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# Stability of polymer jets in extension: physicochemical and rheological mechanisms

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The review is devoted to the fundamental problems of physical chemistry and rheology posed in the analysis of stability loss of polymer jets in extension. Studies of phenomena occurring in deformation of polymeric fluids are of considerable applied interest because extension of polymeric fluids underlies many industrial processes, first of all, fibre spinning. Studies of critical conditions of deformation are based on general principles of fluid mechanics, which are applicable to all fluids and various phenomena in nature and technology. First we discuss solutions to classical problems of instability of liquid jets as the basis for further analysis of the behaviour of polymeric fluids in particular situations. Next, specific features of the deformation mechanisms and appearance of instabilities of polymeric fluid jets are considered as consequences of their physicochemical and rheological properties.
The bibliography includes 162 references.

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## 1. Introduction

Various chemical technological processes involve jet fluid flows. For instance, all homogeneous catalytic reactions proceed under vigorous stirring to ensure contact between the reactant and catalyst molecules; this increases the yield of the desired product and improves its homogeneity. Jet reactors are widely used in gas-phase plasmachemical processes. One more example of jet flow is provided by chlorination of propylene where the process involves the interaction of rotational gas flows.

The aforesaid holds for jet flows occurring in liquid or gaseous media under conditions of chemical reactions between components. However, of great independent significance are free jets moving in air as well as jets moving under the action of external forces, which allows one to fabricate micro- and nanofibres and materials based on them.[1,2] The behaviour of such jets depends on specific features of the rheological properties of polymeric fluids, which underlie the surface and physicochemical phenomena responsible for stability of the flow.

When considering various natural processes and engineering applications, the formation, deformation and breakup of liquid polymer jets are common to all fluids. Determination of stability and conditions for the onset of critical phenomena under deformation conditions is based on the use of universal principles of fluid mechanics. Physicochemical phenomena occurring under uniaxial tension and originating from specific features of the rheological properties of polymeric fluids are of fundamental interest. They also underlie the understanding and realization of basic large-scale industrial processes, such as fibre spinning, fabrication of oriented films and contribute to the understanding of the structure and properties of polymers. Problems in physical chemistry and stretching mechanics of polymer melts and solutions are related to classical problems of the breakup and disintegration of liquid jets in numerous practical applications including those mentioned above.

Extension of this field to polymers introduced a variety of new effects and related theoretical problems. When considering them, the approaches and solutions proposed should be correlated with the results obtained during more than 150 years of research into fluid flow instabilities in

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order to form the basis for further progress in the field. Recently, problems associated with understanding the behaviour of polymeric fluids in extension and determining conditions for the onset of instabilities of different physical nature have been intensively and fruitfully discussed from the standpoint of both basic research and application to validation and optimization of engineering processes.

Theoretical and experimental studies on the dynamics of Newtonian fluid jets made it possible to develop a consistent methodology for explanation of the following main groups of phenomena responsible for understanding the instability mechanisms:

— jet breakup into droplets;

— changes in jet shape and the onset of jet bending instability; and

— the influence of the environment on the jet dynamics.

Meanwhile, fibre spinning from polymer solutions is accompanied by some new phenomena that have been intensively studied recently. Key features of the mechanics of the process are governed by complexity of the rheological properties of polymeric systems and by phase transformations of the systems in question under conditions of intense deformation. The dynamics of polymer jets are described using nonlinear models for viscoelastic media, which means that elastic properties of the medium are considered in explicit form.[3] Such models enable a correct description of stable fibre formation. Recently, there has been an idea that it is the elasticity of polymer solutions that is the key property responsible for stable fibre spinning. No less significant is the fact that the relative importance of elasticity and other characteristics of polymer solutions is directly related to the critical conditions for the onset of different-type instabilities. This understanding of the mechanics of fibre spinning from polymer solutions led to the development of a novel engineering process called mechanotropic spinning.[4]

The aim of this review is to analyze the state of the art in studies on and the available concepts of specific features of the onset of instabilities in uniaxial stretching of polymer melts and solutions as viscoelastic media, which are natural evolution of general physical models instability of fluid flows. We will consider classical mechanisms and criteria for instability in extension of viscous fluid jets, analyze the mechanics of extension of viscoelastic fluids and the reasons for stability of liquid polymer jets as a consequence of their elasticity, and discuss physics of phase separation of polymer solutions under stretching and also the possibility to develop new engineering processes of polymer fibre fabrication using the mechanisms considered.

The list of notations and abbreviations used in the review is as follows:

$a$ — radius of cylindrical jet;
Bo — Bond number;
$\mathrm{Bo_e}$ — electrical Bond number;
$c$ — concentration of a solution;
$c^*$ — crossover concentration;
$c_{\mathrm{stab}}$ — concentration corresponding to formation of stable jet;
$C$ — total curvature of jet surface;
Ca — capillary number;
$\sigma_{zz}$, $\sigma_{rr}$ — stress tensor components along the $z$ axis and in radial direction, respectively;
$D_0$ — nozzle diameter;
$E$ — electric field strength;
$\varepsilon$ — dielectric constant of a fluid;
$\dot{\varepsilon}$ — jet deformation rate;
F — jet deformation force;
Fr — Froude number;
$\gamma$ — surface tension;
$\Gamma$ — growth rate of jet disturbance;
$\Gamma^*$ — maximum growth rate of disturbance;
$g$ — gravitational constant;
$l^*$ — characteristic length;
$L^*$ — jet length before breakup into droplets;
$l$ — monomer unit length in polymer chain;
$\lambda$ — modulation period of cylindrical jet;
$M$ — mass of a drop;
$N$ — number of monomer units in polymer chain;
$v$ — amplitude of modulation of cylindrical jet;
$v^*$ — initial amplitude of modulation of a jet;
Oh — Ohnesorge number;
$Q$ — fluid flow rate;
$R^*$ — radius of liquid bridge at which polymer chains unfold;
$R^{**}$ — radius of liquid bridge at which polymer chains become fully stretched;
$R(z,t)$ — jet radius;
$R_0$ — nozzle radius;
Re — Reynolds number;
$\rho$ — fluid density;
$\eta$ — fluid viscosity;
$\eta_{\mathrm{ef}}$ — effective viscosity of a solution of extended chains;
$t$ — time;
$t^*$ — critical time to breakup;
$t_{\mathrm{b}}$ — jet breakup time;
$\tau$ — relaxation time of polymeric fluid;
$\tau^*$ — jet disintegration time;
$V$ — jet velocity;
$V_0$ — initial jet velocity;
We — Weber number;
Wi — Weissenberg number;
$z$ — coordinate along the cylinder axis.

## 2. Classical problems

An analysis of liquid jet dynamics has a long history. Main problems in the field were formulated more than 100 years ago and subsequently became the subject of many years of research. Among classical studies, mention should be made of original and fundamental publications by Plateau,[5] Rayleigh[6, 7] and Bohr,[8] who established that basic mechanism of jet breakup is related to surface tension. Plateau[5] pioneered in demonstrating that it is surface tension that underlies instability of a cylindrical filament-like liquid jet and its fission into droplets. He considered disturbance of such a filament and determined the surface area of a cylinder whose radius is modulated by the harmonic function

$$R(z) = a + v\cos kz \tag{1}$$

where $a$ is the average radius; $z$ is the coordinate along the axis of the cylinder; the amplitude of modulation of the radius $v$ meets the condition $v \ll a$; and the projection of the wave vector $k$ is related to the modulation period $\lambda$ as follows:

$$\lambda = \frac{2\pi}{k} \tag{2}$$

If $\lambda$ exceeds the jet circumference $2\pi a$, the surface area of the modulated cylinder is always smaller than that of the

initial cylinder provided that both have equal volumes. It was concluded that the cylinder should break into segments of minimum length $\lambda = 2\pi a$.

More recently, Rayleigh [6] studied the growth dynamics of disturbances with periods $\lambda > 2\pi a$. The time-dependent harmonically modulated radius of the cylinder was represented by

$$R(z,t) = a + v\mathrm{e}^{\Gamma t}\cos kz \tag{3}$$

where $\Gamma$ is the growth rate of jet disturbance. Based on the fluid dynamics equations, Rayleigh found a mode corresponding to the maximum growth rate $\Gamma = \Gamma^*$, which is responsible for the characteristic breakup time of liquid cylindrical filament

$$\tau^* = \frac{1}{\Gamma^*} \tag{4}$$

Ignoring viscous forces, the wavelength of this mode and the breakup time are respectively equal to [6]

$$\lambda \approx 9.02\,a \tag{5}$$

$$\tau^* \approx 8.46\left(\frac{a^3\rho}{\gamma}\right)^{1/2} \tag{6}$$

where $\rho$ is the density and $\gamma$ is the surface tension. Rayleigh also for the first time determined[7] the breakup time of inertialess fluid jet (fluid viscosity is $\eta$):

$$\tau^* \approx \frac{6\,a\,\eta}{\gamma} \tag{6a}$$

In this case, one has $\lambda \to \infty$. The results obtained allow one to estimate with ease the critical length of a free jet that emerges from a nozzle at the velocity $V_0$ and retains continuity up to fission into droplets:

$$L^* = V_0\tau^* \ln\frac{R_0}{v^*} \tag{7}$$

Here the time $\tau^*$ is determined using expression (6) or (6a), $R_0$ is the radius of the nozzle and $v^*$ is the initial amplitude of the fastest growing mode. Clearly, in the inertialess mode the critical jet length increases with increasing viscosity: $L^* \propto \eta$. A common solution to the jet stability problem at arbitrary viscous-to-inertial force ratios can be found in a monograph by Chandrasekhar.[9] The results agree well with experimental data.[10]

In some cases, a liquid jet is surrounded by another fluid, with the fluids being immiscible. This situation was studied by Taylor,[11] who analyzed the mechanism of formation of emulsions and more recently by Tomotika,[12, 13] who reported a thorough theoretical analysis of the onset and development of instabilities in inertialess fluid jets. It was established that the period of the fastest growing mode depends on the ratio of the fluid viscosity in the jet $\eta_0$ to the viscosity of the surrounding fluid $\eta_1$ and is finite.[12] This causes the formation of finite-size drops, as was observed in Taylor's experiments. Only in the limiting cases, where $\eta_0/\eta_1 \to \infty$ (this case was studied by Rayleigh) and $\eta_0/\eta_1 = 0$, the period tends to infinity. One more important result was obtained by Tomotika [13] in a study of the disturbance dynamics of an extending liquid cylindrical filament immersed in another fluid, *viz.*, at certain length scales, extension suppresses the growth of disturbance and stabilizes the filament; this is also in agreement with Taylor's experiment.[11]

Modern studies of jet instabilities are characterized by wide use of numerical methods of solution of the hydrodynamics equations and by carrying out experiments involving high-speed digital cinematography.[14–18] The behaviour of a liquid jet is analyzed within the framework of a few main models. They can be classified with respect to the action of external forces, such as drag forces, gravitational force (free falling jets) or electrostatic forces (electrospraying and electrospinning).

A theoretical analysis of the dynamics of a liquid jet should be performed taking into account the action of all forces, which requires consideration of a number of dimensionless criteria. These are the Reynolds number (Re), or the ratio of inertial-to-viscous friction forces; the Weber number (We), or the ratio of inertial-to-surface tension forces; and the capillary number Ca, or the ratio of viscous-to-surface tension forces. For free falling jets, an important role is played by the Bond number (Bo), or the ratio of gravitational-to-surface tension forces; the Froude number (Fr), or the ratio of inertial-to-gravitational forces. In the case of a charged jet, one should use the electrical Bond number ($\mathrm{Bo_e}$), or the ratio of electrostatic-to-surface tension forces. These criteria are given by the following expressions:

$$\mathrm{Re} = \frac{2\rho VR}{\eta} \tag{8}$$

$$\mathrm{Ca} = \frac{\eta V}{\gamma} \tag{9}$$

$$\mathrm{We} = \frac{2\rho V^2 R}{\gamma} \tag{10}$$

$$\mathrm{Bo} = \frac{4\rho g R^2}{\gamma} \tag{11}$$

$$\mathrm{Fr} = \frac{\mathrm{We}}{\mathrm{Bo}} = \frac{V^2}{2Rg} \tag{12}$$

$$\mathrm{Bo_e} = \frac{2\varepsilon E^2 R}{\gamma} \tag{13}$$

Here $V$ is the characteristic velocity of the jet, $R$ is the radius of the jet, $g$ is the gravitational constant, $\varepsilon$ is the dielectric constant and $E$ is the electric field strength.

Studies on the dynamics of instabilities using the system of Navier–Stokes equations for free boundary flows are highly complicated. A way to simplify the problem is to analyze the behaviour of axially symmetric linear jet in the slender body approximation which allows one to reduce the 3D problem to the 1D case.[14, 15] This approximation is based on weak dependence of the jet radius $R(z,t)$ on the coordinate $z$ along the jet axis, *i.e.*,

$$\left|\frac{\partial R(z,t)}{\partial z}\right| \ll 1 \tag{14}$$

It is also assumed that the tangential component of the jet velocity depends only on $z$ and time $t$, *i.e.*, $V = V(t,z)$. For instance, the dynamics of a jet, ignoring the action of external forces, is described by the fluid volume conservation equation

$$\frac{\partial R^2}{\partial t} + \frac{\partial}{\partial z}\left(R^2 V\right) = 0 \tag{15}$$

and the force balance equation

$$\frac{\partial}{\partial t}\left(\rho R^2 V\right) + R^2 \frac{\partial}{\partial z}\left(\gamma C\right) + \frac{\partial}{\partial z}\left[R^2\left(\rho V^2 + \sigma_{rr} - \sigma_{zz}\right)\right] = 0 \tag{16}$$

Here $C$ is the total curvature of the jet surface

$$C \approx \frac{1}{R} - \frac{\partial^2 R}{\partial z^2} \tag{17}$$

$\sigma_{zz} - \sigma_{rr}$ is the first normal stress difference ($\sigma_{zz}$ and $\sigma_{rr}$ are the components of the stress tensor along the $z$ axis and in the radial direction, respectively). For a Newtonian fluid one has

$$\sigma_{zz} - \sigma_{rr} = 3\eta \frac{\partial V}{\partial z} \tag{18}$$

For polymeric fluids the relation between the stress tensor and the deformation rate (in this case, $\partial V/\partial z$) is given by the rheological equations of state (constitutive equations). Substituting the first normal stress difference for a Newtonian fluid into Eqn (16) and expression (3) into Eqns (15) and (16) gives the parameters of the fastest growing mode

$$\lambda = 2\pi a\left(2 + \sqrt{\frac{a^*}{a}}\right)^{1/2} \tag{19}$$

$$\Gamma = \frac{3\eta}{\rho a^2}\sqrt{\frac{a}{a^*}}\left(2 + \sqrt{\frac{a^*}{a}}\right)^{-1} \tag{20}$$

Here the radius $a^* = 18\,\eta^2/\rho\gamma$ separates the regime where inertial forces dominate ($a \gg a^*$) from the regime governed by viscous forces ($a \ll a^*$). It is easy to show that the limiting cases where one can ignore inertial or viscous forces correspond to the results obtained by Rayleigh.

A study of the competing mechanisms of jet breakup associated with surface tension, inertia and viscosity revealed the decisive role of the Ohnesorge criterion [18]

$$\mathrm{Oh} = \left(\frac{\mathrm{Ca}}{\mathrm{Re}}\right)^{1/2} = \frac{\eta}{\sqrt{\rho\gamma a}} \tag{21}$$

which characterizes the relative importance of two jet thinning mechanisms. Namely, inertial forces and surface tension dominate at $\mathrm{Oh} \ll 1$, while at $\mathrm{Oh} \gg 1$, jet thinning is mainly determined by the surface tension and viscous forces. Three main regimes were specified for Newtonian fluids.[19–23] The inertial regime occurs for large-diameter jets at $\mathrm{Oh} \approx 0$.[19,20] In this case the minimum radius of the jet changes as follows:

$$R_{\min}(t) \propto (t_\mathrm{b} - t)^{2/3} \tag{22}$$

where $t_\mathrm{b}$ is the jet breakup time. The viscous regime dominates the behaviour of small-diameter jets at $\mathrm{Oh} \to \infty$, $\mathrm{Re} \approx 0$ and the jet thinning obeys the expression [17,18]

$$R_{\min}(t) \propto (t_\mathrm{b} - t) \tag{23}$$

The third, inertial-viscous regime, is characterized by $\mathrm{Re} \sim 1$ and jet thinning obeying formula (23).[17,23] Transitions between different regimes have been studied recently.[24]

Fluid flow with gravity can follow various scenarios. At low fluid velocity ($\mathrm{We} \ll 0$), one deals with periodic dripping. The mass of the drop ($M$) is almost independent of the fluid flow rate [25]

$$M = \left(\frac{2\pi\gamma R_0}{g}\right) f\left(\frac{R_0}{l^*}\right) \tag{24}$$

Here $R_0$ is the nozzle radius, $l^* = \gamma/\rho g$ is the characteristic length, which depends on the action of capillary forces, and the function $f$ is determined experimentally. As the Weber number increases, the flow regime is changed to quasi-periodic or random dripping [26] and then to a stable jet.[27] In the last-mentioned case, the question arises as to what is the shape of the jet. It can be answered using Eqns (15) and (16); the latter equation written with inclusion of gravitational force takes the form

$$\frac{\partial}{\partial t}\left(\rho R^2 V\right) + R^2 \frac{\partial}{\partial z}\left(\gamma C\right) + \frac{\partial}{\partial z}\left[R^2\left(\rho V^2 - 3\eta \frac{\partial V}{\partial z}\right)\right] = \rho g R^2 \tag{25}$$

It should be supplemented with the boundary condition at the nozzle outlet. If the flow rate of the fluid at the nozzle outlet is $Q$, from Eqn (15) it follows that the fluid velocity along the $z$ axis in the steady regime is

$$V(z) = \frac{Q}{\pi R^2(z)} \tag{26}$$

The solution of Eqn (25) for the radius ignoring capillary forces was obtained by Clarke.[28]

A systematic study on the shape of stable falling liquid jet using modified Bernoulli equation including viscous energy loss was reported.[29] An analytical solution was obtained to the jet shape problem, which revealed the influence of surface tension on the change in the radius of the jet along the jet length. Namely, the change in the radius was found to be a function of the Fr and Bo numbers.[29] At long distances from the nozzle, where inertial forces dominate, the radius of the jet changes as follows:[30]

$$R \propto z^{-1/4} \tag{27}$$

The theoretical profile of the jet was in good agreement with experimental data. Noteworthy, the role of viscosity in disintegration of the jet was left out of consideration. The asymptotic expression for the radius of the jet can be obtained from Eqn. (25) ignoring capillary and viscous forces

$$R \sim \left(\frac{Q^2}{2g\pi^2 z}\right)^{1/4} \propto z^{-1/4} \tag{27a}$$

The velocity of the jet is determined by the free-fall law

$$V = \sqrt{2gz} \tag{28}$$

It is easy to show that, if the capillary and viscous forces dominate, the dependence of the radius of the jet on the distance has the form [30]

$$R \propto z^{-1} \tag{29}$$

It was repeatedly mentioned that a falling jet of a viscous fluid retains its continuity for unusually long time in spite of little effect of viscosity included in the model for this phenomenon.[30] Meanwhile, it was shown[31] that viscosity can play a significant role since its increase causes a considerable increase in the wavelength of perturbations and subsequent increase in the jet length to breakup. The role of viscosity was re-investigated in an experimental study,[32] which confirmed that the stable jet of highly viscous fluid is much longer than that the jet of low viscous fluid. In the limiting case of highly viscous fluids the dependence of $L^*$ on the parameters of the fluid is given by

$$L^* \sim \left(\frac{gQ^2\eta^4}{\gamma^4}\right)^{1/3} \tag{30}$$

Thus, the length of stable jet is proportional to $\eta^{4/3}$, which agrees with the experimental data.[32] Expression (30) can be derived from Eqn (27) assuming $z \approx L^*$ and from relation (7) using $V \approx Q/R^2$. Of course, this result is only relevant to a particular range of fall regimes of a free jet.

The authors of all known studies on the dynamics of falling jets used only the model of Newtonian fluid. Even in the case of strongly non-Newtonian fluids (*e.g.*, semidilute polymer solution), experimental data were analyzed using the equations of Newtonian fluid dynamics.[33]

The authors of the studies mentioned above considered instabilities originating from the properties of fluids (surface tension, density, viscosity). One more type of instability is due to the interaction between the jet and the environment (see pioneering studies[34, 35] and a more recent publication[36]). Further research into the mechanism of jet fission into droplets was aimed to deeper analyze various surface effects. Factors responsible for the critical jet length are 'summarized' in the following correlation equation for a laminar flow:[35]

$$\frac{L^*}{D_0} = 19.5\left(\mathrm{We}^{1/2} + \frac{3\,\mathrm{We}}{\mathrm{Re}}\right)^{0.85} \tag{31}$$

where $D_0$ is the nozzle diameter.

The influence of flow velocity and viscosity on the stability of liquid jets was analyzed in original publications[37, 38] and in a monograph.[39] Experiments and theoretical estimates showed that the higher the flow velocity the shorter the critical jet length; however, an increase in viscosity causes the latter factor to dominate and thus stabilize the jet. A thorough analysis of studies on jet breakup into droplets and spraying can be found in review articles.[15, 40]

Instability of a liquid jet moving in air can manifest itself not only in jet breakup into droplets, but also in the loss of linear cylindrical shape (jet bending instability). Taking account of the onset of transversal deformations (so-called whipping instability) is of particular importance in studies of electrospinning processes. The problem was posed by the authors of Refs 41 – 44 and more recently comprehensively analyzed in Ref. 45 using a 1D model that describes bending deformation of a liquid jet with retention of cylindrical shape (surface phenomena were ignored). However, it is assumed that jet disintegration into droplets becomes possible when the amplitude of deviation from the vertical axis is a multiple of jet radius.

The jet bending effect was for the first time discussed by Taylor[43] who pointed out that coiling of a jet falling on the surface requires the appearance of normal forces similarly to the case for compression of an elastic cylinder. This idea was critically analyzed in a more recent study,[44] followed by estimation of the critical jet length corresponding the loss of stability.[46] Various coiling mechanisms of falling jets have been discussed.[47] The phenomenon termed 'fluid rope-coil effect' is observed if, *e.g.*, 'a thin stream of honey is poured onto toast'. Three possible mechanisms of the phenomenon were studied[47] numerically: a viscous, a gravitational (falling from a moderate height) and inertial (falling from a great height). When inertial forces dominate, the three mechanisms can act simultaneously.

Bending of a viscous fluid jet incident on a moving surface can be used to fabricate continuous threads.[48]

Theoretical and experimental studies on the dynamics of Newtonian fluid jets made it possible to develop a consistent methodology to explain the following main groups of phenomena:

— jet breakup into droplets;

— changes in jet shape and the onset of jet instability in the form of either breakup into droplets or bending; and

— changes in jet dynamics under the action of external factors.

## 3. Instability of polymeric fluid jets

### 3.1. Main effects

Numerous experimental observations of the behaviour of polymeric fluid jets revealed the appearance of qualitatively new instability effects that are not observed in studies of Newtonian fluids. They can be classified as follows:

— neck formation at large deformations (in other words, extension occurs as continuous transition of the material from the initial state to the neck);

— formation of periodic waves on the jet surface;

— formation of periodic structures of the 'beads-on-a-string' type in extension of moderately dilute solutions of flexible-chain polymers; and

— phase separation of polymer solutions at high deformation rates and(or) upon large deformations.

All these phenomena are related to conformational transformations of polymer chains since extension is accompanied by uncoiling and orientation of polymer chains along the stretching axis. The decisive role is played by a dimensionless criterion called the Weissenberg number (Wi) defined as the product of the deformation rate, $\dot{\varepsilon} = \partial V/\partial z$, of the polymeric fluid by its relaxation time $\tau$

$$\mathrm{Wi} = \dot{\varepsilon}\,\tau \tag{32}$$

At a certain critical value of this parameter (of the order of unity), the polymeric fluid undergoes a relaxation transition from the flow state to the rubber-like state. In other words, the flow under the action of external factors is changed to the development of large recoverable (rubber-like) deformations, which are of crucial importance to mechanics and physical chemistry of polymeric materials.

Thus, the classical mechanism of Rayleigh instability leading to breakup of the jet on extension of the polymeric fluid is only realized at very low deformation rates. The higher the stretching rate the larger the contribution of elastic (rubbery-like) properties to various manifestations of instability.

### 3.2. Instability in extension of polymer melts

Stable extensional flow of polymer melts, which occurs up to the Rayleigh breakup of the jet, is possible at relatively low deformation rates since an increase in flow velocity leads to fast approach to the critical Weissenberg number (Wi ≈ 1). This does not mean that irrecoverable deformations do not occur at high deformation rates. They occur in the transient mode where extensional flow is mainly changed to large rubber-like deformations (up to jet breakup). In this respect melts behave like cross-linked rubbers. The role of chemical cross-link points is played by quasi-stable junctions of the entanglement network whose lifetimes are longer than the deformation time.[49,50] The limiting extension is determined by the length of unfolded macromolecule, which in turn depends on the molecular mass of the polymer.[51,52] The limiting elastic deformations corresponding to rupture of linear polymers are governed by the Weissenberg number. The dependences of the limiting deformations of linear polymers and rubbers (unflowable systems!) on this parameter are similar (Fig. 1).[53] It follows that rupture of both types of materials is induced by their rubber-like deformations rather than surface instability (according to Plateau–Rayleigh).

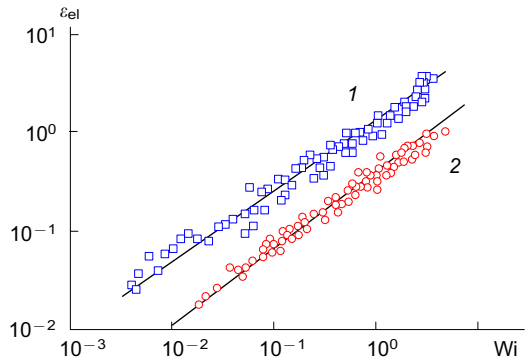



**Figure 1.** Limiting rubber-like deformations of linear polymers (*1*) and rubbers (*2*) plotted *vs.* Weissenberg number.[53]

However, perturbations at large deformations should not always lead to jet breakup since rupture of viscoelastic materials is characterized by durability rather than tensile strength. Disturbances in extension leading to jet breakup develop with time, and the critical time to breakup ($t^*$) can be long enough for large deformations to occur without jet breakup and thus stabilize the fibre spinning regime.

Figure 2 presents the generalized dependence of durability (time $t^*$ normalized using the reduction coefficient $a_T$) on stress (normalized to the elastic modulus, $\sigma_E$, at the rubbery-like plateau). Thus, the key factor is deformation.[55] However, at large deformations the extension becomes nonuniform and instability of the deformation process first of all manifests itself as necking.[56–58] Neck formation in extension of polymers was best analyzed taking solid (both crystalline and amorphous) polymers as examples. Instability at large deformations of crystalline polymers is due to the appearance of dislocations and other structural all correct.† Necking in amorphous polymers is similar to the instability in extension of melts of polymeric fluids since

† Consideration of this issue is beyond the scope of this review.

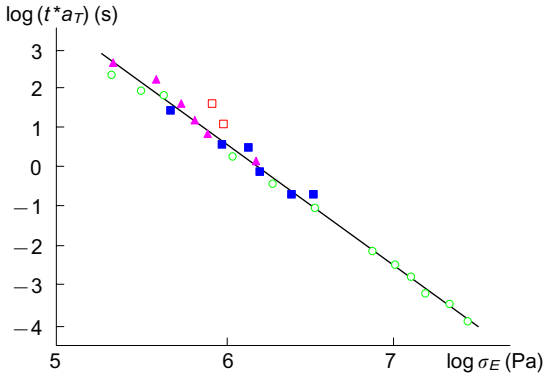



**Figure 2.** Plot of polybutadiene durability under extension *vs.* normal stress.[54]
Normalized $t^*$ values correspond to the temperature range from −10 to 50 °C; different points correspond to the $t^*$ values obtained at different temperatures.

viscoelastic melts behave like solids at high deformation rates. Therefore, the concept of neck formation as a consequence of an increase in the free volume under uniaxial stretching[59] can also be considered in the case of polymeric fluids, although relevant studies are unavailable.

One more macroscopic manifestation of instability under extension of polymeric fluids is the formation of periodic structures, which is usually interpreted as draw resonance. The phenomenon was for the first time observed long ago;[60–64] however, its mechanism is still to be clarified. The formation of a periodic structure along a thread under stable fibre spinning conditions is termed a 'varicose jet'.[60] The process can be accompanied by periodic self-oscillatory variations of the jet diameter (Fig. 3).[62]

The formation of periodic structures was also interpreted as a consequence of ambiguity of solutions to the dynamic equations obtained taking into account peculiar features of the rheological properties of polymeric fluids, such as the non-Newtonian character of flow, the viscoelastic properties of the medium[65,66] and the destabilizing effect associated with the emergence of the jet from the capillary when using more complicated rheological models.[67] The onset of draw resonance (oscillatory variation of the jet diameter) was also associated with a feature of the boundary conditions for the jet in extension, *viz.*, if the force is specified, the extension is always stable, but the draw resonance is 'sensitive' to changes in the jet cross-section.[68] In particular, the onset of draw resonance in the

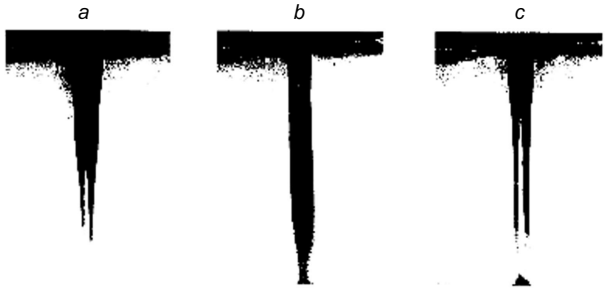



**Figure 3.** Sequentially taken photographs of a jet (*a*–*c*) emerging from the nozzle. Illustration of periodic self-oscillatory variations of the jet diameter in extension.[62] Natural size.

falling jet depends on the relative contributions of inertial forces and gravity.[69] The general formulation of the dynamic problem with inclusion of all factors mentioned above and the output rate of the fluid was considered by researchers from France.[70] One more possible reason for instability of the process in question is non-isothermicity of the viscoelastic jet.[71]

Thus, the main rheological mechanisms of draw resonance in extension of polymer jets usually included dynamic deformations of fluids characterized by constant chemical composition and some rheological properties at different boundary conditions. However, when studying extensional flow of polymer solutions under actual conditions, changes in their chemical composition and physicochemical properties should not be ignored. In addition, mechanisms underlying the stability of extension of polymer solutions should also be investigated taking into account physicochemical processes that occur in the jet and are typical of fibre spinning technology, namely, orientation of macromolecules and the fluid–solid transition.[72] This approach is similar to the mechanism of formation of 'beads-on-a-string' structures (see below), although these phenomena are little comparable. In any case, the rheological properties of the polymer solution (especially, its elasticity) undoubtedly contribute to stabilization of the jet shape.

Tensile deformation plays a significant role in polymer processing technologies, the more so, as particular laws of uniaxial stretching of polymer melts are closely related to structural features of linear and branched polymers.[72–77] Various physical aspects of the breakup of polymer melts and concentrated polymer solutions are still discussed in scientific literature.[78–92] The attention of researchers remains focused on the character of deformation, the breakup mechanism, the nature of strengthening at large deformations as function of long-chain branching,[93] molecular mass and molecular mass distribution,[89] and stretching-induced structural transformations.[94, 95]

The rheological and physicochemical properties of polymer solutions are or particular importance to fibre spinning because they determine the parameters of engneering processes and the properties of the final fibres.[96–99]

### 3.3. Instability in extension of dilute polymer solutions

The presence of a solvent is crucial to extension of semidilute and dilute polymer solutions. In the early stage of research into viscoelastic fluids, it was found that under particular critical conditions, jets form repeating series of spherical droplets connected by nearly cylindrical liquid bridges rather than break up.[100] Further experiments showed that the bridges experience exponential thinning prior to breakup.[101–104] The formation of such a 'beads-on-a-string' structure stabilizes the jet, thus favouring realization of very large deformations without breakup. This type of fluid dynamics is also observed in stretching experiments with highly dilute solutions.[102] In this case, the main stretching and jet-stabilizing mechanism is associated with the action of surface tension forces and elasticity (so-called elasto-capillary thinning).[101–110] The concept of elasto-capillary deformation and breakup was also extended to viscoplastic media with yield stress.[111]

The function describing the thinning of a jet under uniaxial stretching versus time is determined by the dominating physical mechanism. An analysis of the elasto-capillary mechanism of jet deformation[102, 103, 112, 113] showed that the jet diameter should decrease with time exponentially

$$R(t) \propto e^{-t/(3\tau)} \tag{33}$$

The same result was also obtained in experimental study of extensional flow on the microsecond time scale.[114] The process involved stretching of polymer coils, so polymer chains become oriented downstream. This behaviour was qualitatively different from the thinning modes of Newtonian fluid jets observed elsewhere.[14, 15, 24, 115] The authors of yet another experimental study[116] observed a two-step thinning of viscoelastic liquid jet involving the appearance of sinusoidal waves corresponding to the capillary perturbation model followed by transformation of these perturbations into a periodic 'beads-on-a-string' structure.

Middleman[117] pioneered in theoretical analysis of the influence of linear viscoelasticity on the stability of jets. He showed that a viscoelastic fluid jet is less stable than a Newtonian fluid jet under identical dynamic conditions. The result obtained was confirmed more recently[118] using the Oldroyd equation to describe the viscoelasticity. This contradicts to some extent experimental observations;[100, 101] however, the contradiction was removed upon inclusion of nonlinear effects. Goren and Gottlieb[118] studied viscoelastic jets under elastic tension and showed that they are more stable than jets without initial elastic tension.

There are various rheological models for nonlinear viscoelastic media that can be used to analyze the dynamics of polymer jets. Such models provide a correct description of the initial stages of the process. However, predictions of different nonlinear models differ significantly. Predictions of jet thinning dynamics made using different rheological models were compared.[119] The formation and behaviour of drops in a polymer jet was studied in detail using the Oldroyd rheological equation and the FENE-P (see ‡) and Giesekus models.[120–123] A numerical study on the dynamics of drops in the 'beads-on-a-string' structure in viscoelastic fluid jets revealed the decisive role of elastic force in the flow of smaller drops into larger ones by drainage through filaments.[124] The bead evolution patterns predicted in Ref. 124 were observed experimentally.[125]

A computer simulation[126] of the behaviour of a macromolecule represented by a chain of $N$ rigid rods connected by beads showed that the longitudinal Brownian viscosity of the fully extended straight chain increases as $N^3$. At small Weissenberg numbers, the results obtained using this model are qualitatively equivalent to those obtained using the FENE-P phenomenological model. The stability and breakup of the jet were not studied.

The behaviour of semidilute solutions of unentangled polymer is best described by the FENE-P model,[127–129] which includes finite extensibility of polymer chains. This model predicts three main modes of solution behaviour under extension. At low deformation rates, where the Weissenberg number is small ($\mathrm{Wi} \ll 1$), the solution behaves like a Newtonian fluid. The stress tensor components are given by well-known expressions

$$\sigma_{zz} \approx 2\eta \frac{\partial V}{\partial z} \tag{34}$$

‡ FENE-P is an abbreviation, where FENE stands for 'finitely extensible nonlinear elastic' (model) and P stands for the closure proposed by Peterlin.

$$\sigma_{rr} \approx -\eta\frac{\partial V}{\partial z} \tag{35}$$

In this case viscoelasticity plays an insignificant role. As the deformation rate increases (Wi ≈ 1), polymer chains are stretched downstream and the *zz*-component of stress dominates, $\sigma_{zz} \gg \sigma_{rr}$. The rheological equation for the stress tensor is separated into two independent expressions

$$\tau\left(\frac{\partial\sigma_{zz}}{\partial t}+V\frac{\partial\sigma_{zz}}{\partial z}-2\frac{\partial V}{\partial z}\sigma_{zz}\right)+\sigma_{zz}\approx 2\eta\frac{\partial V}{\partial z} \tag{36}$$

$$\tau\left(\frac{\partial\sigma_{rr}}{\partial t}+V\frac{\partial\sigma_{rr}}{\partial z}+\frac{\partial V}{\partial z}\sigma_{rr}\right)+\sigma_{rr}\approx -\eta\frac{\partial V}{\partial z} \tag{37}$$

Finally, at Wi ≫ 1, polymer chains become highly stretched along the flow direction, namely, their longitudinal size $r_z$ is comparable with the chain length $L$, and the behaviour is changed to pseudo-Newtonian

$$\sigma_{zz} \approx 2\eta_{\text{ef}}\frac{\partial V}{\partial z} \tag{38}$$

$$\sigma_{rr} \approx -\frac{2\eta}{3}\frac{\partial V}{\partial z} \tag{39}$$

where $\eta_{\text{ef}} \approx \eta N$ is the effective viscosity ($N = L/l$ is the number of monomer units in the polymer chain, $l$ is the length of the monomer unit). Thus, the viscosity of the solution of stretched polymer chains is $N \gg 1$ times higher than that of the initial polymer solution.

To describe the dynamics of the jet, Eqns (34), (36) and (37) should be analyzed in combination with Eqns (15) and (16). When studying the dynamics of the liquid bridge, Eqn (16) should be augmented with the boundary condition at the drop/jet interface. This means that the jet is extended by the force

$$F = 2\pi R\gamma \tag{40}$$

Considering the polymer solution as highly viscous system and ignoring inertial forces (Oh ≫ 1), from Eqn (16) one gets for the first normal stress difference

$$\sigma_{zz} - \sigma_{rr} \approx \frac{\gamma}{R} \tag{41}$$

A combined solution to Eqns (41), (34) and (15) gives a well-known linear thinning of the jet in the viscous mode and the following expression for the deformation rate:

$$\dot{\varepsilon} \approx \frac{\gamma}{\eta R} \tag{42}$$

When the radius of the jet becomes equal to

$$R = R^* \approx \frac{\gamma\tau}{\eta} \tag{43}$$

(*i.e.*, Wi ≈ 1), polymer chains begin to stretch. Further stress dynamics is determined by Eqns (36) and (37). Combining them with Eqns (41) and (15), one gets

$$R(t) = R^* \approx \mathrm{e}^{-t/(3\tau)} \tag{44}$$

The deformation rate in the bridge is

$$\dot{\varepsilon} = \frac{2}{3\tau} \tag{45}$$

and the first normal stress difference is equal to

$$\sigma_{zz} - \sigma_{rr} \approx \frac{\eta}{\tau}\mathrm{e}^{t/(3\tau)} \tag{46}$$

Stretching of polymer chains takes the time

$$t \approx 3\tau\ln\frac{\eta_{\text{ef}}}{\eta} \approx 3\tau\ln N \tag{47}$$

Thinning causes the bridge radius to decrease by a factor of $N$:

$$R^{**} \approx \frac{R^*}{N} \tag{48}$$

In the pseudo-Newtonian mode [see Eqns (38), (39)], thinning of fully stretched polymer chains obeys a linear law. The bridge breaks up at the time instant

$$\Delta t \approx \frac{\eta_{\text{ef}}R^{**}}{\gamma} \approx \tau \propto N^2 \tag{49}$$

In semidilute polymer solutions (see above) unentangled chains are stretched gradually (coil – stretched coil transition). As to dilute solutions, where polymer coils do not overlap, the stretching of polymer chains occurs as sharp coil – stretched coil transition.[130, 131] Quantitative parameters of the jet structure depend on the polymer concentration in the solution and on the molecular mass of the polymer. It was assumed [109] that an entanglement network exists in solution at polymer concentrations $> c^*$ (see below). It was assumed that the formation of the entanglement network underlies possible formation of polymer solution jets in the form of continuous filaments.[132] However, the behaviour of the polymer jet in extension is determined by not only the initial characteristics of the solution, but also by orientation of macromolecules in the course of extensional flow, by changes in the character of intermolecular interactions and, as a consequence, by changes in the structure and properties of the solution. Therefore, a correct understanding of physics of structural transformations becomes the key point. The situation was formulated in the form of self-explanatory question:[133] 'How dilute are dilute solutions in extensional flows?

What is the minimum concentration of the polymer in solution to form a stable jet? One can assume that the concentration should be high enough to bring macromolecules that form the network into contact with one another. For flexible-chain polymers, intermolecular contacts between macromolecular coils can be formed at the so-called crossover concentration $c^*$ (product of the crossover concentration by the intrinsic viscosity is approximately unity). However, systematic experimental studies of series of different polymers in a wide concentration range showed that a stable jet with a lifetime much longer than the time corresponding to the Plateau – Rayleigh capillary stability condition can also exist at very low concentrations, *viz.*, at $c \ll c^*$.[132] This result is illustrated by Fig. 4. The upper right group of points (region *I*) corresponds to fibre spinning from polymer solutions containing intermolecular entanglements, *i.e.*, above the crossover point. In this region the minimum concentration at which a stable jet ($c_{\text{stab}}$) exists is proportional to $[\eta]^{-1}$. The lower left group of points (region *II*) corresponds to very low concentrations of the solution $c \ll c^*$ at which the formation of a stable jet is also possible; in this region $c_{\text{stab}}$ is proportional to $[\eta]^0$.

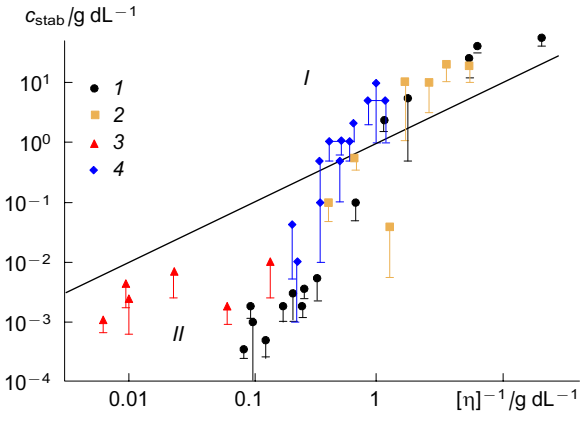



**Figure 4.** Limiting spinnability values ($c_{stab}$) corresponding to stable fibre formation plotted *vs.* reciprocal intrinsic viscosity.[134] Straight line visualizes the condition for the formation of entanglements: $[\eta]c_{stab} \approx 1$. Polymer: polyethylene oxide (*1*), poly(vinyl acetate) (*2*), polyacrylamide (*3*) and polyacrylonitrile (*4*); for *I* and *II*, see text.

The possibility of formation of a stable jet at $c \ll c^*$ can be explained by the fact that stretching is accompanied by the coil–(partially or fully) extended polymer chain transition and subsequent changes in the local concentrations of the polymer.[110] This can lead to changes in the intermolecular interactions between macromolecules and thus stabilize the jet under certain conditions.

In some cases the thinning dynamics of a jet with stretched macromolecules is accompanied by the formation of periodic hierarchical system of drops (blistering pattern) on the jet.[132–139] An example is shown in Fig. 5. Establishment of the nature of this phenomenon is of fundamental importance for understanding the development of large deformations in extension of polymer solutions. A possible explanation[140] is based on the dependence of the diffusion coefficient of polymer chains on not only the concentration of the polymer, but also the mechanical stress.[141–143] Instability of the jet shape at a certain critical deformation is associated with migration of polymer chains in the nonuniform stress field. However, this approach is inapplicable to the high-strain region and gives no description of the formation of blistering patterns.

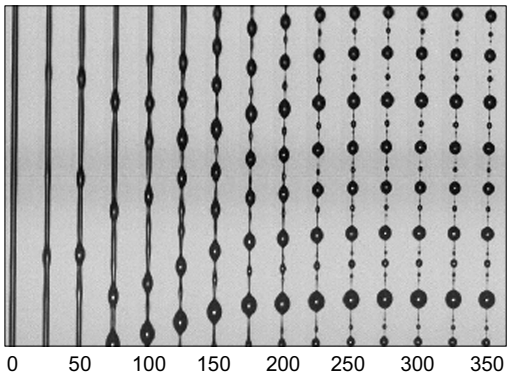



**Figure 5.** Blistering pattern development on stretching a polymer solution.[135]
Numbers denote the time (in ms). Image size: $226 \times 2317$ μm$^2$.

### 3.4. Phase separation of polymer solutions

Oriented polymer jets can also form by af fundamentally different physical mechanism. Stretching of a polymer jet (fibre) can be accompanied by not only the formation of continuous periodic structure, but also phase separation of the polymer solution. In this case the fibre being spun represents an oriented thread bearing solvent droplets.[4, 134, 144, 145] An example of solvent separation from the stretching jet is shown in Fig. 6, while separate drops are clearly seen in Fig. 7. Separation of solvent drops from the polymer solution at large deformations in the final stage of the process was also observed elsewhere.[138]

Using high-speed digital cinematography, it was shown that separation of drops is a complex process. The liquid phase (solvent of low viscosity) is continuously separated on the jet surface as a liquid shell and rolls down the jet surface formed by the oriented and extended (up to fully stretched state corresponding to jet breakup) polymer molecules. The liquid surface has the shape of an unduloid; the thin liquid surface layer decomposes into separate waves by the Rayleigh–Plateau instability mechanism, which results in the formation of a system of liquid drops on homogeneous jet. One actually deals with separate drops rather than segments

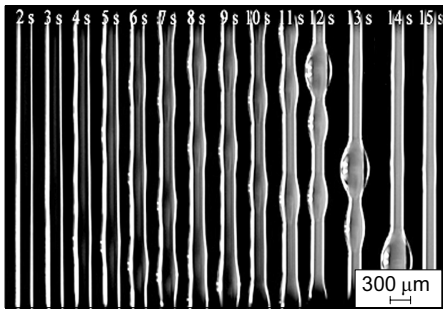



**Figure 6.** Sequential stages of solvent separation from the polymer jet under extension in the course of fibre spinning from polyacrylonitrile solution. For details, see Ref. 145. Numbers denote the time instants (in seconds).

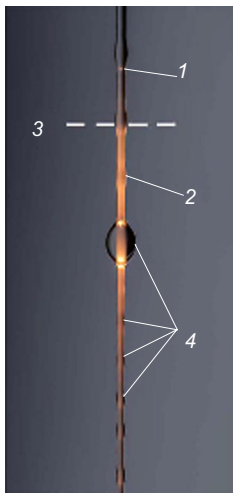



**Figure 7.** A solvent drop on the surface of the solidified jet (fibre).[145]
Liquid segment of the jet (polymer solution) (*1*); solidified segment of the jet (*2*); phase separation boundary (*3*); and separate drops on the jet surface (*4*).

of the jet. This fact is clearly confirmed by the possibility to remove the drops using a piece of cotton wool or soft cloth.

Meanwhile, the 'beads-on-a-string' structures and the blistering patterns look very similar and determination of actual mechanism of the instability in the form of periodic structure deserves additional research and analysis.

Electrospinning is also suitable for the formation of drops on the jet surface. In this case one deals with the loss of longitudinal stability and jet bending occurs. Both mechanisms of flow stability violation can overlap, which eventually leads to jet fission into droplets.[146, 147]

Phase separation causes the formation of elastic threads comprising highly oriented macromolecules. The process can be driven by either stress-induced diffusion or changes in the interaction between macromolecules owing to conformational transitions. According to previous views,[140 – 143] phase separation of a polymer solution originates from the onset of concentration fluctuations, which grow rapidly in the flow regime since is it assumed that the diffusion coefficient depends on external stress.

One more approach to phase separation is based on principles of nonequilibrium thermodynamics.[131, 148 – 150] In this case, phase separation of a polymer solution is driven by violation of the balance between the attractive and repulsive forces acting between macromolecules oriented by the flow. Orientation leads to weakening of inter-chain steric repulsion, *i.e.*, the volume of oriented macromolecules makes a smaller contribution to the interactions. Attractive forces vary only slightly and dominate at high deformation rates, which leads to separation of the solution into the polymer and solvent phases. Studies on the kinetics of phase separation of a solution of oriented chains revealed three main stages of the process.[148 – 150] The first stage involves spinodal decomposition of the solution and the appearance of polymer-depleted and polymer-rich domains of anisotropic shape. The time taken to form the inhomogeneous structure is much shorter than the relaxation time of the polymer chain. Next, transverse compression of the polymer-rich domains occurs, followed by their transformation to microfibrils. The concentration of the polymer in the microfibrils reaches an equilibrium value. Since the length of macromolecules exceeds that of microfibrils, polymer chains pass through several microfibrils, thus linking them to form a network. The characteristic time of formation of the microfibrillar network is of the same order of magnitude as the spinodal decomposition time.

The third stage is characterized by separation of the polymer phase from the solvent. Two mechanisms of the process were studied. First, closely spaced microfibrils aggregate into bundles and the surface energy of the network rapidly decreases. Some proportion of bundles thicken through absorption of smaller bundles. Since the growth of bundles is a very slow process, the other mechanism associated with uniform compression of the network through displacement of the solvent begins to dominate in the final stage. In this case, the energy of the system also decreases and the minimum value of the free energy is attained at complete separation of the polymer and solvent. As a result, the solvent is localized at the jet surface. Clearly, the surface layer of the solvent should break into drops owing to capillary instability. The breakup dynamics is analogous to that reported by Goren,[151] who studied the behaviour of a liquid layer on the surface of a cylindrical body. He showed that the period of the structure formed depends on the thickness of the fluid layer and that for a thin layer one has $\lambda = 4\pi a$ ($a$ is the radius of the cylinder). This result is consistent with the experimental data.[138] In our case (radial collapse of the microfibrillar network) drops grow due to absorption of the solvent displaced from the network and the fibre diameter decreases. With fibre thinning, conditions may arise for the appearance of new smaller droplets. This occurs if the fibre segment between neighbouring droplets becomes shorter than $4\pi a$ and the fibre radius becomes time dependent. This mechanism causes the formation of hierarchical structure of drops (*i.e.*, successive formation of different-size drops) on the fibre surface, which is indeed observed in the experiment. The solvent velocity inside the drops is relatively low, so partial dissolution of the fibre is possible.

Yet another mechanism of solvent displacement on the jet surface is realized in ultrathin jets whose diameter is less than the length of the macromolecule. It is based on the action of capillary forces. As a result, solvent *annuli* are formed on the jet surface. The mechanism has the activation nature and has been studied in detail for a solution of rod-like macromolecules.[152] Since the process is driven by capillary forces, domination of attractive inter-chain forces over repulsive ones is not assumed.

A decrease in the polymer concentration in the solution causes both viscosity and elasticity to decrease. Although experimental determination of parameters of such systems is necessary to understand physics of the phenomena in question, it faces certain difficulties owing to short relaxation times.[153] Therefore, microfluidics rather than extension of jets began to develop. This approach proved itself in studies of rheologically complex elastic fluids under extension and breakup of their droplets. It is based on the use of T-shaped or mutually perpendicular microchannels. As the flow direction of a droplet under study changes, the droplet is stretched and eventually breaks down. This experimental technique has long been proposed by researchers from Keller's group[154, 155] and more recently developed elsewhere.[156 – 158] The method allowed one to observe elasto-capillary breakup and to evaluate the characteristic parameters of weakly elastic media using deformation of droplets of the limiting dilute polymer solutions under extensive flow in microchannels.[159, 160]

## 4. Conclusion

General principles of analysis of the behaviour of jets in nature and in engineering processes are based on solution of the system of balance equations using relevant boundary conditions. The system includes the dynamic (rheological) equation for fluid and the energy and mass conservation equations to respectively describe heat exchange and the interaction between the solution being formed and the environment. Solution to this system of equations for a particular chemical engineering process flow diagram requires the determination of a large number of physical and physicochemical characteristics of the material and process parameters. This also fully applies to theoretical foundations of fibre spinning that were developed long ago (see, *e.g.*, fundamental monographs[161, 162]). The necessary quantitative solutions can be obtained with specified accuracy using modern computational methods provided that characteristics of spinning solutions and the process parameters are known with certainty.

Besides, stability analysis of an engineering process is a must when considering its optimization from the standpoint

of the quality of the final product and performance. This is the subject of the present review. Our approach is based on general physicochemical concepts of the onset and development of deviations from steady-state deformation regime, which leads to instability of the jet up to breakup. When studying polymer melts and solutions, consideration of the ability of polymers to undergo large recoverable (rubber-like) deformations and related relaxation phenomena appeared to be necessary. In the case of uniaxial stretching of jets during fibre spinning these factors favour the onset of specific instability effects, such as necking, appearance of periodic structures and phase separation of polymer solutions.

Extension of polymeric viscoelastic fluids is governed by the Weissenberg criterion characterizing the ratio of the relaxation time of a material to the characteristic time of the action of external factors. The threshold value of this criterion corresponds to transition from the flow state to the dominating development of rubber-like deformations and the fluid now behaves as quasi-cross-linked elastomer. In addition to the constitutive rheological equation, specific features of the properties of polymers (see above) determine the laws of the process of fibre spinning from polymer solutions and the mechanisms of stability loss.

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Figure 5 is courtesy of the AIP Publishing LLP.

## References

1. J.L.Daristotle, A.M.Behrens, A.D.Sandler, P.Kofinas. *ACS Appl. Mater. Interfaces*, **8**, 34951 (2016)
2. J.Xue, T.Wu,Y.Dai, Y.Xia. *Chem. Rev.*, **119**, 5298 (2019)
3. R.G.Larson. *Constitutive Equations for Polymer Melts and Solutions (Butterworths Series in Chemical Engineering)*. (Butterworth-Heinemann, 2013)
4. V.G.Kulichikhin, I.Yu.Skvortsov, A.V.Subbotin, S.V.Kotomin, A.Ya.Malkin. *Polymers*, **10**, 856 (2018)
5. J.Plateau. *Statique Expérimentale et Théorique des Liquides*. (Paris: Gauthier-Villars, 1873)
6. Lord Rayleigh. *Proc. R. Soc. London*, **29**, 71 (1879)
7. Lord Rayleigh. *Philos. Mag.*, **34**, 145 (1892)
8. N.Bohr. *Philos. Trans. R. Soc. London, Ser. A*, **209**, 281 (1909)
9. S.Chandrasekhar. *Hydrodynamic and Hydromagnetic Stability*. (New York: Dover Publications, 1981)
10. R.J.Donnelly, W.Glaberson. *Proc. R. Soc. London, Ser. A*, **290**, 547 (1966)
11. G.I.Taylor. *Proc. R. Soc. London, Ser. A*, **146**, 501 (1934)
12. S.Tomotika. *Proc. R. Soc. London, Ser. A*, **150**, 322 (1935)
13. S.Tomotika. *Proc. R. Soc. London, Ser. A*, **153**, 302 (1936)
14. J.Eggers. *Rev. Mod. Phys.*, **69**, 865 (1997)
15. J.Eggers, E.Villermaux. *Rep. Prog. Phys.*, **71**, 036601 (2008)
16. A.U.Chen, P.K.Notz, O.A.Basaran. *Phys. Rev. Lett.*, **88**, 174501 (2002)
17. J.R.Castrejón-Pita, A.A.Castrejón-Pita, S.S.Thete, K.Sambath, I.M.Hutchings, J.Hinch, J.R.Lister, O.A.Basaran. *PNAS*, **112**, 4582 (2015)
18. A.A.Castrejón-Pita, J.R.Castrejón-Pita, I.M.Hutchings. *Phys. Rev. Lett.*, **108**, 074506 (2012)
19. J.B.Keller, M.J.Miksis. *SIAM J. Appl. Math.*, **43**, 268 (1983)
20. M.P.Brenner, J.Eggers, K.Joseph, S.R.Nagel, X.D.Shi. *Phys. Fluids*, **9**, 1573 (1997)
21. D.T.Papageorgiou. *Phys. Fluids*, **7**, 1529 (1995)
22. D.T.Papageorgiou. *J. Fluid Mech.*, **301**, 109 (1995)
23. J.Eggers. *Phys. Rev. Lett.*, **71**, 3458 (1993)
24. Y.Li, J.E.Sprittles. *J. Fluid Mech.*, **797**, 29 (2016)
25. W.D.Harkins, F.E.Brown. *J. Am. Chem. Soc.*, **41**, 499 (1919)
26. P.Martien, S.C.Pope, P.L.Scott, R.S.Shaw. *Phys. Lett., A*, **110**, 399 (1985)
27. C.Clanet, J.C.Lasheras. *J. Fluid Mech.*, **383**, 307 (1999)
28. N.S.Clarke. *Mathematika*, **12**, 89 (1966)
29. T.Massalh, R.F.Digilov. *Am. J. Phys.*, **81**, 733 (2013)
30. S.Senchenko, T.Bohr. *Phys. Rev. E*, **71**, 056301 (2005)
31. U.S.Sauter, H,W.Buggisch. Stabi *J. Fluid Mech.*, **533**, 237 (2005)
32. A.Javadi, J.Eggers, D.Bonn, M.Habibi, N.M.Ribe. *Phys. Rev. Lett.*, **110**, 144501 (2013)
33. J.K.Lee, G.T.Seo. *Korean J. Chem. Eng.*, **12**, 273 (1995)
34. E.Tyler, E.G.Richardson. *Proc. Phys. Soc. London*, **37**, 297 (1924)
35. E.Tyler, F.Watkin. *Philos. Mag. J. Sci.*, **14**, 849 (1932)
36. K.Adachi, K.Tagashira, Y.Banba, H.Tatsumi, H.Machida, N.Yoshioka. *AIChE J.*, **36**, 7385 (1990)
37. R.P.Grant, S.Middleman. *AIChE J.*, **12**, 669 (1966)
38. R.Tayeb, M.N.Sakib, M.Ali, Q.Islam. *Proc. Eng.*, **56**, 462 (2013)
39. V.G.Levich. *Physicochemical Hydrodymamics*. (New York: Prentice Hall, 1962)
40. S.P.Lin, R.D.Reitz. *Annu. Rev. Fluid Mech.*, **30**, 85 (1998)
41. C.Weber. *Z. Angew. Math. Mech.*, **11**, 136 (1931)
42. P.Debye, J.Daen. *Phys. Fluids*, **2**, 416 (1959)
43. G.I.Taylor. In *Proc. 12th International Congress of Applied Mechanics. (Stanford, 1968)*. (Berlin, Haidelberg, New York: Springer, 1969)
44. D.Buckmaster. *J. Fluid Mech.*, **61**, 449 (1973)
45. V.M.Entov, A.L.Yarin. *J. Fluid Mech.*, **140**, 91 (1984)
46. B.Tchavdarov, A.L.Yarin, S.Radev. *J. Fluid Mech.*, **253**, 593 (1993)
47. N.M.Ribe. *Proc. R. Soc. London, Ser. A*, **460**, 3223 (2004)
48. S.Chiu-Webster, J.R.Lister. *J. Fluid Mech.*, **569**, 89 (2006)
49. A.Ya.Malkin, C.J.S.Petri. *J. Rheol.*, **41**, 1 (1997)
50. A.Ya.Malkin, A.V.Semakov, V.G.Kulichihkin. *Rheol. Acta*, **50**, 485 (2011)
51. S.L.Morelly, L.Palmese, H.Watanabe, N.J.Alvarez. *Macromolecules*, **52**, 915 (2019)
52. H.K.Rasmussen, S.L.Wingstrand, O.Hassager. *Rheol. Acta*, **58**, 333 (2019)
53. A.Ya.Malkin, A.V.Semakov, V.G.Kulichikhin. *Polym. Sci., Ser. A*, **53**, 1198 (2011)
54. A.Ya.Malkin, G.V.Vinogradov. *Polym. Sci.*, **27**, 227 (1985)
55. X.Zhu, S.-Q.Wang. *J. Rheol.*, **57**, 223 (2013)
56. V.C.R.Barroso, R.J.Andrade, J.M.Maia. *J. Rheol.*, **54**, 605 (2010)
57. S.M.Fielding. *Phys. Rev. Lett.*, **107**, 258301 (2011)
58. D.M.Hoyle, S.M.Fielding. *J. Rheol.*, **60**, 1347 (2016)
59. G.P.Andrianova, V.A.Kargin. *Polym. Sci., Ser. A*, **12**, 3 (1970)
60. R.E.Christensen. *SPE J.*, **18**, 751 (1962)
61. H.Isihara, S.Kase. *J. Appl. Polym. Sci.*, **20**, 169 (1976)
62. V.Kulichikhin. *Mol. Cryst. Liq. Cryst.*, **169**, 51 (1989)
63. S.Kase, T.Matsuo. *J. Appl. Polym. Sci.*, **11**, 1455 (1967)
64. H.W.Jung, H.-S.Song, J.Ch.Hyun. *AIChE J.*, **46**, 2106 (2000)
65. L.Kwon, M.-S.Chun, H.W.Jung, J.Ch.Hyun. *J. Non-Newtonian, Fluid Mech.*, **228**, 31 (2016)
66. K.Gupta, P.Chokshi, R.Stepanyan. *J. Non-Newtonian, Fluid Mech.*, **230**, 1 (2016)
67. M.Renardy. *SIAM J. Appl. Math. Soc. Ind. Appl. Math.*, **66**, 1261 (2006)
68. F.Cao, R.E.Khayat, J.E.Puskas. *Int. J. Solids Struct.*, **42**, 5734 (2005)
69. M.Bechert, D.W.Schubert B.Scheid. *Eur. J. Mech., B*, **52**, 68 (2015)
70. Y.Demay, J.-F.Agassant. *J. Non-Newtonian Fluid Mech.*, **18**, 187 (1985)
71. A.T.Serkov, M.B.Radishevskii, Yu.V.Afanas'eva. *Fibre Chem.*, **32**, 165 (2000)
72. H.Münstedt, M.H.Laun. *Rheol. Acta*, **20**, 211 (1981)

73. H.Münstedt, T.Steffl, A.Malmberg. *Rheol. Acta*, **45**, 142 (2005)
74. Z.Starý, M.Papp, T.Burghelea. *J. Non-Newtonian Fluid Mech.*, **219**, 35 (2015)
75. Q.Huang, M.Mangnus, N.J.Alvarez, R.Koopmans, O.Hassager. *Rheol. Acta*, **55**, 343 (2016)
76. S.Sur, M.Chellamuthu, J. Rothstein. *Rheol. Acta*, **58**, 557 (2019)
77. G.Liu, H.Ma, H.Lee, H.Xu, S.Cheng, H.Sun, T.Chang, R.P.Quirk, S.-Q.Wang. *Polymer*, **54**, 6608 (2013)
78. A.Ya.Malkin, A.Arinstein, V.G.Kulichikhin. *Polym. Prog. Polym. Sci.*, **39**, 959 (2014)
79. Y.M.Joshi, M.M.Denn. *J. Rheol.*, **47**, 291 (2003)
80. H.K.Rasmussen, J.K.Nielsen, A.Bach, O.Hassager. *J. Rheol.*, **49**, 369 (2005)
81. J.K.Nielsen, H.K.Rasmussen, O.Hassager, G.H.McKinley. *J. Rheol.*, **50**, 453 (2006)
82. Y.Wang, Sh.-Q.Wang, P.E.Boukany, X.Wang. *Phys. Rev. Lett.*, **99**, 237801 (2007)
83. Y.Wang, Sh.-Q.Wang. *J. Rheol.*, **52**, 1275 (2008)
84. J.Aho, V.H.Rolón-Garrido, S.Syrjälä, M.H.Wagner. *J. Non-Newtonian Fluid Mech.*, **165**, 212 (2010)
85. H.Sun, P.Lin, G.Liu, K.Ntetsikas, K.Misichronis, N.Kang, J.Liu, A.Avgeropoulos, J.Mays, Sh.-Q.Wang. *J. Rheol.*, **59**, 751(2015)
86. S.Cheng, Y. Lu, G. Liu, Sh.-Q. Wang. *Soft Matter*, **12**, 3340 (2016)
87. D.M.Hoyle, S.M.Fielding. *J. Rheol.*, **60**, 1377 (2016)
88. Q.Huang, O.Hassager. *Soft Matter*, **21**, 3470 (2017)
89. Y.Feng, J.Liu, Sh.-Q.Wang, K.Ntetsikas, A.Apostolos. M.Kostas, J.Mays. *J. Rheol.*, **63**, 763 (2019)
90. M.H.Wagner, E.Narimissa, Q.Huang. *J. Rheol.*, **62**, 221 (2018)
91. Q.Huang, H.K.Rasmussen. *J. Rheol.*, **63**, 829 (2019)
92. Sh.-Q.Wang. *J. Rheol.*, **63**, 105 (2019)
93. G.Cui, V.A.H.Boudara, Q.Huang, G.P.Baeza, A.J.Wilson, O.Hassager, D.J.Read, J.Mattsson. *J. Rheol.*, **62**, 1155 (2018)
94. M.Kong, C.Y.Huamg, Y.Lv, Q.Yang, G.Li. *J. Rheol.*, **62**, 11 (2018)
95. S.L.Wingstrand, O.Hassager, D.Parisi, A.L.Borger, K.Mortensen. *J. Rheol.*, **62**, 1051 (2018)
96. V.G.Kulichikhin, S.O.Ilyin, M.V.Mironova, A.K.Berkovich, I.E.Nigant'ev, A.Ya.Malkin. *Adv. Polym. Technol.*, **35**, 21758 (2016)
97. V.G.Kulichikhin, I.Yu.Skvortsov, M.I.Mironova, A.N.Ozerin, T.S.Kurkin, A.K.Berkovich, E.I.Frenkin, A.Ya.Malkin. *Adv. Polym. Technol.*, **36**, 21761 (2016)
98. I.Skvortsov, A.Kalugina, E.Litvinova, A.Malkin, V.Khotimskiy, V.Kulichikhin. *J. Appl. Polym. Sci.*, **136**, 48511 (2019)
99. I.I.Ponomarev, I.Y.Skvortsov, Y.A.Volkova, I.I.Ponomorev, L.A.Vafolomeeva, D.J.Razorenov, K.M.Skurov, M.S.Kuxin, O.A.Serenko. *Materials*, **12**, 3490 (2019)
100. M.Goldin, J.Yerushalmi, R.Pfeffer, R.Shinnar. *J. Fluid Mech.*, **38**, 689 (1969)
101. A.V.Bazilevskii, S.I.Voronkov, V.M.Entov, A.N.Rozhkov. *Sov. Phys. Dokl.*, **26**, 333 (1981)
102. A.V.Bazilevskii, V.M.Entov, M.M.Lerner, A.N.Rozhkov. *Polym. Sci., Ser. A*, **39**, 316 (1997)
103. A.V.Bazilevskii, V.M.Entov, A.N.Rozhkov. *Polym. Sci., Ser. B*, **43**, 716 (2001)
104. A.V.Bazilevskii, A.N.Rozhkov. *Fluid Dynam.*, **49**, 827 (2014)
105. C.Clasen, J.Eggers, M.A.Fontelos, J.Li, G.H.McKinley. *J. Fluid. Mech.*, **556**, 283 (2006)
106. Y.Amarouchene, D.Bonn, J.Meunier, H.Kellay. *Phys. Rev. Lett.*, **86**, 3558 (2001)
107. S.L.Anna, G.H.McKinley. *J. Rheol.*, **45**, 115 (2001)
108. Y.Christanti, L.M.Walker. *J. Non-Newtonian Fluid Mech.*, **100**, 9 (2001)
109. L.E.Rodd, T.P.Scott, J.J.Cooper-White, G.H.McKinley. *Appl. Rheol.*, **15**, 12 (2005)
110. V.Tirtaatmadja, G.H.McKinley, J.J.Cooper-White. *Phys. Fluids*, **18**, 043101 (2006)
111. R.Valette, E.Hachem, M.Khalloufi, A.S.Pereira, M.R.Mackley, S.A.Butler. *J. Non-Newtonian Fluid Mech.*, **263**, 130 (2019)
112. V.M.Entov, E.J.Hinch. *J. Non-Newtonian Fluid Mech.*, **72**, 31 (1997)
113. L.Campo-Deaño, C.Clasen. *J. Non-Newtonian Fluid Mech.*, **165**, 1688 (2010)
114. D.Vadillo, W.Mathues, C.Clasen. *Rheol. Acta*, **51**, 755 (2012)
115. R.F.Day, E.J.Hinch, J.R.Lister. *Phys. Rev. Lett.*, **80**, 704 (1998)
116. Ch.Tirel, M.-Ch.Renoulta, Ch.Dumouche, D.Lisiecki, O.Crumeyrolle, I.Mutabazi. *J. Non-Newtonian Fluid Mech.*, **245**, 1 (2017)
117. S.Middleman. *Chem. Eng. Sci.*, **20**, 1037 (1965)
118. S.L.Goren, M.Gottlieb. *J. Fluid Mech.*, **120**, 245 (1982)
119. M.Renardy. *J. Non-Newtonian Fluid Mech.*, **104**, 65 (2002)
120. A.L.Yarin. *Free Liquid Jets and Films: Hydrodynamics and Rheology*. (New York: Wiley, 1993)
121. H.-C.Chang, E.A.Demekhin, E.Kalaidin. *Phys. Fluids*, **11**, 1717 (1999)
122. M.A.Fontelos, J.Li. *J. Non-Newtonian Fluid Mech.*, **118**, 1 (2004)
123. P.P.Bhat, S.Appathurai, M.T.Harris, M.Pasquali, G.H.McKinley, O.A.Basaran. *Nat. Phys.*, **6**, 625 (2010)
124. J.Li, M.A.Fontelos. *Phys. Fluids*, **15**, 922 (2003)
125. C.Wagner, Y.Amarouchene, D.Bonn. J.Eggers. *Phys. Rev. Lett.*, **95**, 164504 (2005)
126. P.S.Doyle, E.S.G.Shaqfeh, A.P.Gast. *J. Fluid Mech.*, **334**, 251 (1997)
127. R.B.Bird, R.C.Armstrong, O.Hassager. *Dynamics of Polymeric Liquids*. Vol. 1. (New-York: Wiley, 1987)
128. R.B.Bird, O.Hassager, R.C.Armstrong, C.F.Curtiss. *Dynamics of Polymer Liquids*. Vol. 2. (New-York: Wiley, 1987)
129. J.M.Rallison, E.J.Hinch. *J. Non-Newtonian Fluid Mech.*, **29**, 37 (1988)
130. P.G.de Gennes. *J. Chem. Phys.*, **60**, 5030 (1974)
131. A.V.Subbotin, A.N.Semenov. *J. Polym. Sci., Part B: Phys. Ed.*, **54**, 1066 (2016)
132. A.V.Semakov, I.Yu.Skvortsov, V.G.Kulichikhin, A.Ya.Malkin. *JETP Lett.*, **101**, 690 (2015)
133. C.Clasen, J.P.Plog, W.-M.Kulicke, M.Owens, C.Macosko, L.E.Scriven, M.Verani, G.H.McKinley. *J. Rheol.*, **50**, 849 (2006)
134. A.Ya.Malkin, A.V.Semakov, I.Yu.Skvortsov, P.Zatonskikh, V.G.Kulichikhin, A.V.Subbotin, A.N.Semenov. *Macromolecules*, **50**, 8231 (2017)
135. M.S.N.Oliveira, G.H.McKinley. *Phys. Fluids*, **17**, 071704 (2005)
136. M.S.N.Oliveira, R.Yeh, G.H.McKinley. *J. Non-Newtonian Fluid Mech.*, **137**, 137 (2006)
137. R.Sattler, C.Wagner, J.Eggers. *Phys. Rev. Lett.*, **100**, 164502 (2008)
138. R.Sattler, S.Gier, J.Eggers, C.Wagner. *Phys. Fluids*, **24**, 023101 (2012)
139. A.Deblais, K.P.Velikov, D.Bonn. *Phys. Rev. Lett.*, **120**, 194501 (2018)
140. J.Eggers. *Phys. Fluids*, **26**, 033106 (2014)
141. E.Helfand, G.H.Fredrickson. *Phys. Rev. Lett.*, **62**, 2468 (1989)
142. M.Doi, A.Onuki. *J. Phys. II*, **2**, 1631 (1992)
143. M.Cromer, M.C.Villet, G.H.Fredrickson, L.G.Leal, R.Stepanyan, M.H.Bulters. *J. Rheol.*, **57**, 1211 (2013)
144. V.G.Kulichikhin, A.Ya.Malkin, A.V.Semakov, I.Yu.Skvortsov, A.Arinstein. *Eur. Phys. J., E*, **37**, 10 (2014)

145. A.V.Semakov, V.G.Kulichikhin, A.K.Tereshin, S.V.Antonov, A.Ya.Malkin. *J. Polym. Sci., Part B: Phys. Ed.*, **53**, 559 (2015)
146. W.Yang, H.Duan, C.Li, W.Deng. *Phys. Rev. Lett.*, **112**, 054501 (2014)
147. H.H.Xia, A.Ismail, J.Yao, J.P.W.Stark. *Phys. Rev. Appl.*, **12**, 014031 (2019)
148. A.N.Semenov, A.V.Subbotin. *AIP Conf. Proc.*, **1736**, 020086 (2016)
149. A.N.Semenov, A.V.Subbotin. *J. Polym. Sci., Part B: Phys. Ed.*, **55**, 623 (2017)
150. A.V.Subbotin, A.N.Semenov. *Polym. Sci., Ser. C*, **60**, 106 (2018)
151. S.L.Goren. *J. Fluid Mech.*, **12**, 309 (1962)
152. A.V.Subbotin, A.N.Semenov. *J. Rheol.*, **64**, 13 (2020)
153. P.C.Sousa, E.J.Vega, R.G.Sousa, J.M.Montanero, M.A.Alves. *Rheol. Acta*, **56**, 11 (2017)
154. G.P.Pope, A.Keller. *Colloid Polym. Sci.*, **255**, 633 (1977)
155. A.Keller, J.A.Odell. *Colloid Polym. Sci.*, **263**, 181 (1985)
156. C.D.Hudson, F.R.Felan Jr., M.D.Hundler, J.T.Cabral, K.B.Migler, E.J.Amis. *Appl. Phys. Lett.*, **85**, 335 (2004)
157. S.J.Howard. *Biopolymers*, **101**, 287 (2014)
158. J.Husny, J.J.Cooper-White. *J. Non-Newtonian Fluid Mech.*, **137**, 121 (2006)
159. G.F.Christopher, S.L.Anna. *J. Rheol.*, **53**, 663 (2009)
160. A.K.Marshall, T.W.Walker. *Rheol. Acta*, **58**, 573 (2019)
161. A.Ziabicki. *Fundamentals of Fiber Formation*. (London: Wiley, 1976)
162. S.P.Papkov. *Teoreticheskie Osnovy Proizvodstva Khimicheskikh Volokon*. (Theoretical Fundamentals of the Production of Chemical Fibres). (Moscow: Khimiya, 1990)