate the molecular-mass distributions of complexes have been made with the use of statistical simulation methods [16, 17] and semiempirical models of anion equilibria, which were proposed for describing linear and branched chains [18–21], dominant linear ring structures [22], and different anionic complexes [23] with the inclusion of isomers [7, 8], as well as using molecular dynamics methods [24, 25]. Despite these numerous attempts, no satisfactory model that can provide a means for calculating the molecular-mass distribution of complexes has been offered to date [1, 4].

In this paper, we propose a new approach for calculating the molecular-mass distribution of anionic complexes in silicate melts and report on the results of the computations performed for melts with low and moderate degrees of polymerization up to the gelation point of the silicate liquid.

In our work, we use the notion of gelation. According to the *Large Encyclopedic Dictionary on Chemistry* [26], the gelation is defined as follows. Gelation is the transition of liquids to a solidlike state due to the appearance of a three-dimensional structural network in the bulk of the liquid. In polymer melts, the network is formed through chemical cross-linking of linear macromolecules as a result of three-dimensional polymerization or polycondensation of monomers. The instant of time when the reaction mixture loses fluidity due to the cross-linking of growing polymer chains is referred to as the gelation point.

MAIN PRINCIPLES OF THE SIMULATION OF A POLYANIONIC ENSEMBLE

Information on the distribution of silicon–oxygen tetrahedra with different numbers of singly bonded (terminal, nonbridging) and doubly bonded (bridging) oxygen atoms in a polymerized matrix is the input parameter of the model. These Si particles are termed Q^n structons ($0 \leq n \leq 4$) and correspond to structural units that form polymer complexes of different sizes [11, 26, 27]. The Q^4 structon is a monomer in which all four silicon–oxygen bonds are bridging. In the Q^3 , Q^2 , and Q^1 structons, the ratios between the bridging and nonbridging bonds are equal to 3 : 1, 1 : 1, and 1 : 3, respectively. The Q^0 quasiparticle, which involves four oxygen terminal atoms, is the sole structon that coin-

cides with the real anion, i.e., the SiO_4^{4-} monomer, in the polymerized matrix. The distribution (relative concentration) of Q^n structons can be measured using NMR and Raman spectroscopy [28–31]. In a number of cases, it has been assumed that the structon distribution can be described using a Bernoulli distribution [11, 16, 33]. This is equivalent to the assumption that the chemical bonds have the same reactivities and which has been usually used in kinetic models of growth of silicon–oxygen polymer chains [18–21].

In the framework of the model under consideration, a polymerized anion is treated as a random sequence of Q^n structons. The entire ensemble of anions is represented by a set of all possible polymers, i.e., random sequences of silicon–oxygen tetrahedra corresponding to a specified distribution of Q^n structons in the silicate matrix.

The number of O^{2-} ions in the polycondensed system depends on the chemical composition of the melt and the number of newly formed bridging bonds [see reaction (2)] and, hence, is uniquely determined by the distribution of Q^n structons for the melt of the given composition. This circumstance enables us to disregard the presence of free oxygen ions when simulating the ensemble of polyanions with the specified distribution of structons.

The algorithm for reconstructing polyanions can be developed using the sequential assembly of Q^n structons when, at each simulation stage, one Si–O–Si bond is formed according to reaction (2). It is evident that the Q^1 particle in the course of polymerization can form only one bridging bond. This “potentially bridging” bond will be called an unsaturated bond. The Q^2 , Q^3 , and Q^4 structons have two, three, and four unsaturated bonds, respectively. According to the formulated definition, the simulation of polyanions through the sequential assembly of the Q^n structons can be treated as a process of “saturation of unsaturated bonds.” The polymer particle in which all bonds are saturated will be referred to as the formed particle. Therefore, the simulation of the ensemble of polyanions in the melt is reduced to the sequential accumulation of polymers composed of Q^n structons with saturated bridging bonds. The Q^0 particle is the sole particle that does not form bridging bonds. This particle is interpreted as the SiO_4^{4-} ion and added to the model ensemble of polyanions as an independent structural units.

It should be noted that the model allows for the use of different distributions of Q^n structons in glass-forming melts as initial information and, thus, permits us to take into account that terminal oxygen atoms have different reactivities, which reflect in variations in the proportions of Q^n structons at a fixed ratio between the numbers of nonbridging and bridging bonds in the silicate melt [14]. The results of spectroscopic investigations of silicate glasses and melts provide a large

amount of experimental data on the distributions of Q^n structons [29–32].

ALGORITHM FOR SIMULATING THE MOLECULAR-MASS DISTRIBUTION OF POLYANIONS IN A SILICATE MELT

Let us now consider N initial monomers that are represented by Q^n structons distributed in the proportion $x_0 : x_1 : x_2 : x_3 : x_4$ ($x_0 + x_1 + x_2 + x_3 + x_4 = 1$). Obviously, the probability P_n that the next monomer during the process of assembly of the polymer sequence is a Q^n structon is equal to the relative fraction of the given structon; i.e., $P_n = x_n$. The first particle can appear to be a Q^0 monomer with a probability P_0 . If the first randomly occurring monomer is a Q^0 particle, the number of SiO_4^{4-} ions in the silicate melt becomes equal to unity. Subsequently, each occurrence of the Q^0 particle leads to an increase in the number of SiO_4^{4-} ions by unity. When the first occurring monomer is a Q^1 structon (the probability of the given event is P_1), this potential polymer fragment is unsaturated and the choice of the sequence of monomers will be continued. It is clear that the saturation of the bond of the Q^1 structon chosen at the first step is continued only after occurrence of a particle that also has unsaturated bonds. The probability of this event is $(1 - P_0)$, because the occurrence of the Q^0 monomer cannot result in the saturation of bridging bonds and its elimination from the reaction is accompanied by the increase in the number of SiO_4^{4-} ions in the silicate melt. As a consequence, the next monomer in the formed sequence can appear to be a Q^1 structon. The probability of this event for the second monomer in the sequence of reactants is $P_1/(1 - P_0)$. In this case, two unsaturated bridging bonds of two Q^1 structons form one saturated bond of the $\text{Si}_2\text{O}_7^{6-}$ dimer, which is a finished polymer particle (polyanion) and added to the ensemble of particles of the polyanion matrix. After formation of the saturated dimer (like any other particles with saturated bonds), the next polymer sequence will be formed. If the second monomer in the polymer sequence is a Q^2 , Q^3 , or Q^4 particle, the dimer formed as a result of the formation of one bridging bond is not saturated (there are one, two, or three unsaturated bonds) and the formation of a new polymer will be continued. However, when the second monomer in this sequence turns out to be a Q^2 structon and the third monomer is a Q^3 structon, the resulting trimer has no saturated bonds and should be interpreted as a $\text{Si}_3\text{O}_9^{6-}$ ion. The probability of formation of this ion is $P_1^2 P_2 / (1 - P_0)^2$.

In this model, the important constraint is imposed on the formation of polymers: two monomers in one

sequence can be linked together only by one bridging bond. The constraint is equivalent to the fact that the silicate tetrahedra cannot be shared by edges or faces. The silicate tetrahedra can be shared only by vertices. As a consequence, cyclic dimers $\text{Si}_2\text{O}_6^{4-}$ consisting of Q^1 and Q^2 particles or dimers $\text{Si}_2\text{O}_5^{2-}$ composed of two Q^2 particles cannot be formed. In a similar way, other metastable ring structures, such as trimers $\text{Si}_3\text{O}_8^{4-}$ and tetramers $\text{Si}_4\text{O}_{10}^{4-}$, are eliminated from consideration. A minimum cyclic polymer that can be formed in this case is a $\text{Si}_3\text{O}_9^{6-}$ ion consisting of three Q^2 structons. According to our model, this trimer is formed as a result of two sequential events: the formation of the unsaturated trimer that involves three Q^2 particles and has two unsaturated bonds and the subsequent closure (cyclization) due to the formation of the bridging bond between the first and third unsaturated monomers in the trimer. It is evident that the probability of the former event is $P_2^3 / (1 - P_0)^2$. A further behavior of the unsaturated trimer is possible in terms of our model: the trimer can either form the bond with anyone of the unsaturated Q^n particles (which remained in the reservoir of possible reactants) or undergo cyclization, i.e., the formation of the bridging bond between the first and third monomers. Obviously, the conditional probability of the sum of these two events is equal to unity.¹

When the Q^1 structon occurs as the next monomer in our sequence, it can combine with the unsaturated trimer in two ways (according to the number of unsaturated bonds), whereas the cyclization can proceed only in one way (see above). Under the assumption that the probabilities of formation of the bridging bond between any pairs of unsaturated bonds of Q^n structons are equal to each other, the probability of cyclization in the case of the occurrence of the Q^1 particle is equal to 1/3. In the case of the occurrence of the Q^2 particle, this probability is equal to 1/5, because two unsaturated bonds of this structon can form bridging bonds with two unsaturated bonds of the trimer in four ways. For the occurrence of Q^3 and Q^4 particles, the corresponding probabilities are equal to 1/7 and 1/9, respectively. Therefore, the probability of self-closure of the unsaturated bonds in the trimer with the formation of the $\text{Si}_3\text{O}_9^{6-}$ ion can be written in the form

$$P_{\text{Si}_3\text{O}_9^{6-}} = \frac{P_2^3}{(1 - P_0)^3} \left(\frac{1}{3} P_1 + \frac{1}{5} P_2 + \frac{1}{7} P_3 + \frac{1}{9} P_4 \right). \quad (3)$$

¹ The conditional or Bayesian probability is a probability of the occurrence of a given event when another event has already occurred. In our case, the latter event is the formation of the unsaturated trimer from three Q^2 particles.

Table 1. Representation of the compositions of chain and cyclic polymer complexes as sequences of Q^n structons

Linear and branched chains ($j = 0$)					Cyclic complexes ($j = 1$)				
Anion composition	Q^1	Q^2	Q^3	Q^4	Anion composition	Q^1	Q^2	Q^3	Q^4
$\text{Si}_2\text{O}_7^{6-}$	2	–	–	–	$\text{Si}_3\text{O}_9^{6-}$	–	3	–	–
$\text{Si}_4\text{O}_{13}^{10-}$	2	2	–	–	$\text{Si}_4\text{O}_{12}^{8-}$	–	4	–	–
	3	–	1	–		1	2	1	–
$\text{Si}_5\text{O}_{16}^{12-}$	2	3	–	–	$\text{Si}_5\text{O}_{15}^{10-}$	–	5	–	–
	3	1	1	–		2	1	2	–
$\text{Si}_6\text{O}_{19}^{14-}$	2	4	–	–		1	3	1	–
	3	2	1	–		2	2	–	1
$\text{Si}_7\text{O}_{22}^{16-}$	3	3	1	–	$\text{Si}_6\text{O}_{18}^{12-}$	–	6	–	–
	4	1	2	–		2	2	2	–
	4	2	–	1		1	4	1	–
	5	–	1	1		2	3	–	1
$\text{Si}_{10}\text{O}_{31}^{22-}$	5	2	3	–	$\text{Si}_8\text{O}_{24}^{16-}$	2	4	2	–
	3	6	1	–		3	2	3	–
$\text{Si}_{12}\text{O}_{37}^{26-}$	4	6	2	–		1	6	1	–
	5	5	1	1		4	1	2	1

Note: Only dominant low-molecular species are given. The formation of high-molecular complexes can be accompanied by the appearance of numerous isomers, which in the results of calculations will be represented by one chemical composition corresponding to the anions of the general formula $(\text{Si}_i\text{O}_{3i+1-j})^{2(i+1-j)-}$.

In the general case, if an unsaturated polymer has m unsaturated bonds that can form with each other k allowed bridging bonds, the probability of formation of the cyclic bond is represented as follows:

$$P_c = \frac{\frac{k}{m+k}P_1 + \frac{k}{2m+k}P_2 + \frac{k}{3m+k}P_3 + \frac{k}{4m+k}P_4}{1 - P_0}, \quad (4)$$

$$P_c < \frac{k}{m+k},$$

where P_c is the cyclization probability.²

Therefore, the proposed statistical model is reduced to random connections of all possible sequences of Q^n

structons by bridging bonds with the formation of linear, branched, or cyclic polymer complexes. Each sequence is constructed to the complete saturation of bridging bonds in the formed polymer structure with due regard for the constraint that a given pair of monomers can be linked only by one bridging bond. For the polymer sequence involving unsaturated monomers, the probability of self-closure is given by relationship (4) and the probability of growth of the sequence of Q^n particles (an increase in the polymer size) is defined by the expression

$$P_{Q^n} = \frac{nm}{nm+k}P_n, \quad (5)$$

where P_{Q^n} is the probability of growth of the polymer sequence through a Q^n monomer and the probability P_n corresponds to the mole fraction of Q^n structons in the initial system. Examples of a number of compositions of low-molecular species (including isomers) that can be constructed using the aforementioned statistical simulation are presented in Table 1.

² The proposed scheme of cyclization is not the sole possible scheme. In the framework of our approach, it is possible to consider one more mechanism according to which the probability of cyclization is determined by the ratio between the number of unsaturated bonds inside the polymer particle and the number of pairs formed by the unsaturated bonds of the given polymer particle with unsaturated bonds of other particles in the system. The probability of cyclization according to this mechanism is lower than that in the aforementioned mechanism.

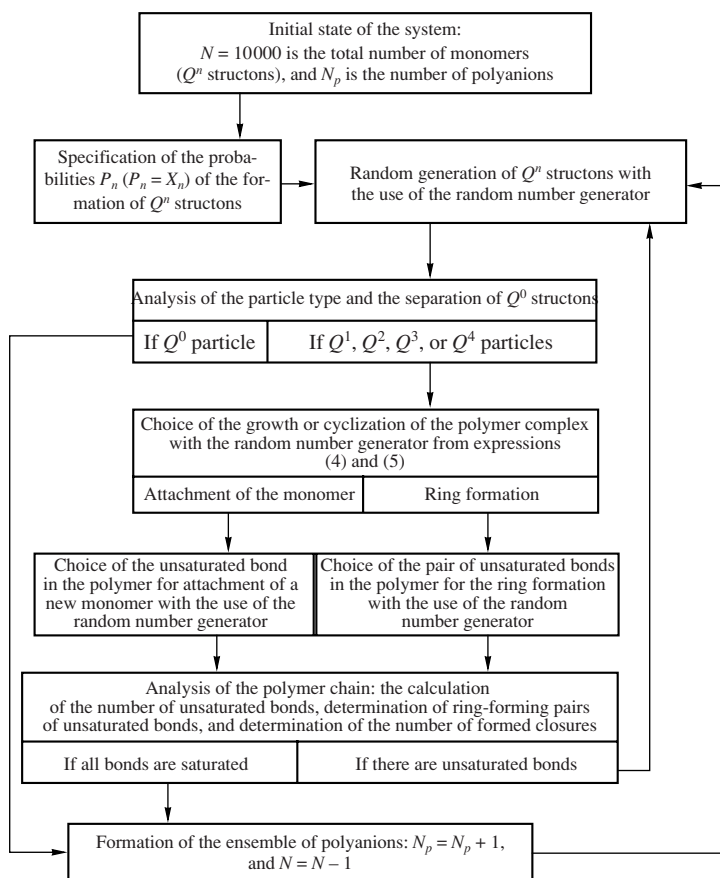


Fig. 1. Schematic flow chart of the STRUCTON computer program (version 1.1, 2006) developed for simulating the molecular-mass distributions of polyanions in silicate melts according to the specified distributions of Q^n particles.

COMPUTER IMPLEMENTATION OF THE MODEL

In order to perform practical calculations in the framework of the proposed stochastic model, we developed the computer program STRUCTON with the use of the Monte Carlo method. The program flow chart is shown in Fig. 1. The calculations according to this program are carried out using a standard generator of (pseudo)random numbers. This generator is included in the software of the high-level language Borland Pascal and uniformly generates in the interval from 0 to 1 in the number axis. The generator allows one to simulate easily a discrete random quantity ξ that takes on values ξ_n ($n = 0, 2, \dots, 4$ in accordance with the number of Q^n structons) with probabilities P_0, P_1, \dots, P_4 . For this purpose, the interval $[0, 1]$ was divided into five segments each P_n in length. A number between 0 and 1 was obtained with the use of the random number generator. The value of ξ_n was assigned to the random quantity depending on the number n of the segment containing the obtained random number. This simple procedure provided the basis of the applied method.

The initial stage of calculations with the STRUCTON program involved the specification of the relative proportions of Q^n structons in the system. The found probabilities P_n were used for generating a random number determining the occurrence of the Q^n particle (Fig. 1). If the first structon was a Q^0 monomer, the number of SiO_4^{4-} ions in the simulated melt was increased by unity. When the first structon was an unsaturated Q^n particle, the number of unsaturated bonds in the polymer chain was calculated and a random number was generated so that it took on one of the two values corresponding to the cyclization or attachment of a new Q^n monomer. The probabilities of ring formation [expression (4)] and increase in the size of the polymer complex [relationship (5)] are equal to $k/(nm + k)$ and $nml/(nm + k)$, respectively. At the next stage, the pairs of unsaturated bonds closed inside the polymer and unsaturated bonds to which a new Q^n particle was attached were simulated under the assumption that the probabilities of formation of bridging binds by any pair of unsaturated bonds of Q^n structons are identical to each other. Upon saturation of all bonds in the polymer chain, i.e., after completion of formation of the

polyanion, the composition [formula (2)], size, and charge of this polyanion were written in a special file. Correspondingly, the number of polymer particles was increased $N_p = N_p + 1$, and the number of potential Q^n structons in the initial reservoir was decreased by unity $N = N - 1$. The calculations were terminated at the current value $N = 0$.

The above scheme of computations (Fig. 1) characterizes one model calculation (one realization) at the specified distribution of Q^n structons. With due regard for the probabilistic character of the model, it is necessary to perform the corresponding calculations at least several tens of times by evaluating the reproducibility and statistical parameters of the calculated distributions. In the testing calculations described below, we carried out 50 these realizations for each distribution of Q^n structons. Taking into account that the number of initial Q^n monomers used in each realization is $N = 10000$, the final results of the simulation of the molecular-mass distributions can be treated as those obtained for 500000 Q^n structons. The corresponding update of the random number generator was performed using the procedure "randomization" after each 10000 steps.

RESULTS OF THE SIMULATION

Three variants of the distribution of Q^n particles corresponding to the condition $2Q^1 + Q^2 > Q^3 + 2Q^4$ (Table 2) were chosen for testing calculations. This condition ensures that the number of nonbridging oxygen bonds exceeds the number of Si–O–Si bonds and the system does not reach a gelation point at which polymer sequences are characterized by unlimited growth (see below). As a result of $3 \times 50 = 150$ realizations, we succeeded in simulating a large number of states from the state containing predominantly SiO_4^{4-} monomers and a small number of $\text{Si}_2\text{O}_7^{6-}$ ions (variant I) to a strongly polymerized matrix involving more than one hundred of species of silicon–oxygen particles (variant III). A variety and reproducibility of model ensembles and the relative concentration of polyanions are illustrated by Table 3, which is constructed using the results of calculations for the first distribution of Q^n structons (Table 2). The calculations simulate a moderate degree of polymerization of the system, in which the SiO_4^{4-} ions ($i = 1, j = 0$) amount to approximately 40% of model particles and the other particles are contained in complexes. These particles, together with SiO_4^{4-} monomers, form, on average, 5320 ± 34 particles from each 10^4 initial structons. Therefore, the mean mole fraction of SiO_4^{4-} ions among polyanions is approximately equal to 0.75 ($\sim 0.40 \times 10000/5320$). The concentration of the other chain and ring structures decreases progressively with an increase in the polyanion size i and the number of cyclizations j (Table 3).

Table 2. Variants of relative proportions (distributions) of Q^n structons in testing calculations

Structon type	Variant I	Variant II	Variant III
Q^0	0.40	0.15	0.05
Q^1	0.30	0.45	0.30
Q^2	0.20	0.25	0.35
Q^3	0.10	0.10	0.25
Q^4	–	0.05	0.05
Characteristics of the model ensembles of anions			
Polymer species	46 ± 3	74 ± 4	141 ± 10
Mean number of particles	5320 ± 34	3210 ± 41	1166 ± 59
Mean anion size	1.87 ± 0.01	3.12 ± 0.04	8.60 ± 0.44

Note: The mean parameters were estimated from the results of 50 realization, and each realization involved 10^4 structons. The standard deviations correspond to $\pm 1\sigma$.

The variance of the model concentration of polymers can serve as a measure of "stability" of model ensembles. This variance is calculated as the standard deviation (1σ) estimated for each particle species from the results of 50 calculations and normalized to the corresponding mole fraction (in Table 3, these values are given in parentheses). For dominant low-molecular species ($i \leq 8, j \leq 1$), the standard deviations of the calculated quantities vary from 0.6% (for SiO_4^{4-} ions) to 21.3% ($\text{Si}_8\text{O}_{24}^{16-}$ rings). In this case, the accuracy in the simulation of chain structures is, on average, higher than that of ring structures. This circumstance is in agreement with the general tendency of statistical calculations: the higher the mean concentration of anions, the higher the reproducibility of this concentration according to the results of the simulation. The standard deviations for high-molecular complexes with a content of $\sim 10^{-4}$ of the total number of particles, as a rule, lie in the range 100–300%.

Similar inferences can be made from the analysis of the results of calculations for the second variant of the distribution of Q^n structons (Table 4). In this case, the ensemble with a larger number of various anions involves SiO_4^{4-} monomers and 130 chain and ring structures, which appeared no less than four times in the given series of calculations. It should be noted that these complexes include the entire variety of polymers observed in the simulation for 500000 particles. This variety is never reproduced in practical calculations of one polymer sequence at $N = 10^4$. According to the results of 50 calculations, the mean number of polymer species is equal to 74 ± 4 . A higher degree of polymerization is responsible for the decrease in the total number of particles from 5320 to 3210 and the increase in

Table 3. Mole fractions of anionic complexes and their variances according to the results of 50 calculations for the first distribution of Q^n structons (Table 2, variant I)

Anion size i	Number of closures (cyclizations) j of intramolecular bonds			
	$j = 0$ (chains)	$j = 1$	$j = 2$	$j = 3$
1	0.751894(0.62)			
2	0.063264(5.8)			
3	0.041642(6.0)	0.004861(20.2)		
4	0.030698(8.9)	0.009247(12.2)	0.000951(53.4)	0.000034(265.3)
5	0.021107(10.7)	0.008027(15.6)	0.001015(42.6)	0.000026(319.5)
6	0.014006(12.3)	0.006685(16.1)	0.000778(53.9)	0.000045(196.3)
7	0.009017(14.1)	0.004685(21.0)	0.000688(55.3)	0.000030(229.1)
8	0.005655(18.9)	0.003583(21.3)	0.000706(48.6)	0.000045(177.9)
9	0.003512(21.2)	0.002485(26.7)	0.000575(55.9)	0.000053(202.5)
10	0.002440(27.1)	0.001781(30.1)	0.000481(61.7)	0.000038(244.9)
11	0.001519(34.8)	0.001248(38.0)	0.000425(58.5)	0.000049(200.7)
12	0.001046(46.5)	0.000839(45.1)	0.000278(87.7)	0.000045(177.9)
13	0.000669(55.1)	0.000526(58.9)	0.000248(81.0)	0.000053(160.3)
14	0.000380(71.1)	0.000376(67.9)	0.000139(96.6)	0.000049(168.7)
15	0.000214(89.3)	0.000263(80.7)	0.000109(129.4)	0.000026(286.0)
16	0.000135(118.1)	0.000150(93.6)	0.000075(150.0)	0.000026(286.1)
17	0.000098(134.7)	0.000139(145.3)	0.000113(129.1)	0.000015(339.1)
18	0.000087(152.0)	0.000049(185.1)	0.000023(317.8)	
19	0.000049(168.7)	0.000068(173.5)		
20	0.000038(200.0)	0.000026(247.8)	0.000030(229.1)	
21	0.000019(300.0)	0.000019(300.0)	0.000038(244.8)	
22		0.000015(339.1)	0.000026(319.5)	

Note: The variances are given in parentheses and represent the standard deviations ($\pm 1\sigma$) expressed in percent of the molar concentration. There are 73 complexes that appeared no less than four times in the series of calculations involving 50 realizations (the total number of Q^n structons is equal to 0.5×10^6). The number of anion species observed in each realization is, on average, equal to 46 ± 3 , and the mean number of polymer particles amounts to 5321 ± 34 .

the mean polymer length from 1.87 to 3.12 (Tables 2–4). One more important observation following from the examination of the data listed in Tables 3 and 4 concerns a finiteness of the ensemble of polyanions. This manifests itself in a limited chain length ($i \leq 23$) and a limited size of ring complexes, which are truncated polymer sequences decreasing with an increase in the number of cyclizations j . As was noted above, the main factor responsible for the limitation of the maximum size of chain anions is the self-closure of terminal oxygen atoms, whereas the factor hindering the cyclization (especially, in the case of small-sized species) is asso-

ciated with the fact that silicon–oxygen tetrahedra cannot be shared by edges and faces.

The dependences of the content of polymer chains ($j = 0$) and complexes with different degrees of cyclization ($1 \leq j \leq 4$) on the polyanion size i according to the data presented in Table 4 are plotted in Fig. 2. It is worth noting that the concentration of high-molecular anions gradually decreases in the case of chain structures, whereas the distribution curves for ring complexes exhibit maxima. The “peak” distributions of ring complexes at $j = 4$ reflect a statistical character of the method and that a number of 0.5×10^6 initial structons

Table 4. Mole fractions of anionic complexes according to the results of 50 calculations for the second distribution of Q^n structons (Table 2, variant II)

Anion size i	Number of intramolecular closures j (cyclizations) of bonds					
	$j = 0$ (chains)	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$
1	0.465760					
2	0.160941					
3	0.088948	0.005250				
4	0.055388	0.008118	0.000417			
5	0.039258	0.010479	0.001156	0.000062		
6	0.026776	0.010370	0.001443	0.000193		
7	0.018875	0.009172	0.001727	0.000206	0.000025	
8	0.012355	0.007884	0.001995	0.000274	0.000031	
9	0.008190	0.006434	0.001632	0.000336	0.000044	
10	0.005774	0.004819	0.001692	0.000398	0.000056	
11	0.003927	0.004148	0.001673	0.000393	0.000100	
12	0.002607	0.003023	0.001252	0.000392	0.000050	
13	0.001719	0.002268	0.001165	0.000386	0.000081	
14	0.000964	0.001677	0.001091	0.000392	0.000087	
15	0.000853	0.001310	0.000861	0.000336	0.000068	0.000025
16	0.000612	0.000910	0.000710	0.000317	0.000069	
17	0.000318	0.000680	0.000654	0.000236	0.000094	
18	0.000380	0.000561	0.000556	0.000237	0.000031	
19	0.000174	0.000444	0.000386	0.000212	0.000087	0.000038
20	0.000075	0.000249	0.000324	0.000187	0.000099	
21	0.000050	0.000261	0.000268	0.000131	0.000050	0.000043
22	0.000062	0.000119	0.000132	0.000143	0.000075	
23	0.000063	0.000112	0.000118	0.000137	0.000031	0.000025
24		0.000094	0.000168	0.000100	0.000063	
25		0.000088	0.000081	0.000125	0.000050	
26		0.000050	0.000081	0.000063	0.000044	
27		0.000050	0.000044	0.000037		
28			0.000044	0.000062	0.000038	
29					0.000031	
30		0.000025	0.000025			
31				0.000025		

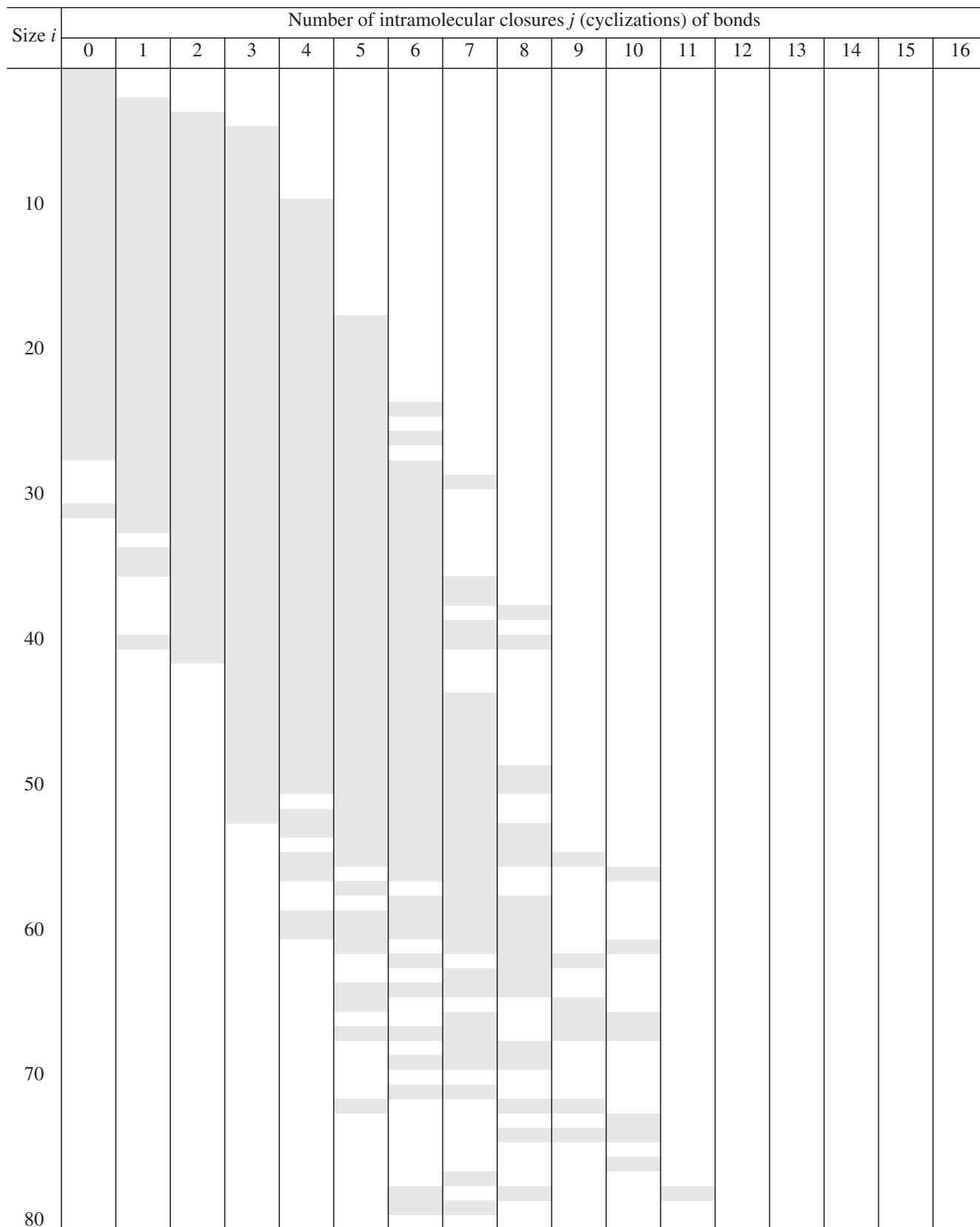
Note: There are 131 complexes that appeared no less than four times in the series of calculations involving 50 realizations (the total number of Q^n structons is equal to 0.5×10^6). The number of anion species observed in each realization is, on average, equal to 74 ± 4 , and the mean number of polymer particles amounts to 3210 ± 41 .

is insufficient for a good reproduction of the results at mole fractions of $\leq 10^{-4}$.

As the gelation point of the silicate liquid is approached, the total degree of polymerization of the

system increases rapidly. As a rule, the degree of polymerization is expressed as the ratio between the number of bridging bonds and the total number of oxygen bonds in the silicate matrix; that is,

$$\alpha = (Q^1 + 2Q^2 + 3Q^3 + 4Q^4) / [4(Q^1 + Q^2 + Q^3 + Q^4)]. \quad (6)$$

Table 5. Ensemble of polymer anionic complexes according to the results of 50 calculations for the third distribution of Q^n structons (Table 2, variant III)

Note: There are 131 complexes that appeared no less than four times in the series of calculations involving 50 realizations (the total number of Q^n structons is equal to 0.5×10^6). Moreover, the calculations revealed 14 particles of size $81 \leq i \leq 139$ corresponding to $9 \leq j \leq 16$.

Table 6. Example of a separate calculation and mean characteristics of the model ensembles for variant **III** (Table 2)

Fifth calculation (among 50)					Mean parameters of anion distribution				
Particle	Number	x , mole fractions	Mean charge	Mean size	Particle	x , mole fractions	($\pm 1\sigma$)	Mean size	($\pm 1\sigma$)
SiO ₄	429	0.37599	-4.0	1.00	SiO ₄	0.4281	0.0187		
		Chains					Chains		
Si ₂ O ₇	212	0.18580			Si ₂ O ₇	0.1750	0.0154		
Si ₃ O ₁₀	101	0.08852			Si ₃ O ₁₀	0.0696	0.0084		
Total	461	0.40403	-9.7	3.87	Total	0.3683	0.0185	3.78	0.17
		Rings					Rings		
Si ₃ O ₉	2	0.00175			Si ₃ O ₉	0.0054	0.0020		
$j = 1$	110	0.09641	-22.2	11.12					
$j = 2$	59	0.05171	-32.1	17.05	Total number of rings ($j = 1$)	0.0845	0.0119	9.66	0.66
$j = 3$	21	0.01840	-47.8	25.91					
$j = 4$	11	0.00964	-53.3	29.64					
$j = 5$	11	0.00964	-61.6	34.82	Remaining rings ($j \geq 2$)	0.1191	0.0123		
$j = 6$	6	0.00526	-98.0	54.00					
$j = 7$	6	0.0526	-101.7	56.83					
$j = 8$	4	0.00351	-108.0	61.00					
$j = 9$	1	0.00088	-116.0	66.00	Total	1.00000		8.60	0.44
$j = 10$	5	0.00438	-152.0	85.00					
$j = 11$									
$j = 12$	1	0.00088	-278.0	150.00					
$j = 13$	2	0.00175	-151.0	87.50					
$j = 14$	3	0.00263	-200.0	113.33					
$j = 15$	1	0.00088	-236.0	132.00					
$j = 16$	1	0.00088	-206.0	118.00					
Total	1141	1.00000	-18.0	8.76					

Note: In separate calculations for the specified distribution of Q^i structons, there appear single high-molecular species of size $i \geq 1000$ with a number of closures $j \geq 100$. This indicates the approach of the gelation point, at which polymer complexes are characterized by unlimited growth.

For the third variant of calculations, the degree of polymerization is $\alpha = 0.4875$ (Table 2). This means that almost half the silicon–oxygen bonds is represented by Si–O–Si bridging bonds, which allow for an unlimited growth of polymer complexes and the formation of high-dimension structures. In this case, the tabular and graphical representations of the total distribution of model anions are complicated by the presence of high-molecular complexes of size $i \geq 50$ and a small number of polymer particles involving up to 1500 silicon atoms. For this reason, the mole fractions of individual anions are not given in Table 5, which illustrates the total distribution of particles of size $i \leq 80$. This model ensemble should be complemented by high-molecular

structures, such as the Si₂₆₅O₇₆₂⁴⁶⁴⁻, Si₄₁₃O₁₁₉₇⁷⁴²⁻, Si₁₀₀₉O₂₉₃₄¹⁸³²⁻, or Si₁₃₉₅O₄₀₃₅²⁴⁹⁰⁻ particles. Apparently, in this case, it is possible to analyze the initial stages of unlimited growth of polymer structures, i.e., the onset of gelation.³ The formal representation and the evaluation of weighted-mean characteristics of similar model ensembles are possible in terms of the approach developed by Esin [7, 8], who proposed to use the summation of polyanions in the sequence corresponding to the

³ In our model, the gelation point corresponds to $\alpha = 0.5$, which is in agreement with the data obtained in [9, 18–20].

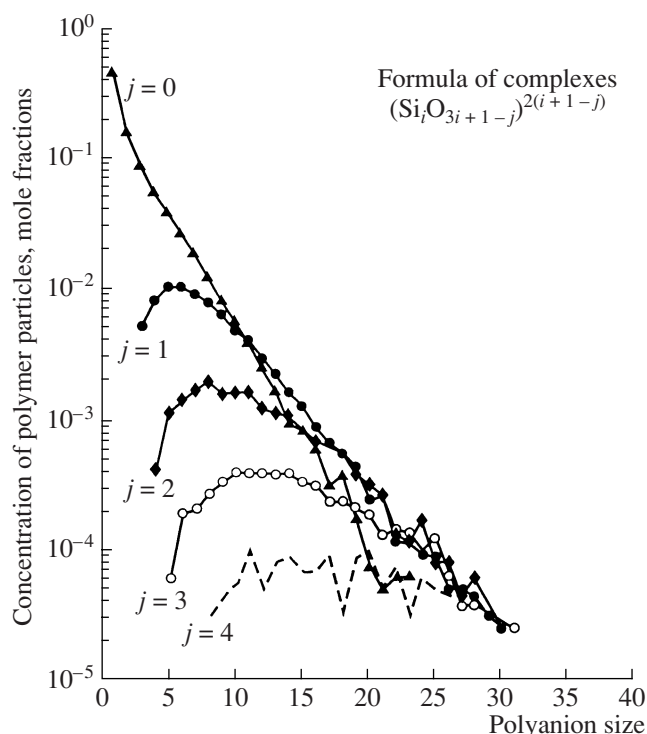


Fig. 2. Molecular-mass distributions of chain ($j = 0$) and ring ($1 \leq j \leq 4$) complexes according to the results of 50 calculations with the STRUCTON program for variant II of the distribution of Q^n structons (Table 2). The total ensemble of anions involves, on average, 3210 ± 41 polymerized particles (from 10^4 initial Q^n structons) representing more than 130 different complexes of size $1 \leq i \leq 31$. The presence of isomers (Table 1) is implicitly taken into account by calculating the mean concentration of polymers of a specific composition [relationship (2)] irrespective of their geometry.

same number of cyclizations j (see vertical columns in Tables 3–5). This permits one to compare more correctly the results of calculations at moderate (Fig. 2) and high degrees α of polymerization of the system [relationship (6)]. The results of this extension for one of the calculations for the third variant of the distribution of Q^n structons (the fifth realization characterized by the absence of formation of strongly polymerized complexes is chosen among 50 realizations) are presented in the left-hand side of Table 6. The results of statistical processing for all 50 realizations are listed in the right-hand side of Table 6. It can be seen from Table 6 that the method used for generalizing structural chemical information virtually does not affect the accuracy in the reproducibility of SiO_4^{4-} monomer and chain polymer species dominant in the concentration.

CONCLUSIONS

Thus, a new statistical model was proposed for describing an equilibrium structure of polymer anionic

complexes with the use of a specified number and a known distribution of Q^n structons in silicate melts. The model is based on the representation of polyanions as a sequence of Q^n particles, i.e., monomers with different numbers of bridging bonds ($1 \leq n \leq 4$). In the framework of the model, an ensemble of polyanions is described as a set of all possible linear, branched, and cyclic silicon–oxygen polymer structures. Relationships were proposed for calculating the probability of growth and intramolecular cyclization of polymers as a function of the content of Q^n structons of different types. In this case, the constraint is imposed on the sequence of the interaction of Q^n structons: two monomers can be linked together only by a Si–O–Si bond. The constraint is equivalent to the fact that the silicate tetrahedra cannot be shared by edges or faces.

The proposed statistical model was used to develop an algorithm for calculating the molecular-mass distributions of silicate complexes of the general formula $(\text{Si}_i\text{O}_{3i+1-j})^{2(i+1-j)-}$. According to this algorithm, the structure of silicon–oxygen complexes is simulated by saturating unsaturated bonds in the course of sequential assembly of a polymer particle from randomly chosen Q^n structons. The polymer particle with all saturated bonds is treated as a finished particle and added to the model ensemble of polyanions. The Q^0 structons are interpreted as SiO_4^{4-} ions and considered an independent species of particles in the final ensemble of silicate complexes. Within the given algorithm, the simulation of the molecular-mass distribution of complexes is performed using a random number generator and represents a variant of the statistical Monte Carlo method.

The algorithm for simulating the molecular-mass distributions of polyanions was implemented in the form of the STRUCTON computer program (version 1.1, 2006) intended for calculating the composition and proportions of polyanions at different degrees of polymerization of the system up to the gelation point of the silicate liquid. The executable code was implemented on personal computers. The input parameters of the program are specified distributions of Q^n structons. The distributions can be obtained experimentally (from Raman and NMR spectroscopic data) or calculated theoretically. The special option of the STRUCTON program makes it possible to calculate the molecular-mass distributions of polyanions in terms of the equal reactivity principle with the use of the relative fraction of nonbridging oxygen bonds as the input parameter [34].

The testing calculations were performed for three initial distributions of Q^n particles corresponding to different degrees of polymerization $0.25 \leq \alpha \leq 0.49$ for the model system containing 10^4 initial structons. The results of the statistical simulation of the equilibrium distribution of anions demonstrated that a limited ensemble of polymer complexes is formed in the system, so that the mean number of different species of

complexes varies from 46 to 141. This correlates with an increase in the mean size of anions from 1.87 to 8.60 and a decrease in the total number of polymer particles in the model system by a factor of more than four (from 5320 to 1166).

The proposed statistical model and the first results of the simulation of the molecular-mass distribution of polyanions can be considered the first step on the road to the construction of a more universal program that provides a way of simulating polymer equilibria outside the gelation point and in the presence of other complex-forming components. The possibility of combining the given algorithm with the formalism of the theory developed by Toop and Samis [35] for $MeO-Me_2O-SiO_2$ systems enables one to estimate the mole fraction of O^{2-} ions in the anion matrix for silicate melts with different sets of modifier cations [34].

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