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Advanced Applications of Evolution processes in Solutions of Interacting Polymers

In this work the experimental technique, which allows investigate the processes of artificial evolution, is offered. Artificial evolution processes occur in solutions of polymers capable to form hydrophilic interpolymer associates. Those processes are caused by external action, for example, periodical heating of solution of interacting polymers. The observation of phase transition shows that evolution processes can be governed by external action in special way. Here we show the relationship of experiments that ensure artificial evolution in systems of the specified type in physical chemistry of polymers with processes in nanotechnology and processes in sociology and economic disciplines. Such approach is prevalent for systems having large number of elements and specified relations between its elements.

Key words: artificial evolution, hydrophilic interpolymer associate, phase transition.

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Әрекеттесетін полимерлердің ерітіндісінде жасанды эволюцияны пайдаланудың жаңа мүмкіндіктері

Жұмыста жасанды эволюцияның процесстерін зерттеуге мүмкіндік беретін эксперименталды техника ұсынылған. Зертеліп жатқан жасанды эволюцияның процесстері гидрофильді интерполимерлі ассоциаттар құрастыра алатын полимер ерітіндісінде өтеді. Эволюциялық процесстерді ерекше амалымен басқарылатыны фазалық өткелдердің экспериментaлды зерттеуі көрсетті. Бұл жұмыста келтірілген типтегі жүйелерде жасанды эволюцияның жүрісің камтамасыз ететін эксперименттердің тек полимерлердің физикалық химиясына емес, басқа да нанотехнология мен әлеуметтік-экономикалық ғылым сияқты салаларға тән екені көрсетілген. Бұл тәсілдеме әр элемент басқа элементтермен белгілі бір жолмен әрекеттесетін сансыз элементтерден құрылатын жүйелерді зерттеуде кең таралған болып келеді.

Түйін сөздер: жасанды эволюция, гидрофильдік интерполимерлік ассоциаттар, фазалық өткел.

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Новые возможности использования процессов искусственной эволюции в растворах взаимодействующих полимеров

В работе предложена экспериментальная техника, позволяющая исследовать процессы искуственной эволюции. Исследуемые процессы искуственной эволюции протекают в растворах полимеров, которые способны образовывать гидрофильные интерполимерные ассоциаты. Экспериментальное исследование фазовых переходов показало, что процессы эволюции могут управляться с помощью внешнего воздействия специфичным образом. В данной работе показана связь экспериментов, обеспечивающих протекание искуственной эволюции в системах указанного типа, характерных не только для физической химии полимеров, но и для других отраслей, включая нанотехнологии и социально-экономические науки. Данный подход является распространенным при исследовании систем, состоящих из большого числа элементов, где каждый элемент системы взаимодействует определенным образом с другими элементами.

Ключевые слова: искусственная эволюция, гидрофильные интерполимерные ассоциаты, фазовый переход.

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ADVANCED APPLICATIONS OF EVOLUTION PROCESSES IN SOLUTIONS OF INTERACTING POLYMERS

Introduction

The question about the nature of evolution mechanisms, which preceded the biological one, still remains open [1-3]. In many respects, it is connected with the fact that till today there are no generally accepted means of experimental check of the hypotheses designed for finding the way on which prebiological evolution occurred.

In work [3] the concept which allows to dig up the mechanism of prebiological evolution on the basis of the new alternative to the Darwinist point of view, using hypothesis of casual mutations (wider – fluctuations) with the subsequent fixing of favorable signs as the driving force of evolution was formulated. The concept [3] is based on the proof of analogy between partially dissociating macromolecule and a neural network. It is possible to show [3] that any molecule of polymer getting an electrostatic charge due to partial dissociation of functional groups automatically becomes analog of the Hopfield's neuroprocessor in which the role of separate neurons is played by the functional groups capable to get a nonzero charge at the expense of dissociation. Electrostatic fields created by no compensated charges go in the role of feedback. The output state of neurons analogs is described by logical variables (1 – there is a charge, 0 – there is no charge).

Based on the analogy between partially dissociating macromolecule and a neural network, it is possible to offer the following mechanism of prebiological evolution [3]. According to [3], the system of any nature is treated as «complex» on condition that there is complementary to it an analog of a neural network.

At the first stage of evolution the complexity is in transformation of communications between its elements which is treated as evolution of a neural network (or its analog), complementary to the system under consideration. At the second stage, the neural network carries out the directed «choice» of the elements, which are most answering to a new state.

Consideration of a number of social and economic systems [4,5] allows to show that such mechanism of evolution, apparently, is the general, i.e. it is applicable to the description of any nature systems. It can be explained as follows. The nature of new quality which appears in complex system at the first stage of evolution can be only informational: this quality corresponds to simple set of system elements in the same way as the consciousness of the person corresponds to set of neurons that make up a human brain.

Comparison to social and economic systems (in particular, being considered in [4,5]) is important due to the fact that the appearing new quality can be treated as the macroscopic regulator, not only the providing selection of system elements, but also showing such functions as the distributed memory, specific reactions to external influences, etc. In other words, at this stage of evolution the system, in a certain extent, gains property of self-directing its further development.

This conclusion is nontrivial and far from the conventional. This is why it is extremely important to find the experimental evidence of the adequacy of proposed evolution mechanism, which is the main goal of this work.

Experimental

Materials. Polyacrylic acid (PAA) with molecular weight $2.5x10^5$ (Aldrich Chemical Co., USA) was used without additional purification.

N-vinylcaprolactam (Aldrich) was freshly distilled. Polycaprolactam was prepared by radical polymerization in glass ampoules in the presence of AIBN initiator. N-vinylcaprolactam 11, 64 g (83.62 mmol) and 27 mg (0.16 mmol) of AIBN were dissolved in 71 g of toluene and the polymerization solution was purged for 30 min with argone to remove oxygen. Polymerization was conducted for 24 hrs at 70 °C. After the polymerization, the solution was cooled to room temperature and poured to the excess of diethylether. The precipitated polymer was purified by intensive reprecipitation from toluene to diethylether (3x) and dried to constant weight.

Molecular weight characteristics and polydispersity of obtained polymers was detected by gel permeation chromatography. Gel permeation chromatography was performed by GPC Aligent 1100 series RI detector.

Methods. The scheme of the used installation gathered to initiate a process which can be treated as artificially stimulated evolution is submitted in Fig. 1. Ditch (1) is filled with the studied solution, its walls are made of the plane-parallel glasses polished with an optical accuracy. In the center of ditch the heating spiral (2) made of a nichrome wire 0,1 mm in a diameter in the form of a ring is located.

The optical system provides registration of the optical transmission coefficient of the medium, which changes as a result of interpolymer reactions.

Heating of a spiral is carried out periodically, and the range of temperature fluctuations captures the temperature at which phase transition occurs due to the formation of insoluble and/or partially soluble component. In other words, at such fluctuations, the hydrogen bonds [6, 7] stabilizing a product of interpolymer reaction (hydrophilic interpolymer associate, HIA) are destroyed, then formed again. They represent grids/fragments of the grids existing in the dynamic mode, and one of the interacting polymers acts as the cross-agent. It is necessary to emphasize that HIA is the new and low-studied class of interpolymer reactions products. However, already at this stage of research it can be stated that HIA forms the whole range of interpolymer reaction products [6,7] that should be expected due to the liability of their structure.

Destruction and formation of communications in such labile system as HIA can be considered, taking into account results [3], in terms of the change of weight coefficients of neural networks formed by fragments of polyelectrolyte macromolecules. (Weight coefficients are defined by distances between functional groups.) In other words, at formation and destruction of the hydrogen communications stabilizing HIA rewriting of information actually takes place.

Further, at repeated rewriting of information (that is provided with periodic nature of temperature indignation) the system of considered type aspires to certain rather steady state. Mathematically it can be described as transition to a limit of the following type.

$$S_{n=1} = (I = A)\, S_n, \qquad n \rightarrow \infty \qquad (1)$$

where S_n is a vector, describing the state of the system at the n-rated iteration, A is an operator of information rewriting, I is the unit operator. The existence of this limit already means that the system evolves, as some steady state capable to reproduction of information appears in it. (This, obviously, is the primary necessary condition for the appearance of inherited information.)

Thus, in despite of the simplicity of the used technique, it really can be used for initiation of artificial evolution, at least, understood in the sense of generating self-replicating information.

Results and discussion

The example of the data registered by means of the scheme in Fig. 1 is presented in Fig. 2. The schedule represents a fragment of dependence of relative intensity of an optical signal from time at periodic heating in the set mode. Measurements were made using 2% polyvinylkaprolactam solution (PVK)

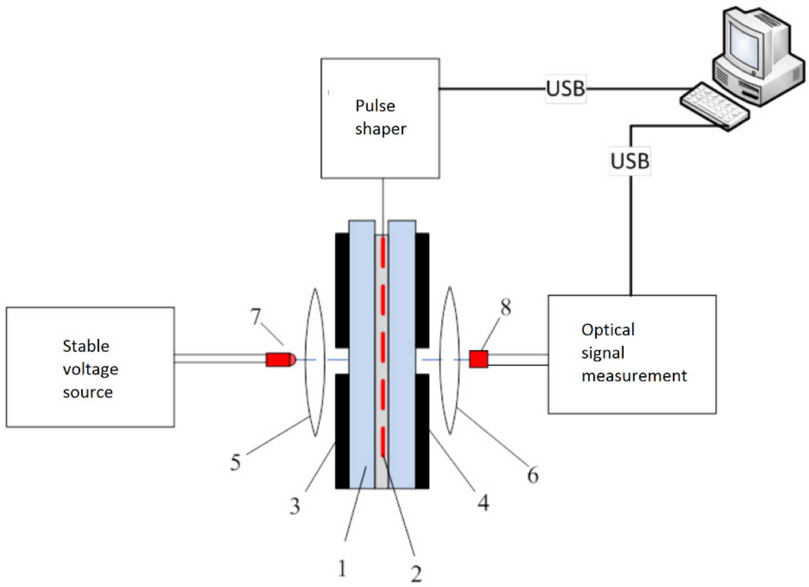

Figure 1 – The scheme of experimental installation providing start of artificial evolution processes by means of periodic heating; 1 is a ditch with the studied solution, 2 is a heating spiral, 3,4 are iris diaphragms, 5 is lens providing formation of a parallel beam of light, 6 is the focusing lens, 7 is the light source, 8 is the optical receiver.

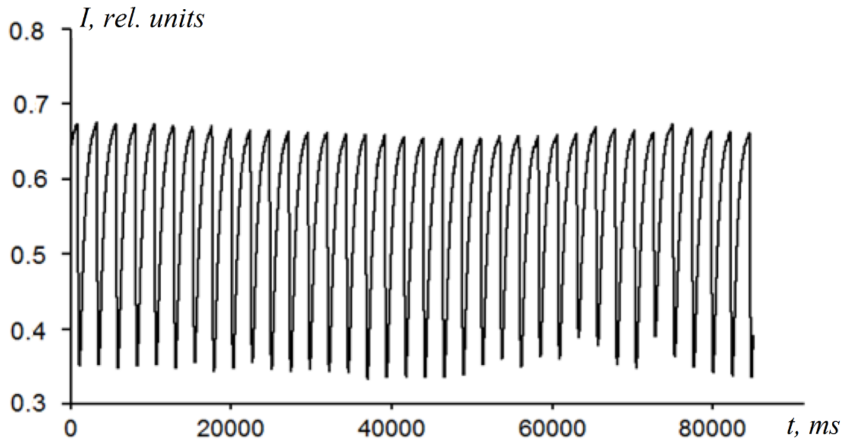

Figure 2 – Dependence of relative intensity of an optical signal from time, C (PVK) = 2%, T = 2400 ms, τ = 30 ms

It can be seen that the shape of the observed oscillations is noticeably different from the square and that allows tracing kinetics of phase transition. It is also visible that in this case (pure solution) effects connected with any transformations of the environment don't take place.

Addition low-molecular salt in solution, as it is known in [8], leads to an increase in speed of phase transition. (It seems to be connected with the bigger amplitude of local change of thermodynamic variables.) At a concentration of 0.3% sodium chloride more complex fluctuations occur in the system. The corresponding example is presented in Fig. 3.

It is evident that in the spectrum of the detected signal additional low-frequency components appears. As it is well known [9], the modulation of oscillations induced by external influences, in a nonlinear system takes place when such system possesses own resonant properties. In this case conditions when own damped oscillation is sustained due to energy of an external source are realized.

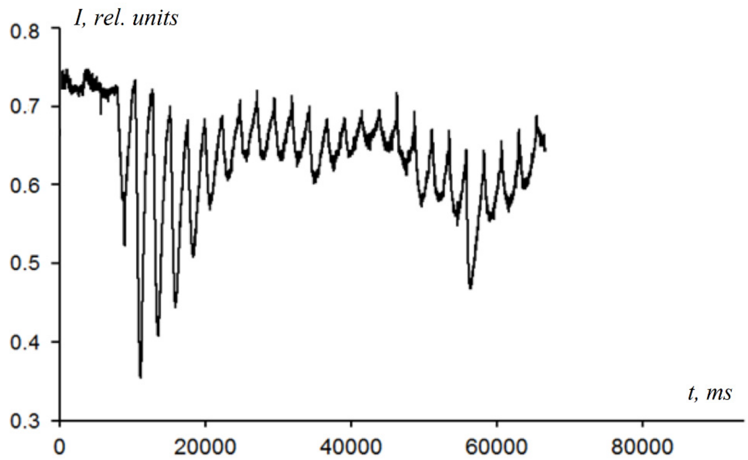

Figure 3 – Relative intensity of the optical signal from the time, C_{pol} = 1%, C_{NaCl} = 0,3%, T=2400 мс, τ =30 ms; time countdown is made from the beginning of measurements

It is also visible in Fig. 3 that the studied system spontaneously can pass from one mode into another, and this transition is carried out by jump. The new state is characterized by hyper sensibility of system to external influences that is expressed in sharp increase in amplitude of fluctuations, and also in appearance of additional low-frequency components in a range of the registered signal.

The regular fluctuations or fluctuations close to the regular ones are mainly observed in solution which contains only one polymer. If the solution contains two interacting polymer (the system of PAA + PVK which as it was noted above, forms a hydrophilic interpolymer associate, and an interpolymer complex) then observed fluctuations, as usually, lose their regularity. The corresponding example is presented in Fig. 4 (the data obtained in a stoichiometric concentration ratio of PAA and PVK). Comparing this result with the data in [5,6], in which it was shown that in the region of HIA existence interpolymer reaction between PAA and PVK provides a wide range of products, we can see that the system is really experiencing major transformation.

Thus, periodic indignation of the solution containing polymers capable to form both HIA, and PKI really provides effects that can be interpreted as restructuring of the supramolecular structures formed by interaction of macromolecules.

Conclusion

Thus, in work the simple technique that provides periodic destruction and formation of the communications stabilizing HIA and/or interpolymer complexes is offered. The analogy between partially dissociating macromolecules and neural networks allows considering such periodic process in terms of repeated rewritable information in separate fragments of macromolecules. The transition to equilibrium state is achieved by multiple direct and reverse phase transitions in this case is interpreted as the appearance of the structure carrying the reproducible information. Adequacy of this conclusion follows from comparison to results of works [4,5] in which it was shown that emergence of any steady network automatically provides realization of the evolutionary mechanism offered in [3]. Namely stability of a network provides «the choice» of quite certain elements that are mostly answering to a new condition of system.

Presumably, this mechanism could underlie the occurrence of primary elements which served as a prototype of macromolecules capable to bear the genetic information. It is necessary to emphasize that under certain conditions [10] periodic fluctuations of temperature in non equilibrium systems can arise spontaneously, too. Therefore, conditions in which there is a repeated overwriting of data in the neural network of molecular level, can also be implemented naturally.

Certainly, the hypotheses stated in this work need further confirmations, however already at this stage of research it is admissible to assume that initiation of artificial evolution of molecular structures represents not only the academic, but also practical interest as one more instrument of receiving nanostructures.

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