Polymer Globule as a Nanoreactor

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ABSTRACT: Peculiarities of chemical reactions inside polymer globules with sizes falling in the nanometric range have been theoretically studied. The simplest example of a polymer-catalyzed bimolecular reaction between two low-molecular-weight compounds has been considered to illustrate the advantages of conducting chemical transformations in globular solution of macromolecules. Under theoretical examination of polymer-analogous transformations of polymer molecules, the possibility has been shown of reaction-induced conformational transitions between their coil and globular states. Besides, a pronounced effect has been revealed of the preferential sorption of low-molecular-weight reagents on composition of copolymers formed.

Introduction

The rate of chemical reactions between reagents A and B can be increased by localizing them in minute volume microreactors. The role of such microreactors can be efficiently performed by polymer globules with sizes falling within nanometric scale. If the thermodynamic affinity of low-molecular-weight reagents to the polymer essentially exceeds that of the solvent, their concentrations within the globule will be considerably higher than those outside it. In addition, because of the distinction in thermodynamic affinity to the polymer of reagents A and B, their molar fractions inside and outside the globule may differ substantially. Such a phenomenon referred to as "preferential sorption" is well-known in the thermodynamics of dilute polymer solutions.[1–7] This phenomenon is essential exclusively in cases of rather dense polymer globules, inasmuch as the concentration of monomeric units in a polymer coil is too small to induce a significant difference in concentrations of the reagents inside and outside its domain.

Preferential sorption is of crucial importance in free-radical copolymerization where only its allowance makes possible to explain a number of significant experimental results falling outside the traditional interpretation of the mechanism of this process.[8–20] Its quantitative theory has been developed,[21,22] taking into account the sorption of monomers into the growing macroradical being in the globular conformation state. The basis for this theory is thermodynamic relations connecting the concentrations of low-molecular-weight reagents inside and outside a globule. These relations are of rather general character since for their derivation the number of different low-molecular-weight components of the polymer solution (reagents and solvents) as well as the types of quasi-components (monomeric units in macromolecules) were presumed to be arbitrary. The thermodynamic model used in ref 21 is fully characterized along with stoichiometric parameters by the set of the Flory parameters $\{\chi_{\alpha\beta}\}$, describing the pair interactions between different types of components and quasi-components. The set $\{\chi_{\alpha\beta}\}$ may be conveniently considered as a manifold of elements of the cellular matrix

$$\chi = \begin{pmatrix} \chi^{LL} & \chi^{LP} \\ \chi^{PL} & \chi^{PP} \end{pmatrix} \tag{1}$$

where superscripts P and L of the submatrices denote respectively "polymer" and "low-molecular-weight components". Following the notation used earlier,[21] we further will enumerate rows and columns in each of matrices χ^{LL} and χ^{PP} separately. That is why in every such a matrix the elements $\chi^{LL}_{\alpha\beta}$ and $\chi^{PP}_{\alpha\beta}$ can exist with identical pair (α, β) of subscripts. As for elements $\chi^{LP}_{\alpha\beta}$ and $\chi^{PL}_{\alpha\beta}$ of matrices χ^{LP} and χ^{LP}, their first and second subscript refers respectively to the first and the second superscript.

In this brief article we will present the results of our theoretical consideration of three types of reaction systems using the thermodynamic equations derived in ref 21 describing the equilibrium sorption of reagents by polymer globules. The system of the first type is a dilute solution of homopolymer macromolecules in the globular state and two low-molecular-weight compounds A and B. These latter enter in a chemical reaction with one another, resulting in the formation of a final product C that tends to leave the globule. The polymer acts in this system as a catalyst for this bimolecular reaction, so that its rate turns out to be proportional to the concentration of monomeric units in the nanoreactor. Experimental data reported in the literature testify to high efficiency of polymer catalysts, provided their macromolecules are in the globular state. Among the latter are, for example, some partially quaternized tertiary amine polymers exhibiting reversible coil–globule transition.[23,24] It was shown[25–27] that in the presence of macromolecules of such polymers the rate of hydrolysis of some compounds increased by 3–4 orders of magnitude when conformational state of these macromolecules changes from coil to globule.

The second reaction system considered also concerns a dilute solution of macromolecules whose units A, however, contain functional groups. Their reaction with a low-molecular-weight compound Z also present in the solution results in the transformation of units A into units B. In the course of such a polymer-analogous reaction (in short PAR), the homopolymer macromolecules turn into macromolecules of binary heteropolymer to convert finally into homopolymer with units B.

Finally, the third reaction system considered only differs from the previous one by the presence in the dilute polymer solution of two reagents, Z_1 and Z_2, instead of one. The final product of PAR inside the homopolymer globule will now be a binary copolymer. Its composition may markedly differ, due to the

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preferential sorption of reagents, from that obtained under the homogeneous regime of PAR.

Below, neglecting the change in reagents' concentrations in the course of the chemical transformations, we will present the calculation of selected examples of the hypothetical reaction systems of the above-mentioned three types to illustrate the key peculiarities connected with the localization of the reactions inside polymer globules.

Results and Discussion

We will start with the system of the first type concerning the reaction between two low molecular compounds in the presence of homopolymer globules. The local rate of reaction between them per unit volume is determined by the expression

$$w = kPZ_1Z_2 \tag{2}$$

where k is the rate constant of this chemical reaction and P stands for monomeric units' concentration, whereas Z_1 and Z_2 represent the concentrations of the reagents. The overall rate of a reaction in a nanoreactor, W_G, equals the product of the local rate of this reaction in a globule, ω_G, by its volume V_G. The effect of the preferential sorption on the reaction rate can be characterized by a coefficient K equal to the ratio of this rate W_G in the globule to that in the coil W_C at the same composition of the reaction mixture

$$K = \frac{W_G}{W_C} = \frac{kV_GP_GZ_1Z_2}{kV_CP_CZ_1^0Z_2^0} = \frac{Z_1Z_2}{Z_1^0Z_2^0} \tag{3}$$

This coefficient, as it follows from formula 3, is determined only by the product of ratios of reagents' concentrations in the globule and in the coil, being independent of the number of monomeric units in the macromolecule.

The volume physical interactions are characterized by a symmetric matrix of the Flory parameters (1), which for the system of interest has six independent elements

$$\chi = \begin{pmatrix} 0 & \chi_{12}^{LL} & \chi_{13}^{LL} & \chi_{11}^{LP} \\ \chi_{21}^{LL} & 0 & \chi_{23}^{LL} & \chi_{21}^{LP} \\ \chi_{31}^{LL} & \chi_{32}^{LL} & 0 & \chi_{31}^{LP} \\ \chi_{11}^{PL} & \chi_{12}^{PL} & \chi_{13}^{PL} & 0 \end{pmatrix} \tag{4}$$

Here numbers 1, 2, and 3 of the low-molecular-weight compounds correspond respectively to the first and second reagents and the solvent. For the vast majority of pairs of solvents, reagents and monomeric units the values of the Flory parameters fall within the interval (0, 2), although in some cases large and even negative values are known.[28] An example of these latter is the solution of poly(ethyl methacrylate) in toluene, where $\chi_{31}^{LP} \approx -1$.[29] Positive and negative values of the Flory interaction parameter for every pair of (quasi)components correspond respectively to the loss and gain in the free energy at the contact between the constituents of this pair. Therefore, the thermodynamic affinity of any pair of (quasi)components rises when its Flory parameter decreases.

Because the number of thermodynamic parameters in the system under consideration is six, a complete analysis of the results in the six-dimensional parameteric space is hardly possible. Our calculations of coefficient K (3) at a considerable number of points of this space brought us to the conclusion that at many of them the values of this coefficient far exceed unity. The calculation results for some hypothetical systems presented in Figure 1 illustrate the efficiency of a globular nanoreactor whose employment enables the rate of the chemical reaction to be substantially increased.

For each curve depicted in this Figure 1, the increase in χ_{23}^{LL} leads to substantial larger values of the coefficient K due to the
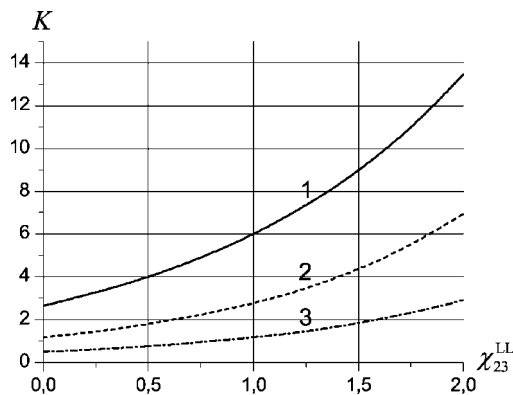

Figure 1. Dependence of coefficient K (3) on parameter χ_{23}^{LL} describing the interaction of the second reagent with the solvent at values of parameter χ_{21}^{LP} equal to -1, 0, $+1$ (curves 1, 2, 3, respectively). The other matrix (4) elements are chosen as $\chi_{12}^{LL} = 0$, $\chi_{13}^{LL} = 2$, $\chi_{11}^{LP} = 0.1$, $\chi_{31}^{LP} = 2$, whereas the molar fractions of the reagents and solvent in the solution are $y_1^0 = y_2^0 = 0.025$, $y_3^0 = 0.95$, respectively.

increased second reagent sorption into the globule. So, the ratio of the value of the second reagent concentration inside the globule to that outside it changes from 1.1 to 5.5 along line 1, from 0.5 to 2.8 for line 2, and from 0.22 to 1.2 for line 3. This has a simple explanation. Indeed, for larger values of χ_{23}^{LL} the contacts of the second reagent with the solvent become progressively more unfavorable, and thus the latter opts for going into the globule where the concentration of the solvent is less. As Figure 1 shows, the decrease in χ_{21}^{LP} also enhances the second reagent sorption due to the energetic benefit from its contacts with monomeric units. For these changes in the Flory parameters, the concentration of the first reagent in the globule remains virtually unchanged, being about 2.5 times higher than its external concentration. This is also favored by the values of parameters χ_{13}^{LL} and χ_{11}^{LP} of the first reagent interaction with the solvent and polymer as well as small value of parameter χ_{12}^{LL}, which does not prevent the increase in concentrations of both reagents in the globule.

The type of the conformational state of the macromolecule in dilute solution is primarily controlled by the value of parameter χ_{31}^{LP}. For this state to be globular, inequality $\chi_{31}^{LP} \gtrsim 0.5$ should necessarily hold, provided the remaining Flory parameters (4) fall within the interval (0, 2). Note, the value of χ_{23}^{LL} tangibly affecting coefficient K just slightly influences the volume fraction Φ of monomeric units in the globule. In fact, the value of along curves 2 and 3 in Figure 1 decreases from 0.87 to 0.85 and 0.81, respectively. Hence, for this kind of system the rise in the reaction rate in a globule practically does not depend on the concentration of monomeric units inside it. Essentially, the enhancement of the thermodynamic affinity of the solvent to the polymer (resulting in a more pronounced swelling of a globule and facilitating thus the penetration in it of the solvent) leads to the displacement of the reagents outside the globule. This obviously deteriorates the efficiency of the nanoreactor. So, for the set of parameters, corresponding to the largest value of K in Figure 1, the change of χ_{31}^{LP} from 2 to 0.75 reduces K from 13 to 7 and Φ from 0.74 to 0.49.

The second type reaction system consists of dilute solution of homopolymers with units A each containing a functional group that upon reaction with low-molecular-weight compound Z turns into unit B. The rate of the polymer-analogous reaction between reagent Z and initial units A can be written as follows

$$\frac{dp}{dt} = k(1 - p)Z \tag{5}$$

where p is the conversion of the initial units, k represents the rate constant of the second-order chemical reaction, and Z
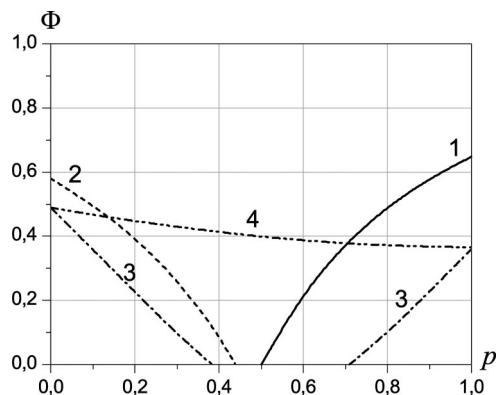
Figure 2. Volume fraction of globule Φ occupied by monomeric units versus conversion of the initial units at molar fractions of the reagent and solvent $y_1^0 = 0.05$, $y_2^0 = 0.95$. Values of the Flory parameters for each curve plotted in this figure are presented in Table 1.

Table 1. Sets of the Flory Parameters Characterizing Four Hypothetical Reaction Systems Where the PAR Proceeds inside a Polymer Globule

	χ_{12}^{LL}	χ_{12}^{PP}	χ_{11}^{LP}	χ_{12}^{LP}	χ_{21}^{LP}	χ_{22}^{LP}
1	0.1	0.1	0.1	0.1	0.1	1.0
2	0.1	0.1	0.1	0.1	0.9	0.1
3	0.1	1.0	0.1	0.1	0.8	0.7
4	0.1	0.1	0.1	0.1	0.8	0.7

denotes the concentration of the reagent in the globule. The value of the latter in the course of a PAR proceeding inside a coil is approximately the same as the reagent's concentration Z^0 in the solvent volume. That is why eq 5 admits a simple analytical solution

$$p = 1 - \exp(-kZ^0 t) \qquad (6)$$

The matrix of the Flory parameters for the system under consideration just as matrix (4) has six independent elements

$$\chi = \begin{pmatrix} 0 & \chi_{12}^{LL} & \chi_{11}^{LP} & \chi_{12}^{LP} \\ \chi_{21}^{LL} & 0 & \chi_{21}^{LP} & \chi_{22}^{LP} \\ \chi_{11}^{PL} & \chi_{12}^{PL} & 0 & \chi_{12}^{PP} \\ \chi_{21}^{PL} & \chi_{22}^{PL} & \chi_{21}^{PP} & 0 \end{pmatrix} \qquad (7)$$

Here numbers 1 and 2 of the low-molecular-weight compounds correspond respectively to the reagent and solvent. Numbers 1 and 2 of the monomeric units correspond to initial and reacted units. In line with eq 5, the enhanced sorption of reagent into the globule can accelerate, as in the case of the previously considered reaction system, the transformation of initial units A into units B. However, it is of some interest to address other effect, namely, the evolution of the conformational state of a macromolecule in the course of the PAR induced by the difference in thermodynamic affinity of the solvent to the initial and reacted units. This effect is exemplified by Figure 2, where the curves are calculated on the basis of the data reported in the Table 1. This figure presents four types of evolution of the volume fraction Φ in the globule occupied by the units of the macromolecule during its chemical modification. Along with the simplest type of the evolution (curve 4), there are other ones which involve transitions between the coil and globular state.

Curve 1 in Figure 2 corresponds to the system where the solvent being thermodynamically good for the initial units is moderately poor for the reacted units. Because of this, in the beginning of the reaction the macromolecule is in the coil state, but as soon as the fraction of the reacted units reaches a critical value, the chain undergoes the coil−globule transition. Line 2

corresponds to the opposite case, when the solvent is moderately poor for the initial units and good for the reacted units. Finally, line 3 is calculated for the reaction system in which macro-molecules of each homopolymer consisting of the initial and reacted units are in dilute solution in the globular state. However, within an intermediate interval of conversions, the coil state of a macromolecule proves to be preferable, since the reduction in the number of contacts in coil between thermodynamically incompatible initial and reacted units provides a considerable gain in free energy, thus inducing a globule−coil transition. If these units are compatible (small values of parameter χ_{12}^{PP} correspond to this case), the volume fraction Φ changes steadily.

The third type reaction system differs from the above one by the presence of two competing elementary reactions instead of one

$$\text{A} + \text{Z}_1 \xrightarrow{k_1} \text{B}_1, \ \text{A} + \text{Z}_2 \xrightarrow{k_2} \text{B}_2 \qquad (8)$$
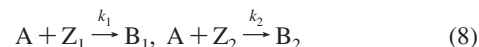
Their kinetics is characterized in terms of variables p_1 and p_2 denoting the fractions of reacted units B_1 and B_2

$$\frac{dp_1}{dt} = (1 - p_1 - p_2)k_1 Z_1, \ \frac{dp_2}{dt} = (1 - p_1 - p_2)k_2 Z_2 \qquad (9)$$

Just as in the second type reaction system, these equations for the case of the reaction taking place inside a coil have a simple analytic solution

$$p_\alpha = X_\alpha^C(1 - \exp(-\tau))$$
$$X_\alpha^C = \frac{k_\alpha Z_\alpha^0}{k_1 Z_1^0 + k_2 Z_2^0} \ (\alpha = 1, 2), \ \tau = t(k_1 Z_1^0 + k_2 Z_2^0) \qquad (10)$$

It follows from expressions 10 that the final composition of the macromolecule X_α^C equal to the fraction of units B_α is determined in this case by the ratio of products $k_1 Z_1^0$ and $k_2 Z_2^0$.

For convenience, we introduce æ to denote the ratio of the rate constants of chemical reactions of molecules Z_1 and Z_2 with groups A and x_1^0 for the composition of the reaction mixture in solution

$$æ = \frac{k_1}{k_2}, \ x_1^0 = \frac{y_1^0}{y_1^0 + y_2^0} \qquad (11)$$

where y_1^0 and y_2^0 represent the molar fractions of reagents Z_1 and Z_2 in the solution. The composition X_1^0 in terms of parameters (11) is expressed by the following formula

$$X_1^C = \frac{x_1^0}{1 + (-1)x_1^0} \qquad (12)$$

The matrix of the Flory parameters (1) for the current system of interest comprises 15 independent elements. Depending on their values, the sorption of reagents into globule, by analogy with the above-considered reaction systems, affects the rates of chemical transformations. Besides, it also can induce con-formational transitions of the macromolecule in the course of PAR due to the difference in the thermodynamic affinity of monomeric units B_1 and B_2 with the solvent. Below we will dwell on one more interesting phenomenon, connected with the effect of the preferential sorption of the reagents on the final composition of the copolymer. Note that an analogous phe-nomenon is well-known in free-radical copolymerization as the "bootstrap effect".[8–20] Centrally important for this effect is the interplay of physical and chemical factors manifesting itself as follows.

For simplicity sake, let us consider a system where the reagents showing identical affinity to the polymer are present in the solution in equimolar fractions. Let us also presume the
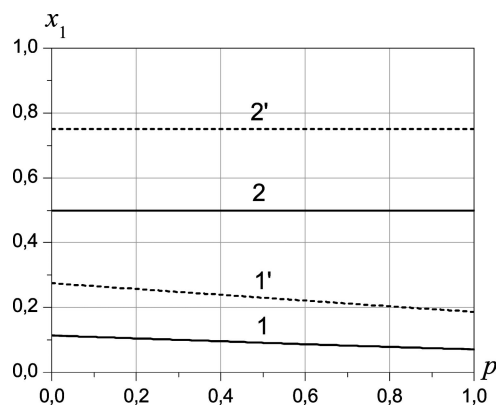
Figure 3. Composition x_1 of the reagents' mixture inside the globule versus conversion of the initial units A. Lines 1, 1′ and 2, 2′ correspond to PAR conducted inside globule and coil, respectively. All lines are calculated at the same value of æ equal to 9, solvent volume fraction $y_3^0 = 0.95$, and composition of reaction mixture in solution $x_1^0 = 0.5$ (1, 2); $x_1^0 = 0.75$ (1′, 2′). Values of the remaining parameters used to construct curves 1 and 1′ are presented in matrix (13), where the first three rows and columns correspond respectively to the reagents Z_1, Z_2 and the solvent, while the last three correspond to the monomeric units A, B_1, and B_2.

first reagent to be more reactive than the second one. Then, at the initial stage of the PAR, the fraction of B_1 units in the macromolecule will be substantially larger than the fraction of B_2 units. If the contacts of B_1 units with reagent Z_1 prevail over those with reagent Z_2, the mixture of reagents in the globule will also get progressively enriched with the first of them. This, in turn, will favor further preferable formation of B_1 units. Such a positive feedback can lead to a pronounced distinction in composition of the final product of the PAR proceeding inside a globule and inside a coil.

One more interesting example of the influence of the preferential sorption on the composition of the final product of the PAR occurs in a system where A units prefer to have contacts with molecules Z_2 whose reactivity is markedly less in comparison with molecules Z_1. In this case, at the initial stages of the PAR in a nanoreactor, the reaction mixture inside the globule will be enriched by the less reactive reagent. As a result, the rates of the formation of B_1 and B_2 units can become comparable. The values of these rates will just slightly differ at later stages of the PAR, if the reacted units of both types tend to the contacts with reagent Z_2. This situation is illustrated by Figure 3. Its inspection shows that the composition of the reagents' mixture inside the globule practically does not change in the course of the PAR remaining approximately equal to 0.1. Consequently, the ratio of the fractions of each of units B_1 and B_2 to their overall fraction undergoes no alteration as well, being close to 0.5 because the ratio of the kinetic constants k_1 to k_2 equals 9.

$$\chi = \begin{vmatrix} 0 & 0.1 & 0.1 & 1.6 & 2.0 & 2.0 \\ 0.1 & 0 & 1.3 & 0.3 & 0.2 & 0.1 \\ 0.1 & 1.3 & 0 & 1.5 & 1.6 & 2.0 \\ 1.6 & 0.3 & 1.5 & 0 & 0.2 & 0.2 \\ 2.0 & 0.2 & 1.6 & 0.2 & 0 & 0.5 \\ 2.0 & 0.1 & 2.0 & 0.2 & 0.5 & 0 \end{vmatrix} \qquad (13)$$

Of particular theoretical and applied interest is a comparison of the character of the dependence of the composition of the final products of the PAR proceeding inside a globule and inside a coil. In the last case this dependence is described by the simple analytic expression (12) used to draw the curves 2 and 2′ in Figure 4. It shows that the preferential sorption can substantially decrease the content of B_1 units formed during the reaction of group A with the more reactive reagent Z_1. For the pair of
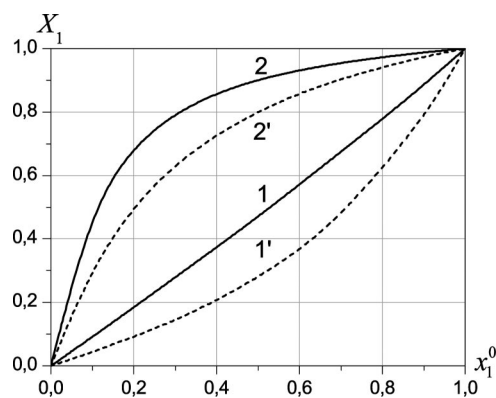

Figure 4. Dependencies of fraction X_1 of units of type B_1 in chain of final polymer on the reaction mixture composition x_1^0 in solution for the products of PAR inside globule (curves 1, 1′) and inside coil (curves 2, 2′). The solvent fraction in solution $y_3^0 = 0.95$ the value of parameter æ equals 9 (curves 1, 2) and 4 (curves 1′, 2′); values of thermodynamic parameters are the same as those used when calculating the lines in Figure 3.

lines 1 and 2 the difference in concentrations of reagents in the globule due to their preferential sorption almost completely compensates for the distinction in their reactivities. As a result, the dependence of X_1 on x_1^0 is given by a straight line. For the other pair of curves, 1′ and 2′, the difference in reactivities of reagents Z_1 and Z_2 turns out to be insufficient to compensate for the effect of their preferential sorption into globule. That is why the final products of the PAR conducted inside the globule prove to be enriched with B_2 units.

Conclusion

Finally, we will discuss some assumptions underlying the model used to perform the calculations. First, all chemical reactions were presumed to proceed under a kinetically controlled regime. This assumption is certainly true, provided the globule is not in glassy state, because the characteristic time scales of the diffusion of low-molecular-weight reagents into the globule are normally far less than the time scales of their chemical transformations. In the opposite limiting case, when the reaction proceeds under the diffusion-controlled regime, the so-called "protein-like" heteropolymers are formed.[22] The macrokinetics of such PARs has been theoretically studied in papers.[30,31]

Second, in line with ref 21 we considered only homogeneous heteropolymer globules in "volume approximation", ignoring their narrow surface layer. This approximation is known to work rather well outside the immediate vicinity of the coil−globule transition point.[32] As for leaving out of consideration inhomogeneous heteropolymer globules with varying concentrations of monomeric units at different points, the appearance of such globules can be expected only at sufficiently large values of the Flory parameter describing the pair interaction of these units. The assumption on the thermodynamic and kinetic stability of a globular solution of macromolecules with respect to their aggregation in the course of chemical transformations in a reaction system is of utmost importance. This assumption holds the better the lower is the concentration of globules and the faster are chemical reactions proceeding in them.

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