DYNAMIC STRUCTURIZATION IN SOLUTIONS OF HYDRODYNAMICALLY ACTIVE POLYMERS

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It has been established experimentally that, under the condition of elongational flows, dynamic structurization and periodic processes may originate in the solutions of flexible polymers due to self-regulation in these systems.

In recent years the processes of ordering and self-regulation in nonlinear systems have been attracting great attention because understanding the principles of self-regulation and its thermodynamics can become a clue to many physical phenomena, specifically, to the Toms effect [1]. An example of a self-regulating system in hydrodynamics has long since been known. It is the so-called Benard instability [2]. The formation of benards is a spatial self-regulation. Systems are also known which are able to order both spatially and temporally. A classic example is the Belousov–Zhabotinskii reaction [3] when the break of a spatial homogeneity and the development of a spatial–temporal order bring about a periodic process in a reactive system.

Both the simplest and most complex systems in living and nonliving nature are capable of ordering, but the fundamental principles of self-regulation, established by I. Prigozhin and his school [2], are identical in all cases. The system must be open (must exchange energy and mass with the environment), nonlinear (a reaction to outer effects is not proportional to them), and supercritical (a restructuring from chaos to order is only possible on passing over a critical point away from the state of thermodynamic equilibrium, i.e., the so-called bifurcation point). Self-regulation is always accompanied by energy dissipation.

The tests dealt with in the current study revealed that spatial and temporal self-regulation can be observed in the solutions of hydrodynamically active polymers under the condition of elongational flows.

To create a hydrodynamic elongational field we used the flow of a Newtonian liquid (water, acetone, dioxane) converging to a small opening with $0.3 \cdot 10^{-3}$ m diameter. Into the same flow, at a sufficient distance from the opening, we injected jets of solutions of hydrodynamically active polymers, viz., polyethylene oxide (PEO) or hydrolyzed polyacrylamide (HPAA) with molecular mass $6 \cdot 10^6$ and $4.5 \cdot 10^6$ and characteristic viscosity 2.42 and 3.70 m^3/kg, respectively. The degree of hydrolysis of polyacrylamide was 5%. Investigated concentrations ranged within 0.001-0.1%. The velocity of the polymer solutions at the injection points coincided with the velocity of the main flow of the liquid. The flow was visualized in the entrance region of the opening via dye additions to the injected polymer solution.

At low outflow velocities, dyed jets of the polymer solution make streamlines of the main flow visible (Fig. 1). In this case, the behavior of the jets of PEO and HPAA solutions differ in no way from the water jets injected into the convergent liquid flow. After the liquid flow rate through the opening has attained a certain critical value, the flow character of the polymer solution jets changes abruptly. Fairly thick polymer jets transform into thin cords, whose length varies with time (Fig. 2). Observing the dynamics of formation and collapse of individual cords (which is the essence of the pulsational motion character of submerged polymer jets) reveals the following regularity. Initially, with the polymer jets approaching the opening, their smooth curving toward the opening is observed. In this case, they begin to be ever more noticeably accelerated along these curvilinear trajectories, which is testified to by thinning of the jets. Near the opening, a stepwise (for PEO solutions) decrease in the thickness of the jets is observed, and they transform into a thin cord. The region where a thick jet transforms into a thin cord starts drifting up the jets, thus causing extension of the cords. The variation in the jet thickness for aqueous HPAA solutions is more even than for PEO solutions. Since the jets approach the opening nonsimultaneously, at each instant of time the length of the cords spinned by the flow out of the individual polymer jets is not the same. A double refraction is observed in the region of jet emergence.

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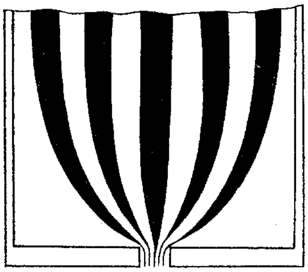

Fig. 1

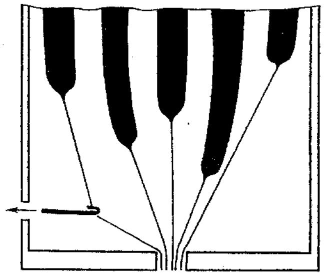

Fig. 2

Fig. 1. Flow pattern in the entrance region of the capillary at injection of the polymer solution into water with a subcritical mode of outflow.

Fig. 2. Flow pattern at the instant when a wire probe (on the left) has an effect on the polymer cord spinned by the hydrodynamic field ($M_{PEO} = 6 \cdot 10^6$; $C_{PEO} = 0.03\%$; $\bar{U} = 2.5$ m/sec).

On reaching a certain critical length, the cord breaks in the immediate vicinity of the opening. Thereafter, the cord that remained above loses elasticity and dips, marking one of the streamlines of the main flow. When the polymer jets have approached the opening once more, everything is repeated anew. This process resumes with a period varying from fractions of a second up to several seconds, depending on the mode of the main flow, the molecular mass of the polymer, its type, the solvent quality and temperature, as well as on the polymer concentration in the solution.

A rise in the discharge velocity of the convergent water flow and an increase in the molecular mass and concentration of the polymer entail an extension of the cords and a decrease in the frequency of their length variations. A rise in the temperature leads to the opposite effect. Tests with acetone and dioxane (which are solvents of worse thermodynamic quality than water [4]) showed that, for the same supercritical velocities as in the tests with water, the pulsation frequency of the cord length is greater and the amplitude of these variations is smaller than in the case of injection of the polymer solution into water. It is to be noted also that for concentrated (according to Debye [5], $[\eta]_0 \cdot C > 1$) polymer solutions, there are such outflow modes when the formed polymer cords do not collapse throughout the time of observation.

Consideration was also given to the effect of the initial (unperturbed by the hydrodynamic field) dimensions of the molecular coils, which for polyelectrolytes (HPAA) are functions of the pH value of the medium, on the flow character of the HPAA solution jets injected into the water flow. The experiment has demonstrated that, at a pH of the water main flow equal to 2, the length of the polymer cord decreases suddenly (by 3-4 times for a concentration of 0.05%), whereas frequency of variation of the cord length increases by 1.5-2 times. Increasing pH from 7 up to 9.5 does not actually affect the flow character.

Basic regularities of the behavior of the polymer jets when injected into an elongational flow, such as the main liquid flow is [6, 7], are the same as in the case of the polymer solution outflow through short capillaries [6-9]. Consequently, the observable singularities of the behavior of submerged polymer jets in the elongational flow are stipulated by a very strong unrolling of the polymer coils by the action of the hydrodynamic field (the degree of their unrolling amounts to about 60% [7, 9]). The unrolling of macromolecular chains results in a reduction of their flexibility, which in certain conditions causes a phase separation under the action of the hydrodynamic field [10], i.e., induces dynamic structurization.

The following experiment can serve as confirmation of the dynamic structurization by the action of a stretching hydrodynamic field. A thin wire with a facility for capturing the polymer cord is located in the entrance region of the opening at subcritical modes of the outflow. Travel of such a wire in the plane perpendicular to the jets does not alter the flow pattern, i.e., the polymer jets are permeable to the wire at these flow modes. If the same experiment is repeated at a supercritical mode of the liquid outflow, one or several polymer cords can be captured at the instant of their growth and drawn aside, as is illustrated in Fig. 2. This is possible only with a fairly strong interaction between the polymer molecules, i.e., with the origination of a supermolecular structure, occurring in the this case by the action of the stretching hydrodynamic field. The minimal concentration of aqueous PEO solutions, when a cord spinned by the hydrodynamic field might yet be warded off, was equal to 0.008%, which corresponds to the region of dilute solutions ($[\eta]_0 \cdot C < 1$).

The results presented and those obtained in studying convergent flows of polymer solutions [6-9] allows us to state that the solutions of hydrodynamically active polymers ought to be subdivided into at least three regions of concentrations. The first is a region of dilute polymer solutions, where the macromolecules are subjected to strong deformational effects (to unrolling) under the action of the hydrodynamic field but still weakly interact with one another. The second is a region of semidilute solutions (an intermediate region), where with subcritical flow modes the solutions are dilute, but with supercritical flow modes they are already concentrated, because supermolecular structures have emerged from the displacement of the phase separation curves under the effect of the hydrodynamic field [10]. These dynamic structures should be referred to the class of dynamic phase transitions, treated by the theory of dissipative structures [2]. The last region is that of concentrated solutions ($[\eta]_0 \cdot C > 1$), where significant macromolecular interactions exist even with no hydrodynamic field. Attention should be drawn to the fact that the first two regions pertain to strengths of the Toms effect manifestation [11].

Thus, the results considered in the current study indicate that a dynamic structurization and periodic processes, obeying the Prigozhin principles of self-regulation [2], may originate in the solutions of hydrodynamically active polymers under the conditions of an elongational flow. Apparently, the effect of a reduction in turbulent friction by polymer additives is related exactly to the initiation of dynamic structurization. Therefore, the results of the current work and of [7, 12-14] are of great importance for substantiating the model of a continuous medium, in which the Toms effect is displayed.

NOTATION

$[\eta]_0$, characteristic viscosity; C, polymer concentration in the solution; $\bar{U}$, mean velocity of liquid outflow through the opening.

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