

1. Introduction Polymeric stars attract the attention not only due to the own technological properties [1-3], which can be varied by a length  $N$  of the rays and by their number  $s$ , but also as the complicated and interesting object of the statistical physics of polymers. Experimental data concerning to the properties of the polymeric stars are not numerous [4-7] and doesn't give the sufficient well-defined picture. In particular, an investigation of the low-angle scattering of the neutrons [5, 6] for the diluted solutions of the star-like polybutadienes with 3, 4, 8 and 12 rays, one among which is deuterated, points on the fact, that the gyration radius of the tagged ray is increased at the number of the rays growing, but at this in diluted solutions the gyration radius is more, than in a melt. Rheological investigations [7] of the regular polystyrene stars which are differed by a number of the rays (6, 12 and 22) and by the structure of the branching center (one or two covalently connected molecules of fullerene) also give the contradictory results: the characteristic viscosity of their solutions in chloroform is weakly increased at the molar mass of the star growing (with index = 0,2 in MKH equation ), whereas it is decreased in tetrahydrofurane, in other words, has the negative index = -0.06. Theoretical analysis of the polymeric stars in Daud-Cotton's model [8], which considered them as spherical polymeric brushes in quasi-plate approximation [9-12] leads to the dependence of the conformational radius of polymeric star on a number of rays  $s$  and their length  $N$  in a form ( $d$  - is dimensionality of a space): , (1) The expression (1) has an essential lack: at  $s = 2$ , that is, under condition of the polymeric star degeneracy into the linear chain by  $2N$  length, it wrongly illustrates of this situation. Besides, the experimental value of the so-called branching index  $g$ , determining by ratio , (2) in which  $R$  is the conformational radius of the linear polymeric chain containing as same as the star of  $sN$  links, , (3) is disagreed with the theoretical values , calculated accordingly to (1)-(3). In statistical physics like to the linear chains for polymeric stars two main tasks are solved. First is the estimation of a number of allowed configurations  $L$  with the calculation of indexes and in the scaling expressions by following type [13]: (4) for linear chain and (5) for the star. In expressions (4) and (5)  $z$  is not strictly determined; at the scaling approach the effective coordination number of  $d$ -measured lattice, parameters and are assumed as universal scaling indexes. For linear chain at  $d = 3$  the value = 1,1596 0,002 was obtained [14] using the method of a group of the field theory renormalization. Index for polymeric star calculating by several methods including the groups of the field theory renormalization [15-18], methods of molecular dynamics [19-20] and Monte-Carlo's method [21-23] is sharply decreased at the  $s$  growing, taking more negative values even at  $s > 8$  (for example, at  $s = 32$  an estimation with the use of Monte-Carlo's method [23] gives the value 29); this prejudices the universality of this scaling index. Theoretical calculation of the  $L$  and  $L$  in statistics of the self-avoiding random walks (SARW) is represented in the next paper of this collection book. Here let's consider the second main task, which consists in the estimation of the distribution function of the end of a chain from its beginning. More often the distribution function

$P(N)$  of the distance  $r$  between the ends of the linear chain by the  $N$  length is written in the scaling form [24-25]: , (6) In which  $R$  is the conformational radius of Flory (7) Function represented by two asymptotes: at  $x \rightarrow 1$  (8) at  $x \gg 1$  (9) with indexes, for example,  $\nu = 0,273$  [26] and  $\nu = 2,5$  [27]. The same scaling ratios (6), (8) and (9) are used for the polymeric stars, but the indexes and are function on the number of rays. Let's note, finally, that the scaling approach to the description of the distribution function in a form (6) in spite of its universality is approximate and limited. In particular, it not covers the most important field of the parameter  $x$  in (8) and (9) between  $x \rightarrow 1$  and  $x \gg 1$  change, in which  $P(N)$  takes the maximal values corresponding to the most probable conformational state of the polymeric chain. That is why, even the calculation of the indexes and doesn't give the possibility to describe the thermodynamical properties of the conformational state of polymeric chains and their transformation, for example at the deformation; this is not allow strictly to estimate the elastic properties of the conformational volume. Exact form of the distribution function and following from it thermodynamical properties of linear polymeric chain conformation are strictly determined in the SARW statistics for ideal diluted [28] and concentrated [29] solutions. Here this approach is spread on the regular polymeric stars in diluted and concentrated solutions with the description of their thermodynamical and dynamical properties.

## 2. Diluted solution of polymeric stars

### 2.1. Self-avoiding random walk statistics

Let polymeric star with the  $s$  rays by the same length  $N$  is inserted into  $d$ -measured lattice space with the parameter of a cubic cell equal to the statistical length of a monomeric link of the rays of star, and let  $Z$  is the number of cells of the lattice space, in which there are the all  $sN$  links of a star. We will be neglect by the effects of interactions, assuming that the all possible configurations of polymeric star are energetically equal. Let mark any undefined pair of rays and will be considered it as the linear polymeric chain by length of  $2N$ . Let fix its one end as the referenced position of the Gaussian phantom walks of the second end. Let define via steps of walks the end of the marked chain relatively its beginning along the  $i$  directions of  $d$ -measured lattice space, limited by the condition of the normalization (10) The number of methods for the realization of walks along the  $i$  direction is equal to , where the numbers of the steps into positive and into negative directions connected via the ratio . Since the a priori probability of a choice of the positive or negative direction for every step is the same and is equal to  $1/2$ , the probability of that under given will be done of positive and negative steps, will be determined by the Bernoulli's equation: (11) Inputting the numbers of the resulting steps via the ratio , we have ,. Then the (11) can be rewritten as follow: (12) For the walks along the all directions of the  $d$ -measured space we have (13) The condition of the absence of self-intersection trajectories of walks requires from the point of view of the links of star per cells distribution that in every cell of the lattice space should be exist not more than one link of a star. The links of a polymeric chain are continuous; they cannot be separated one from other and located upon the cells into the undefined order. Therefore, the

number of a links in a chain is its essential distinctive feature. The links of the different rays are also distinguishable. That is why the number of different methods location of sN distinguishable links of a star per Z similar cells under condition that in every cell cannot be more than one link is equal to  $Z$ . Due to the identity of the cells, a priori probability of fact that the presented cell will be occupied by a link is equal to  $1/Z$ , will be not occupied -  $1 - 1/Z$ . Therefore, the probability of sN distribution of the distinguishable links of a star per Z identical cells under condition, that in every cell can be not more than one link, will be determined by the Bernoulli's distribution: (14) Distribution (13) describes the trajectory of the walks of undefined marked linear chain by the length  $2N$ , whereas the expression (14) determines the distribution of the all sN links of a star upon the Z identical cells. That is why the probability of the common fact consisting in that the trajectory of the random walk for the chosen chain by the  $2N$  length is the trajectory without the self-avoiding is equal (15) Here the index  $2/s$  is the result of the division of  $2N$  on sN, Using the Stirling's formula by the following type at  $N \gg 1$ ,  $s \gg 1$ , and decomposition  $s = N + (s - N)$ , in accordance with the condition  $s - N \ll N$ , and assuming  $N(N-1) = N^2$ , we will obtained the asymptotic form (15) with the accuracy to the constant multiplier neared to the one: (16) The transition to the metric d-measured space is possible via the introduction of the variable of the displacement along the i direction of the end of a chain from its beginning,  $x_i$ , (17) and also of the standard deviation of the Gaussian part in (16) (18) Accordingly to the condition of the normalization (10) the following relationship is superposed on the value  $\Omega$ : (19) The expression (16) is true for any undefined chosen pair of the rays representing by itself the linear chain by the length  $2N$ . Therefore, for the all of them Z is general parameter characterizing in metric space the conformational volume of polymeric star: (20) So, taking into account the (17)-(20), a distribution (16) can be rewritten as follow: (21) Distribution (21) in metric space determines the probability of fact that the trajectory of the self-avoiding walk of any undefined pair of rays representing by itself the linear chain by  $2N$  length, under the given values of s, N and will be finished into elementary volume  $\Omega$ , locating on the surface of ellipsoid with the semi-axes  $x_i$ ,  $i = 1, d$ .

## 2.2. Thermodynamics of conformation and deformation of polymeric stars

Without taking into account of the energetic effects of the interactions, the main factor determining the thermodynamic properties of the conformational state of polymeric star is the entropy of the self-avoiding random walks, which accordingly to the Boltzmann is determined by the thermodynamical probability of a state, that is by the number of methods of its realization; such methods are the trajectories of the self-avoiding random walks or configurations. A connectedness of the links in polymeric chain imposes the first and essential limitation on the trajectories of walks – an inhibition of the step backwards. Consequently, the number of variants of a step of walk trajectory cannot be more than  $2d-1$ . Only the first step has  $2d$  variants of the motion. This means, that the maximal number of the trajectories of walk for undefined pair of rays will be equal (22) If the presented state is realized by L methods, then its probability is equal to  $1/L$ , that is why let determine the

number  $L(2N)$  of configurations for the undefined chosen pair of the rays via expression: (23) It's follow from this: (24) For polymeric star the number of independent pairs from  $s$  rays is equal to  $s(s-1)/2$ . That is why, the number of methods  $L(sN)$  for the realization of conformational state of polymeric star will be equal: (25) Therefore, in accordance with Boltzmann, the general entropy of the conformational state of polymeric star can be represented as two components: (26) The first term is positive and is more than the second one; it takes into account the all trajectories of walk with imposed on them singular limitation of the connectedness of the links into a chain, and doesn't accept the reverse step. The second term is negative ( ); it takes into account the additional limitations on the trajectories of walk by requirement of their self-intersection absence. At this, the first term at given data  $s$ ,  $N$ ,  $d$  is the constant value, whereas the second term via is the function on the conformational state. That is why let assume only the second term in (26) as the entropy  $S$  of the conformational state of a polymeric star: (27) Negative value of determined in such a way entropy of the conformation permits to consider the conformation as the statistical form of the self-organization of polymeric stars, and the numerical measure of this self-organization is entropy accordingly to (27). Free energy of the conformational state without taking into account of the energetic effects is equal to . By combining of (21) and (27), we will obtain: (28) Next, among the all possible conformational states let mark the most probable or thermodynamically equilibrium conformational states, to which the maximum  $S$  and the minimum  $F$  correspond in accordance with the condition at . By differing of (28), we have (29) By equaling of the right part to zero and solving the system consisting of the algebraic equations for the all  $i$ , we will find the most probable or equilibrium values of , which are the semi-axes of the equilibrium conformational ellipsoid: (30) Under the absence of the external forces and into the ideal solution the all directions of the walk are equiprobable accordingly to condition ; that is why parameters in accordance with the (18) take the same value equal to: (31) The substitution of values in (30) based on (31) makes the semi-axes of the equilibrium conformational ellipsoid the same and equal to the conformational radius of the polymeric star: (32) Let's estimate the branching index determined by the ratio (2) with the use of the expressions (3) for and (32) for : (33) Calculations accordingly to (33) for variant  $d = 3$  at  $s = 3$  and  $s = 12$  give the values equal to 0,73 and 0,24 respectively, which are good agreed with the experimental data 0,78 and 0,24 [31]. Under the action of external forces along the axes of  $d$ -measured space appearing in particular at the transition of polymeric star from the ideal solution into the real one, and spherical conformational space of the polymeric star is deformed into the ellipsoid with the semi-axes accordingly to (30), equilibrium as to . We assume the following variables as a measure of the conformational volume deformation: (34) , (35) which represent by themselves the multiplicities of linear and volumetric deformation respectively. In accordance with the condition of normalization (10) the values of cannot accept the undefined values. Let's determine the relationship

between them by introducing the secondary parameters: (36) It follows from the determinations of from (18) and of from (31): (37) By substitution of the values in (30) and taking into account (34) we will find (38) Therefore, , (39) so (40) Accordingly to (37) and (40) we have (41) An analysis of (41) shows, that under any deformation of the spherical conformational volume of polymeric star, to which the values of  $\alpha$  and  $\beta$  correspond, into the conformational ellipsoid, the multiplicity of the volumetric deformation is decreased ( $\Delta V < 0$ ); that means the compaction of the conformational volume of polymeric star. Next, let's determine a free energy of the equilibrium conformational ellipsoid by substitution in (28) of values : (42) Here (43) That is why it can be also written: (44) For strainless state , that is why a work of its transition into a deformed state in the system of the mechanics signs will be equal: (45) Such work is positive, that is in the system of the mechanics signs it's realized under the system. If, however, the conformational volume is changed from the one deformed state with into another deformed one with , then the deformation work will be equal to: , (46) and can be characterized by any sign. Let's determine the pressure of conformation P of polymeric star via usual thermodynamic expression (47) as a measure of relationship between free energy and volume of conformation. Since the conformational volume is equal to we have (48) By differing the (42) and (44) upon we will obtain respectively: , (49) (50) It follows from the comparison of (42) and (49), that the pressure of conformation numerically is equal to density of free energy: . Next, by multiplying of this expression on and taking into account the (42) and (49), we will find the equation for the conformation state of the polymeric star in a form (51) where  $\text{const} = \frac{2}{3} \pi^2 \rho$  (52) So, the values are integrals of the process of equilibrium deformation of the conformational volume of polymeric star.

### 2.3. Modulus of elasticity

Under approximation of the isotropy of conformational volume of polymeric star its relative deformation in  $i$  direction of  $d$ -measured space under the action of the all main forces let's express via the differential form of the Poisson's equation: (53) Here:  $Y$  is the Young's modulus,  $\nu$  is the Poisson's coefficient,  $\sigma_i$  is the tension in  $(d-1)$ -measured plate normal to the  $i$  direction; and  $S_i$  are values of the areas which are normal to the forces and respectively. Let's rewrite (53) respectively to the Young's modulus: (54) In the system of the mechanics signs , that permits to use the expression (29). Under equilibrium values these forces (but not their derivatives) are equal to zero. That is why by differing of (29) upon  $\sigma_i$  and  $\sigma_j$ , and next by substituting of the equilibrium values we will obtain , (55) (56) By substituting of these derivatives in (54) with change of on the equilibrium values we will find (57) Comparing the (57) and (49), we find the relationship between the Young's modulus and the pressure of conformation: (58) From the other hand, in general case of the  $d$ -measured space the relationship between  $Y$  and  $P$  can be expressed via the volumetric modulus (59) by the ratio (60) It follows from the determination of (59) and the equation of state (51):  $E = 2P$  (61) Substituting of (61) into (60) we will obtain another equation of relationship between  $Y$  and  $P$ : (62) Comparing the (62) and (58) we find the expression for the Poisson's coefficient: (63)

Next, we determine the shear modulus via the Young's modulus and the Poisson's coefficient for d 2-measured space (64) which is also the function on the pressure of conformation: (65)

## 2.4. Main forces and the work of deformation

It follows from the determination of the main forces in accordance with the (29) that at the equilibrium values these forces are equal to zero. That is why let's determine the main forces as those, which should be applied to the strainless conformational volume, for which the conformational radius is equilibrium, with respect to, in order to transform it into the deformed state of the conformational ellipsoid with the semi-axes, equilibrium with respect to. This determination means, that in expression (29) parameter should be replaced on, and values should be replaced on. Then we will obtain: (66)

Substituting of in (66) we will obtain: (67)

It follows from this, that in the accepted system of the mechanics signs the positive forces correspond to the stretching along i axe (), and the negative forces correspond to the compression (). That is why the main forces of deformation cannot be undefined, but they are ordered to the equation of the relationship (as it is following from the (67) and (41)): (68)

A work of the deformation under the action of the all main forces let's describe by the expression: (69)

Using of the ratio (67) and (70) after the integration of (69) we will obtain the expression (71) which is wholly identical to the obtained earlier (45). This proves the correctness of the determination of the main forces accordingly to (66) and (67).

## 2.5. Dynamical properties

### 2.5.1. Characteristic time of the transition and the coefficient of diffusion

Characteristic time of the translational motion of the strainless polymeric star (here we will be specialized on the analysis only of this situation) let's determine as a time needed for the transfer of its equilibrium frozen conformation on the characteristic distance. At the transfer of of the links on a distance it is necessary to do steps, every of which is realized for a time, which can be called as the characteristic time of the segmental motion. Thereby, (72)

Substituting the expression (32) for in (72) we will obtain (73)

As it was shown in [32], the diffusion coefficient at multivariate random transfer of the macromolecule is determined via expression: (74) which is the analog of the Einstein's equation for low-molecular substances. At the analysis of the directed transfer of macromolecule along i direction of the d-measured space, for example, under the action of gradient of chemical potential, it is necessary to use other determination of the diffusion coefficient: (75)

Substituting the expressions (73) and (31) in (75), finally we will obtain for the strainless polymeric star: (76)

### 2.5.2. Characteristic time of the rotational motion and the coefficient of the elastic component of viscosity

Viscous-elastic properties of the polymeric solutions suppose [32] the presence both of the frictional and elastic components of the measured effective viscosity. The elastic component of the viscosity is gradiently dependent value, depends also on a composition of the solution and on the coefficient of the elastic component of viscosity, which is determined via expression: (77)

Here: is the determined earlier shear modulus; is the characteristic time of the rotational motion. As the characteristic time of the rotational motion let's assume a time during which

the strainless polymeric star into the frozen equilibrium conformational state will be rotated around any axis on the characteristic angle, equal to the one radian.

Accordingly to this determination, the links, allocated from the rotation axis on a distance  $r$ , pass a way  $r$  for  $r/a$  steps and for time  $(r/a)$ . Since the allocation of the all  $sN$  links in  $d$ -measured space is unknown, we use the following approach [33] for the estimation of  $\tau$ . Let's design on the  $(d-1)$ -measured rotation plate the all  $sN$  links of the polymeric star. Conformational radius of the rotation plate is equal to  $a$ , but the numbers of the projections should accept such acceptable values  $N'$  and  $s'$ , that to provide the value in  $(d-1)$ -measured space. Then substituting the values  $d-1$ ,  $N'$  and  $s'$  in expression (32) for instead of  $d$ ,  $N$  and  $s$  correspondingly, we will obtain (78) From the comparison of (32) and (78) we will find the acceptable values of  $N'$  and  $s'$  in the rotation plate, (79) Let's select on the rotation plate the linear polymeric chain by  $2N'$  length, consisting of the pair of rays from the  $s'$ . Let  $n$  is the number of the link of presented given undefined chain from the rotation axis. Let's assume, that the distance of this link from the rotation axis is ordered to the same distribution (78), that is: (80) Although for the internal links of a chain this expression is not quite correct [see the previous work in the presented collection book], but the following integration shows, that the main endowment into characteristic time of the rotation has the links with the numbers neared to  $2N'$ . Under the plane of rotation turn on the one radian, the links with the numbers of  $n$  tract a way for  $r/a$  steps and for time  $t$ . For all  $s'N'$  links, distributed upon  $s'/2$  linear chains, the rotation time will be equal to  $\tau$ . At the change of  $n$  on  $dn$  an increment of time consists of: (81) After the integration of (81) via the limits from  $n = 1$  till  $n = 2N'$  with taking into account of (78) we will obtain (82) By change of  $N'$  on  $N$  and  $s'$  on  $s$  accordingly to (79), we finally find (83) Next, using the expressions of (65) and (50) for shear modulus of unstrained polymeric star  $G = 1$ , we have (84) Here Combining the (83) and (84) for determination of the coefficient of elastic component of viscosity in (77) we finally find accurate within a multiplier neared to the one: (85) Let's comment the obtained expressions (76) for  $\tau$  and (85) for  $\eta$ , comparing them with the same expressions for  $\tau$  and  $\eta$  of linear polymeric chains, consisting the same number of  $sN$  links. For this purpose let introduce the branching indexes upon (2) type in form  $\alpha$  and  $\beta$ . For linear polymeric chains containing the  $sN$  links we have (86) (87) Comparing the (87) and (85) and also (86) and (76) we have  $\eta_{star} = \eta_{chain} \cdot \alpha$  and  $\tau_{star} = \tau_{chain} \cdot \beta$ . Thereby, at the same number of links, the polymeric stars are less mobile ( $\beta < 1$ ), but have considerably more coefficient of the elastic component of viscosity ( $\alpha > 1$ ), than the linear chains.

### 3. POLYMERIC STARS IN CONCENTRATED SOLUTION

#### 3.1. Self-avoiding random walks statistics

In concentrated solution the conformational volumes of polymeric stars are overlapped in accordance with the condition  $\rho > \rho_c$ , in which  $\rho$  is a density of the solution upon polymer, is the critical density corresponding to the start of the conformational volumes overlapping. Due to the polymeric star cannot be considered as an independent subsystem, it is necessary to consider the all set of the polymeric stars in conformational volume of the separated system. Let's introduce the screen cubic

d-measured space containing of  $m$  intertwining between themselves uniform polymeric stars. Let's separate from them any undefined star, and in it – any undefined pair of rays, forming the linear chain by  $2N$  length. Its phantom Gaussian walks are ordered to the same distribution law (13) with the same normalization condition (10). However, the probability of the  $msN$  differed links distribution upon  $Z$  identical cells at the condition, that in every cell there is not more than one link, will be determined by a new expression: (88) It follows from this, that the probability of the self-avoiding walks for undefined chosen pair of rays will be equal: (89) Here the index  $2/ms$  was obtained as the ratio  $2N/msN$ . Combining the (13) and (88) into (89) and using as same principles as at the derivation of the (16) equation, we will obtain into the asymptotic limit from (89): (90) The transition to the d-measured space is realizable with the use of the same previous expressions (17)–(20), accordingly to which (91) This distribution is true for any undefined pair of rays of any undefined star in general space .

### 3.2. Thermodynamics of conformation and deformation of the intertwining polymeric stars

The numbers of configurations for pair of rays, polymeric star and  $m$  intertwined between themselves in  $m$ -ball polymeric stars let's determine, correspondingly, by the expressions: (92) (93) (94) Therefore, in accordance with Boltzmann, general entropy of the self-avoiding walks of the intertwined polymeric stars in  $m$ -ball will be equal: (95) As same as earlier, only the second term in (95) we accept as the entropy of the conformation of  $m$ -ball of polymeric stars or as entropy of their self-organization: (96) At the absence of the energetic effects, a free energy of the conformation will be equal to: (97) From the all possible states of the polymeric stars in  $m$ -ball let's choice the most probable or thermodynamically equilibrium states in accordance with the condition  $\Delta F = 0$ . Differentiating of (98), we will obtain: (98) Equaling the right parts of (98) to zero for all  $i = 1, d$  and solving the obtained system of the algebraic equations, let's find the equilibrium semi-axes of the conformational ellipsoid, general for any pair of rays, any polymeric star and  $m$ -ball in the large: (99) At the equiprobability of walks upon the all directions of d-measured space that is reflected by the condition of accordingly to (31), we have the spherical conformational volume with the radius: (100) Deformation of the  $m$ -ball at its transition from the spherical (unstrained) conformational state into the ellipsoid with the semi-axes let's express via the multiplicities of the linear and volumetric deformation via ratios: , (101) which are also ordered to the equation of the relationship (41). Next, substituting the equilibrium values in (97) we will find the equilibrium free energy of the strained  $m$ -ball: (102) It follows from this, that in the system of the mechanics signs a work of the transition of the unstrained  $m$ -ball with into the deformed state of the conformational ellipsoid with 1 will be equal to: (103) Next, determining the conformation pressure via the same thermodynamic ratio (47), in which the conformational volume of  $m$ -ball in general case is equal to , we find (104) Again we have and the equation of the conformational state of  $m$ -ball for intertwined polymeric stars: , (105)  $const =$  (106)

### 3.3. Modulus of elasticity of $m$ -ball for intertwining



polymeric stars An equation of the deformation for the m-ball of the intertwined polymeric stars we write in the same general differential form (53) and transform it relatively to the Young's modulus into the form (54). Corresponding derivatives we find via the differencing of (98) with the following substitution of the equilibrium values : , (107) (108) Substituting of these expressions in (54), we will obtain: (109) Comparing of (109) with the expression (104) for P, we have the relationship between and P: (110) From the other hand, determining of Y via the volumetric modulus  $E = 2P$  by the ratio (60), we will again obtain the relationship by (62) type, comparing of which with the (110), we will obtain the expression for the Poisson coefficient in the well-known form (63). So, the Poisson coefficient both for the linear chains and for the polymeric stars in diluted and concentrated solutions is the universal function only on the Euclidian space. Using the relationship (64), let's express the shear modulus of the m-ball of the intertwined polymeric stars via the conformation pressure in the known form: (111)

3.4. Main forces and a work of the deformation of m-ball of the intertwining polymeric star The main forces of the deformation let's again determine as the forces, which should be applied to the m-ball, in order to transfer it from the unstrained state equilibrated with respect to the , into the deformed state, equilibrated with respect to the . That is why it is necessary again to substitute instead of the value in the expression accordingly to (98), and to change on , that is (112) After the substitution , we have (113) Describing the deformation work of the m-ball by the same equation of mechanics (69) with the use of the expression (113) for the main forces, we will obtain again the expression in accordance with the (103). 3.5. Determination of , , and P as the explicit functions s, N and concentration of polymeric stars in solution

Concentration (density of solution upon polymer) of polymeric stars in concentrated solution is equal to (114) where is the molar mass of a link. At  $m = 1$  we have the critical concentration, to which the beginning of the polymeric stars conformational volumes overlapping corresponds: (115) From the comparison of (114) and (115) follows (116) Determining the density in the volume of a link via expression (117) we find (118) This permits to write for m and the expressions , (119) . (120) via substituting of which in (102) and (104), we will find (121) (122) We can easy find the explicit functions of the modulus of elasticity on N, s and via P in accordance with (122). 3.6. A work of the intertwining of polymeric stars A change of free conformation energy at the transition of the m polymeric stars from the diluted solution into the concentrated one is equal to . In calculation per one polymeric chain we have: (123) In a system of the mechanics signs this value determines a work of the polymeric stars intertwining as a work of the polymeric star transfer from the diluted solution in concentrated one. After the substitution in (123) of the expressions (42), (102) we will obtain: (124) where . From the other hand, expressing the conformational volumes of polymeric chains in diluted solution , and in concentrated , we have (125) Therefore, a work of the polymeric stars overlapping into the m-ball represents by itself a work of the conformational volume compression at the transfer of the star from the diluted

solution into the concentrated one: (126)

### 3.7. Dynamical properties of polymeric stars in concentrated solution

#### 3.7.1. Characteristic time of the transition and a diffusion coefficient

Characteristic time of the translational motion of polymeric stars in concentrated solution let's determine as a time  $\tau$ , for which the m-ball of the intertwined polymeric stars with the frozen equilibrium conformation will be displaced on the effective distance consequently of the random walks upon the all  $d$  directions of space. The next expression corresponds to this determination: (127) in which as before is the characteristic time of the segmental motion. Substituting in this expression the ratios (119) and (120), determining the  $m$  and  $\tau$ , we will obtain: (128)

A diffusion coefficient for the chosen direction, determined earlier by the ratio (75), will be described via expression: (129)

#### 3.7.2. Characteristic time of the rotational motion and the coefficient of the elastic component of viscosity

Characteristic time of the rotational motion of the m-ball of the intertwined polymeric stars let's determine as a time, needed for the turn of the frozen equilibrium conformation of m-ball on the elementary angle equal to the one radian. Let's select the rotation plate by dimensionality  $d-1$  with the same conformational radius and blueprint on it the all  $msN$  links of the m-ball. Obtained projections  $N'$ ,  $s'$  and  $m'$  are ordered to the SARW statistics, that is why the conformation radius in  $d-1$  plate can be write as follow: (130)

Comparing the (130) and (100), we determine the relationships, (131)

Let's select a chain by the  $2N'$  length from the general numbers of the projections. Assuming that the internal links of this chain with the numbers of  $n$  from the rotation center are ordered to the same regularity (130), their rotation radius will be expressed via ratio: (132)

At the turn on an angle by the one radian these projections with the numbers  $n$  from the rotation center pass the distance for  $1/a$  steps and for time  $(1/a)$ . At the change of  $n$  on  $dn$  an increment of time consists of  $\tau$ . By integrating of this expression from  $n = 1$  till  $n = 2N'$ , we will obtain: (133)

For the all chains we have  $\tau$ . Taking into account the relationships (131) we finally find: (134)

We determine the coefficient of the elastic component of viscosity of concentrated solution of polymeric stars via the characteristic time and the shear modulus  $G$ . Using the ratios (111) and (122) at  $\alpha=1$  for  $\tau$  and (134) for  $G$ , we find: (135)

Here the value for  $d = 3$  space neared to the one, that is why it can be written: (136)

## 4. Conclusion

Self-avoiding random walks statistics completely describes the thermodynamic and dynamic properties of the polymeric stars in diluted solutions as the function on a length and the number of rays; in concentrated solutions additionally as the function on the concentration of polymer.