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Computer simulation of polymer networks: mesoscopic heterogeneity of the structure and topological parameters

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Samples of networks of reacting bi- and trifunctional monomers have been obtained by the dynamic Monte Carlo method for the two dimensional lattice model. Systems with various densities and numbers of chemical junctions have been studied. The steady-state structural factor, the number of the degree of conversion, and topological parameters of samples appear to depend strongly on the initial (random) spatial configuration and the size of the Monte Carlo base cell. Deviations of structural parameters calculated by ensemble and time averaging are statistically significant, which makes it possible to classify networks of this type as so-called non-ergodic fortuitous media that exhibit this property for scales of ~10^2 nm. Newly developed facilities for topological analysis allow one to observe the kinetics of changes in individual components of the system: trees, circuits, and other more complex structures.

Key words: polymeric networks, Monte Carlo method, structural heterogeneity, topological parameters.

Polymeric networks obtained in polymerization or polycondensation reactions are always characterized in fact by heterogeneities of chemical composition, molecular mass distribution, and spatial structure. These heterogeneities are usually considered as an undesirable factor, which exerts a negative effect on mechanical properties, although there are exceptions. For example, microheterogeneities of the structure of cross-linked polymers can play an important role in processes of controlled transport of low- or high-molecular substances through networks (in particular, for gel electrophoresis). In the latter case, the preparation of materials with optimum parameters requires studying the reasons for the appearance of network heterogeneities and the development of

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facilities for controlling them. The reasons for the appearance of network heterogeneities are still unclear.[1] Proceeding from modern theoretical views, the maximum spatial scale for structural heterogeneities should not exceed the mean size of the network cell (it corresponds to several nanometers for close-linked systems). However, the recent precision experiments on light scattering and small-angle neutron scattering[2] unambiguously indicate that there are structural heterogeneities of considerably large scale corresponding to tens or even hundreds of nanometers.

In this work, we tried to study some regularities of the appearance of heterogeneities in polymeric networks during their chemical synthesis by the Monte Carlo method using a rather simple model.

Model and method of calculation

The use of traditional lattice models for studying the formation and properties of thick cross-linked polymers encounters nearly invincible calculation difficulties due to the restricted freedom of movement of chain regions, which participate in the formation of chemical junctions. Therefore, we used a special model without this disadvantage. The so-called model of the chain with fluctuating bonds[3] is used as the prototype; it assumes that lengths of chemical bonds between particles (atoms) are not fixed and can change their values within a certain interval. Like usual lattice models, each lattice point can contain only one particle. However, in this case, any particle that occupies a lattice point makes inaccessible for other particles all adjacent points that belong to the first coordination sphere (it is evident that the number of these points is equal to eight for the quadratic lattice). The movement of particles is controlled by the Monte Carlo method: a randomly chosen particle can "jump" to any of the adjacent eight points (at the distance of 1 or $\sqrt{2}$ of the lattice constant) with an equal probability of 1/8. However, if this point is occupied or the conditions implied by the maximum possible chemical bond length are not fulfilled, the particle remains at the original position. It is noteworthy that in the initial model[3] the particle moves only the unit distance, which makes the system as a whole less mobile and, hence, less suitable for studying networks. It is evident that the minimum chemical bond length corresponds to two lattice constants. Since we used the two-dimensional quadratic lattice, it is easy to understand from the geometric considerations that the maximum allowable bond length is the $\sqrt{13}$ lattice constants. Exceeding this value does not fulfill the condition of chain self-noncrossing and does not retain the network topology. It should be mentioned that the model considered does not result in artifacts, which appear when bonds of fixed length are used in standard lattice algorithms, and is very efficient for computer calculations due to its discrete nature (in this case, all calculations can be based on integer arithmetic). It should also be noted that comparing our model to real polymers one should keep in mind that each molecule in this case corresponds not to an individual atom or repeating unit of a macromolecule, but to the statistical segment of the chain, which consists of ~10 units in typical cases.

A single attempt of the particle to move is called the Monte Carlo microstep. From the dynamic viewpoint, the unit ("quantum") time is the number of attempts (both successful and unsuccessful) of moving all particles of the system modelled. In further considerations, time τ will be measured in these standard units, which we call the Monte Carlo step (MCS).

Bi- and trifunctional monomers consisting of two and three particles and including two and three chemical bonds, respectively, are used as initial reacting molecules (three particles bonded to a chemically inert, but also mobile, central particle are reactive in the second type monomers, which are three-rayed "stars"). In further discussions, these monomers will be denoted as d and t. It is assumed that when two unbound reactive groups during their movement over the lattice get into points separated by the minimum possible "chemical distance," the chemical bond between them appears immediately and is retained for the whole subsequent time.

In the model considered, only steric (volume) repulsion forces act between any two unbound particles due to the fact that particles cannot be spatially superimposed; in other words, we model athermal conditions without any thermal effects.

The initial number of functional groups per one particle is determined as

$$f = \frac{2N_d + 3N_t}{N_d + N_t},$$

where N_d and N_t are specified numbers d and t of monomers. Chemical reactions between functionally active groups result in the association of monomers in larger structures, and the number of functional groups correspondingly decreases with time τ. The degree of conversion

$$k(\tau) = \frac{f(0) - f(\tau)}{f(0)},$$

which is the time function varying from 0 to 1 is a convenient parameter of this process.

All particles are localized in the base quadratic cell with the specified length L of the edge (lengths will be expressed in units of the lattice step). Usual periodic boundary conditions are applied on the cell. The numerical mean density of particles in the system is determined as $\rho = 4(2N_d+4N_t)/L^2$, where the factor of 4 appears due to the intrinsic quadruple volume of each particle. The majority of calculations are performed at $L = 128$, $N_d = 512$, and $N_t = 128$; in this case $f(0) = 2.2$.

Each sample of the network is generated at three stages:

1. The specified number of monomers is randomly (but in such a way that no steric conflicts appear be-

tween particles) arranged within the base cell. Then the system is homogenized, *i.e.*, local concentrations of monomers are equalized due to diffusion without chemical reactions between them.

2. The reaction between d-monomers (the d+d type), which provides the growth of linear chains and simple circuits, is switched on. Monomers t remain chemically inert and participate only in the overall diffusion process. This stage is completed after a twofold decrease in the number of functional groups, *i.e.*, when $k = 0.5$ is achieved.

3. Trifunctional monomers enter the reaction at the final stage. They play the role of a linking agent for chains, but do not react themselves. Thus, d+d and d+t type reactions occur in the system. The reaction is ceased when the limiting degree of conversion is achieved, *i.e.*, at approximately a constant value of k. This usually requires a time of $\sim 10^4$ MCS.

Each sample of the network prepared by the method described above is subjected to prolonged relaxation before the calculation of structural parameters. Only after this the required structural parameters are determined (as the average over rather long time of $\sim 10^4$ time steps). This procedure is called the time averaging for individual realization (for a given sample of the network). Repeating of all stages considered above at different positions of monomers in the cell gives another sample of the system. An averaging over the set s of similar independent realizations is the averaging over the selected ensemble of the model system (ensemble averaging).

Results and Discussion

To describe structural and topological parameters of networks, we have developed special analytical procedures.

Let us consider some topological parameters of the system. Structures of various types can appear during reactions involving bi- and trifunctional monomers. The simple classification in terms of the theory of graphs allows one to classify these structures as trees (open chains are also considered as trees), circuits (simple and complex, *i.e.*, containing one and more internal bridges), and mixed structures called "lattice animals." At each instant the maximum population of bound particles can be found in the system, *i.e.*, it is a cluster of the maximum size. When this cluster is extended to the whole cell, it is reasonable to identify it to the gel fraction, and the remaining fragments are identified to the sol fraction. We have developed theoretical graph methods for analysis, which make it possible to identify any of structural types mentioned. In addition, the calculations of so-called topological indices have been performed for all structures to describe quantitatively topological properties in the integral form. In particular, we have determined the cyclomatic rank *Ci* (the number of trivial contours in the combined circuit) and the Wiener index *Wi* (which is equal to the half-sum of the shortest distances between all pairs of particles in a given graph).[4] Of course, topological properties of the two-dimensional model considered strongly differ from those of real three-dimensional systems; nevertheless, there are all grounds to believe that the two-dimensional model reflects correctly general regularities of the behavior of the system.

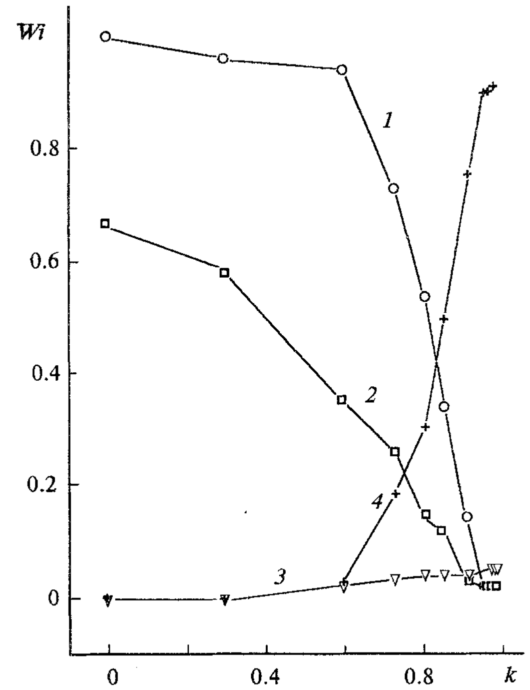
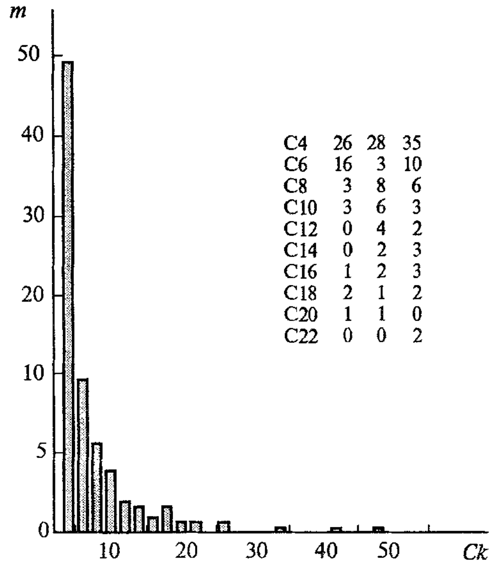


Fig. 1. Kinetic dependences of the relative mass content of trees (*1*), chains (*2*), circuits (*3*), and other more complex structures (*4*) for the system at $L = 128$, $N_d = 512$, and $N_t = 128$.

Let us consider some examples of calculation of topological parameters. Figure 1 presents the relative "mass" content, *Mi*, of structures of different types as a function of the degree of conversion k (the value of *Mi* is proportional to the content of the given ith structure in the mixture and to the number of particles, n_i, which compose the mixture). It can be seen that the content of open chains and trees decreases rapidly as the chemical reaction occurs. At the same time, the number of simple circuits increases, although their relative fraction always remains small, because the majority of chains does not close up and succeeds to bind to trifunctional monomers. All structures mentioned enter the sol fraction. At $k > 0.6$ the fraction of complex structures increases impetuously (the cluster of maximum size grows as well).

Typical histograms of distribution over the number of structures of different types in the system of reacted monomers are presented in Figs. 2 and 3. Figure 2 corresponds to three independent realizations for the system, which in the initial state consists only of dimers. Of course, only chains and simple circuits are present in this case, and compositions of the mixture do not differ



C4	26	28	35
C6	16	3	10
C8	3	8	6
C10	3	6	3
C12	0	4	2
C14	0	2	3
C16	1	2	3
C18	2	1	2
C20	1	1	0
C22	0	0	2

Fig. 2. Histogram of distribution over the number of simple circuits in the reacted system of dimers. The numbers of circuits of the given size (*Ck*) for three independent calculations at L = 128 and N_d = 1030 are indicated, *m* is the number of circuits.

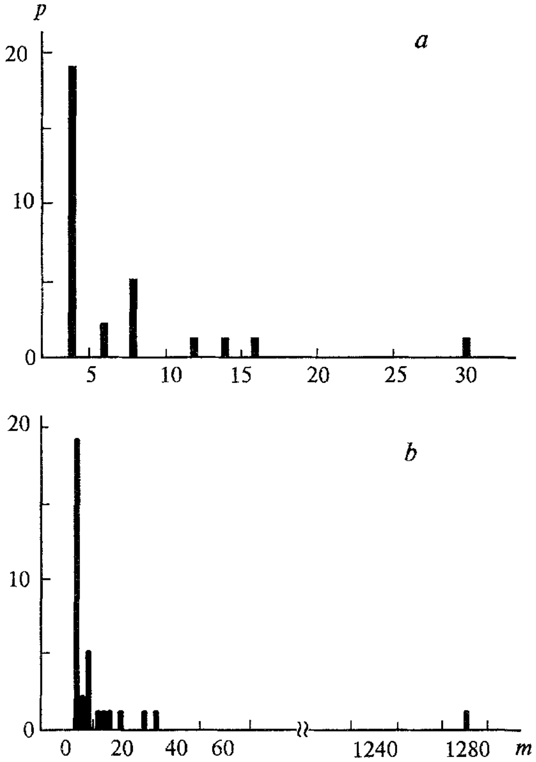


Fig. 3. Histograms of distribution over the number of structures of different types (*a*, simple circuits; *b*, trees and other complex structures). The calculations are performed at L = 128 for the 512d+128t systems (*p* is the number of structures, *m* is the number of particles).

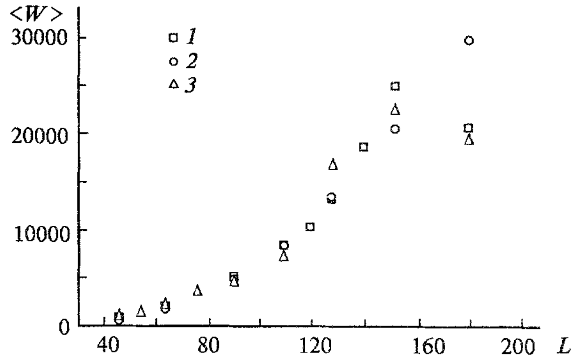


Fig. 4. Dependence of the mean value of the partial Wiener index <*W*> on the size of the base cell *L*. Three examples at different values of *f*(0) are considered: *1*, 2.2; *2*, 2.306; and *3*, 2.091.

too much in repeated realizations for fairly large cells with $L \geq 100$. One can draw a conclusion from Fig. 3 that in this case one large cluster (with the number of particles $n_i = 1281$) and many considerably finer structures entering the sol fraction are present in the system of reacted dimers and tetramers.

Let us determine the partial Wiener index

$$W = \sum_{j=1}^{G} Wi_j / n_j ,$$

where G is the number of all structures (graphs) in the system and Wi is the Wiener index if the given *j*th structure consisting of n_j particles. It can be said that W characterizes the topological complex nature of the system as a whole.

Figure 4 presents the dependence of the Wiener index $\langle W \rangle$ averaged over different initial realizations on the size of the base cell L. The number of independent realizations s is accepted to be equal to 10; the overall density of particles in the cell is maintained constant (ρ = 0.19), and only the ratio between dimers and tetramers in the initial mixture is varied (the following three examples are considered: $f(0)$ = 2.2, 2.306, and 2.091). It can be seen that the topological complex character of the system increases rapidly as its size increases, and the value of $\langle W \rangle$ depends on the initial composition of the reaction mixture at the same overall density ρ of particles. The mean partial cyclomatic rank $\langle C \rangle$ determined in a similar way at $L > 60$ reaches nearly the constant value, which increases proportionally to the parameter $f(0)$ for ρ = const. The dispersion of the W value, $D(W)$, which characterizes fluctuations of topological properties of the system, demonstrates an unusual behavior. The example of the calculation of $D(W)$ as a function of L is shown in Fig. 5.

It is evident that the dispersion $D(W)$ should be zero for very small L due to the uniqueness of the final topological composition. On the other hand, when the size of the system increases arbitrarily, the dispersion also must approach to zero, because in this case the final result is independent of different initial realizations at fixed parameters ρ and $f(0)$. For the model studied, the $D(W)$ values reach a maximum at $L \approx 120$ to 160 in the considered range of parameters. It is the case which

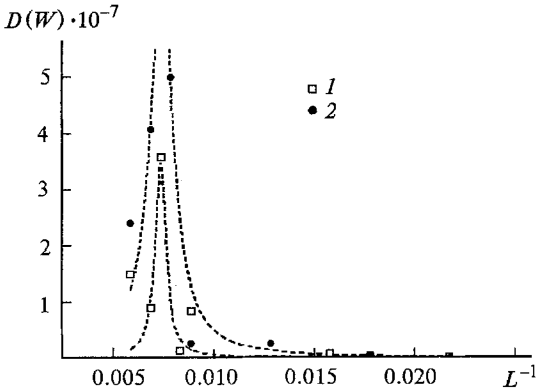


Fig. 5. Dependence of the Wiener index dispersion W on the size of the Monte Carlo base cell for the reacted system of dimers and tetramers at the density $\rho = 0.19$ and two values of the parameter $f(0)$: *1*, 2.2; *2*, 2.091.

demonstrates the largest fluctuations of reaction products. A rough comparison to real systems shows that rather large spatial scales of ~10^2 nm, which are considerably greater than the mean size of the network cell, correspond to this cell. It is noteworthy that the real experiments on dynamic light scattering and thermal neutron scattering on gel networks also show considerable fluctuations of structural parameters, especially when gel is scanned by narrow-collimated beams, which allow one to observe microvolumes of a system.[2]

Like in the real experiment, the collective structural factor $S(q,\tau)$, depending in the general case on the module of the wave vector $q = |\boldsymbol{q}|$ and time, is the main observed structural function. For the steady-state regime $S(q,\tau) \equiv S(q)$. The calculation of the function $S(q)$ for the lattice system should be commented.

For an arbitrary system of N particles in the general case we have

$$S(q) = \frac{1}{N}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\left\{\left\langle \exp[i\boldsymbol{q}\cdot(\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta)]\right\rangle\right\}, \qquad (1)$$

where $i = \sqrt{-1}$, $\boldsymbol{r}_\alpha$ is the radius-vector of the particle α in a given configuration (at a certain instant τ), and angular brackets <> indicate the mean configuration value. When assumed that the system always retains the spatial isotropy (it is quite justified for our problem), the right part of Eq. (1) can be angle averaged. For the two-dimensional system, the integration gives

$$S(q) = \frac{1}{N}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\left\langle J_0(qr_{\alpha\beta})\right\rangle, \qquad (2)$$

where $r_{\alpha\beta} = |\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta|$ is the distance between particles in pair and $J_0(x)$ is the zero-order Bessel's function. The fact that the lattice is discrete and the size of the base cell is finite implies restrictions on the number of possible values of q and $r_{\alpha\beta} = |\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta|$. For example, the minimum value of q is limited by the value of $2/L$, and a set of admissible q values is determined by the final set of all various modules of vectors compatible with the reverse Brave lattice $L \times L$ in size. If interparticle distances of this configuration are grouped in intervals as the histogram $h(r_i)$ (*i.e.*, each value of $h(r_i)$ is the number of distances $r_{\alpha\beta}$ equal to r_i), the "instant" value of $S(q)$ for this configuration is given by the expression

$$S(q) = 1 + \frac{2}{N}\sum_{i=1}^{N_h} h(r_i)J_0(qr_i), \qquad (3)$$

where N_h is the number of different distances r_i, *i.e.*, the number of non-zero elements of the massive $h(r_i)$. The normalization of $S(q)$ at $q = 0$ follows from Eq. (3):

$$S(0) = 1 + \frac{2}{N}\sum_{i}^{N_h} h(r_i) = $$
$$= 1 + \frac{2}{N}\cdot\frac{1}{2}(N-1)N = N. \qquad (4)$$

At $q \to \infty$ we have $S(q) \to 1$ as it should be. It is expedient to remove (subtract) the background contribution, which corresponds to the uniform particle distribution in the system at their given density, from the function $S(q)$. For this purpose let us write the pair correlation function $g(\boldsymbol{r}) = \langle\rho(0)\cdot\rho(\boldsymbol{r})\rangle/\rho^2$. For the spatially isotropic system, $g(\boldsymbol{r})$ is equivalent to the radial function of the particle density distribution $g(\boldsymbol{r}) = \langle\rho(\boldsymbol{r})\rangle/\rho$, where (r) is the local density of particles at the distance r from a chosen particle. For the lattice model, each layer dr thick and removed from the beginning of reference at the distance r has only the final and strictly determined number of accessible positions. Let us denote this number as $d(r_i)$. Then, by definition, for some configuration the "instant" value of $g(r)$ is

$$g(r) = \frac{2L^2 h(r_i)}{N^2 d(r_i)} \qquad (5)$$

with the evident condition of normalization

$$\rho\sum_i d(r_i) = \rho\sum_i g(r_i)d(r_i) = N - 1. \qquad (6)$$

When the particle distribution in the system is random, $g(r) = 1$. Therefore, in this state $h_0(r_i) = N^2 d(r_i)/(2L^2)$, and the background function $S_0(q)$ is given by the expression

$$S_0(q) = 1 + \rho\sum_i d(r_i)J_0(qr_i). \qquad (7)$$

It is clear that the function in Eq. (7) is independent of a particular configuration and is determined only by the density and the linear size of the system. Then the structural factor, from which the background contribution (7) is subtracted, is denoted as $S(q)$. In further calculations, the value of $S(q)$ will be determined not for all particles, but only for those which are the centers of tetramers and, hence, directly enter network points.

It has been assumed in the analysis of the experimental data[2] that structural heterogeneities of networks at intermediate scales (~10 to 10^2 nm) reflect their nonergodic nature. This hypothesis could be confirmed by

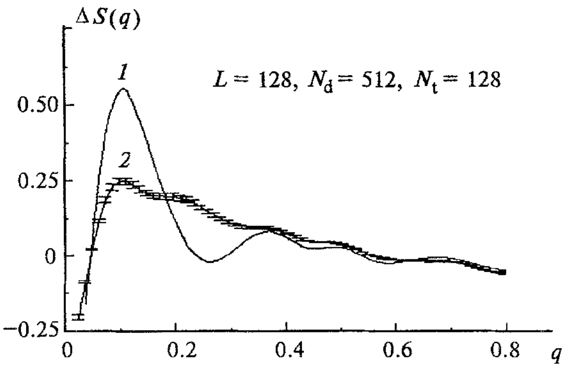


Fig. 6. Time (curve *1*) and ensemble (curve *2*) averaged structural factors for networks. In both cases, the contribution corresponding to the initial system of "ruptured" monomers was subtracted from the function *S*(*q*). The calculations were performed at $L = 128$ for the 512d+128t systems. The 95 % confidence intervals are indicated.

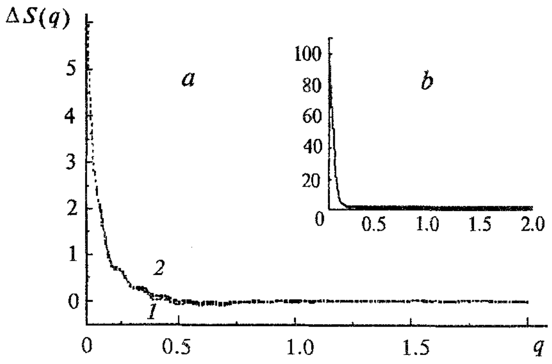


Fig. 7. *a.* Time (curve *1*) and ensemble (curve *2*) averaged structural factors for the unreacted monomeric system. *b.* The functions *S*(*q*) for nine individual realizations are shown. In all cases, the background contribution corresponding to the uniform spatial particle distribution was subtracted from *S*(*q*). The calculations were performed at $L = 128$ for the 512d+128t systems.

the difference in structural parameters obtained by ensemble averaging (*i.e.*, averaging over different independent initial realizations) and time averaging.[5] The logic pattern is the following. It is evident that for the infinitely large system both of the averaging methods must always give identical results. On the contrary, in small volume elements of the real system, which approximately correspond to sizes of individual monomers, fluctuations of density are very high, which results in drastic differences in properties determined by the two methods. Therefore, one can set up a problem concerning the estimation of the maximum size of the model system at which these differences remain significant. Unfortunately, the complete realization of the program planned is rather doubtless due to large calculation expenditure. Therefore, in this work we restrict our consideration to discussion of the results obtained for the single but fairly large system with the size of the base cell $L = 128$ (which is considerably greater than the mean distance between network points).

The computational experiments show that we always have at least one sample of the system, which noticeably differs in the *k* value from the sampling mean $<k>$, of ~50 independent random realizations of the network generated under the same conditions over the time intervals, which certainly guarantee achieving the limiting degree of conversion *k*. Let us choose this structure and average its structural factor, calculating *S*(*q*) in time intervals of 10 MCS during the long evolution period of 10^5 MCS. For enzemble averaging, let us use other realizations corresponding to the same time interval of $3 \cdot 10^4$ Monte Carlo steps. The results are presented in Fig. 6.

It is seen that the differences in the functions *S*(*q*) obtained by ensemble and time averaging are fairly considerable. This fact directly confirms the non-ergodic nature of the system for the spatial scales considered. According to approximate estimations, this scale corresponds to ~10^2 nm, which, as mentioned, is much greater than the mean size of the network cell (*i.e.*, the mean distance between network points). Moreover, the estimation presented is the lower boundary. Probably, it can be increased by about an order of magnitude.

The reasons for the effects observed are rather clear. In fact, when the network is formed, transitions of molecules between some regions of the system become forbidden, and some zones of the phase space become inaccessible. This is the basic reason for the appearance of heterogeneities of mesoscopic scale. These regularities are inherent in polymeric networks with a rather great number of chemical junctions and are not observed for weakly linked systems or "ruptured" monomers. This can be illustrated by Fig. 7, which presents the structural factors calculated by time and ensemble averaging for the mixture of bi- and trifunctional monomers.

It can be seen that in this case both averaging methods give in fact identical results, which coincide within statistical errors.

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