

From Capillary to Elastic Instability of Jets of Polymeric Liquids: Role of the Entanglement Network of Macromolecules[†]

A. V. Semakov, I. Yu. Skvortsov, V. G. Kulichikhin, and A. Ya. Malkin

Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii pr. 29, Moscow, 119991 Russia

e-mail: alex_malkin@mig.phys.msu.ru

Received April 6, 2015; in final form, April 22, 2015

By example of a series of polymers with molecular masses in a wide range, it has been shown that mechanisms of the instability of jets formed by diluted and moderately concentrated polymer solutions are different. A change from the capillary mechanism of breakup of a jet to the phase-separation instability inherent in polymer solutions occurs above the critical value of the dimensionless parameter—the product of the concentration and the intrinsic viscosity. This transition is determined by the conditions of the appearance of the entanglement network, which is also responsible for the possibility of large strains at the extension of a solution. The stability of a jet is achieved only at quite high strain rates at which a transition from the liquid solution to a rubbery-like oriented jet separated from the solution occurs.

DOI: 10.1134/S0021364015100136

It is known that a liquid filament is unstable. It can exist only for a finite time determined by the relation between capillary, inertial, and viscous forces. According to the Plato–Rayleigh model, the lifetime of the filament is determined by the relation between the inertial force and surface tension or viscosity:

$$\tau_{\text{in}}^* = \left(\frac{\rho r^3}{\gamma} \right) \quad \text{and} \quad \tau_{\text{vis}}^* = \frac{6\eta r}{\gamma}, \quad (1)$$

where ρ is the density of the liquid, r is the radius of the jet, γ is the surface tension, and η is the viscosity. However, it is also well known that jets of polymer solutions have a significantly larger “vitality” and can be extended by many times under certain conditions. In this case, the picture of breakup is different [1]. Typical examples of such phenomena are the expansibility of filaments produced by bombyces and spiders and of saliva, as well as the extension of jets in the production of chemical fibers. Malkin and Petrie [2] showed that large strains at the extension of melts of polymers are possible because they are not due to a flow, but are rubbery elastic deformations. It was shown in [3–5] that the breakup of jets for a wide range of concentrations of polymer solutions is described by the nonlinear Oldroyd equation under the assumption of a finite extensibility of a jet. However, it is still unclear how the transition from the capillary to elastic mechanism of the breakup of jets occurs and what is a criterion of their stability because of the deformation-induced transition to a rubbery-like state. This work is an attempt to answer this question with the use of new

experimental data concerning the correlation between the concentration of a polymer solution at which the mechanism of instability of a jet changes from capillary to elastic and the concentration at which the entanglement network is formed.

OBJECTS AND METHODS

We studied solutions of polyacrylonitrile in dimethyl sulfoxide of a chemical purity. We used a series of 17 samples of homo- and copolymers of polyacrylonitrile with the mean-weighted molecular mass M_w in the range from 84 to 836 kDa and the degree of homogeneity from 1.7 to 8.1. The detailed characteristics of these polymers are given in the supplemental materials to this article.

The state of a solution was characterized by the dimensionless product of the volume concentration c and the intrinsic viscosity $[\eta]$ measured by standard methods. The product $c[\eta]$ is usually considered as a measure of the volume filling by solved macromolecules. At $c^*[\eta]$ about 1 (where c^* is often called the crossover concentration), a transition from dilute solutions, where contacts between macromolecules are absent, to semidilute solutions, where such contacts exist, is observed [6].

The conditions of the breakup of jets were determined by the visualization method at the original setup shown in Fig. 1. The extension of polymer solutions was performed in the regime of uniform acceleration of a carriage with an acceleration of 4.3g at zero initial velocity (g is the gravitational acceleration).

The process of extension of the jet was studied by high-speed video recording by a Nikon v2 camera with

[†]See the supplemental materials to this article at the website www.jetpletters.ac.ru.

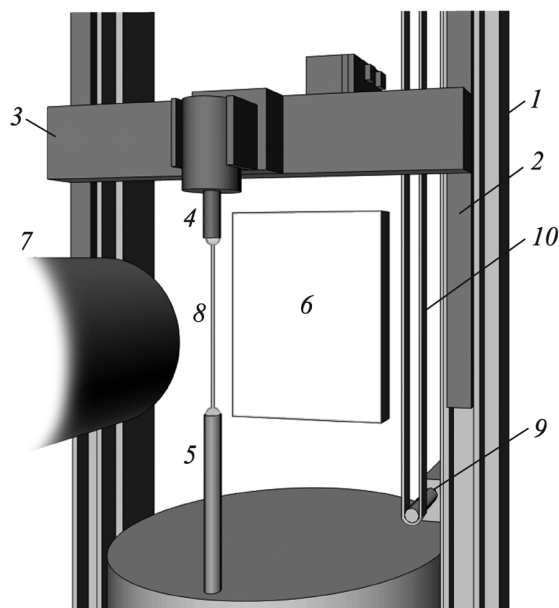


Fig. 1. Setup for the visualization of the extension of polymer solutions and determination of the beginning of fiber formation: (1) frame, (2) sliders, (3) carriage, (4) mobile cylinder fixed on the carriage, (5) immobile cylinder, (6) LED display, (7) camera, (8) jet of a polymer solution, (9) engine, and (10) belt drive.

a rate up to 1200 fps. For macro recording, we used a Tokina 100f 2.8D zoom objective at the position with the maximum magnification. Jets were recorded in backlight against the background of a bright planar photodiode serving as a display. As a result, we obtained clear 320×120 -pixel images of jets with a physical resolution of $16 \mu\text{m}$ per pixel at the 0.83-ms time resolution of the process of extension.

RESULTS AND DISCUSSION

The analysis of the video recording of the process of extension of jets of solutions with various concentrations made it possible to separate three main types of behavior of extended drops. Figure 2a shows the corresponding frames of high-speed recording for polymer solutions with various concentrations for a polymer with $M_w = 836 \text{ kDa}$.

A jet of the solution with the lowest concentration ($c = 0.001\%$) is stretched and decays into *separate drops* through the Rayleigh instability mechanism (Fig. 2a). The estimates of the characteristic times of instability of the liquid filament of this solution by Eqs. (1), $\tau_{\text{in}} = 0.3 \text{ ms}$ and $\tau_{\text{vis}} = 0.4 \text{ ms}$, correspond to the experimental data: the filament is thinned in the second frame and is joined in the third frame (the time of one frame is 0.83 ms); the next frame demonstrates the break of the jet.

At a high (three orders of magnitude higher) concentration of this polymer of 1%, the behavior of the

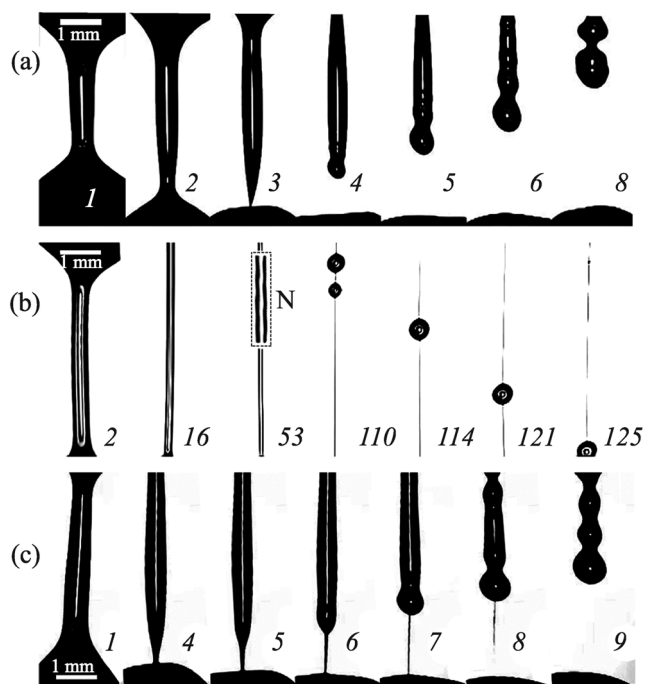


Fig. 2. Frame of high-speed recording of the tension of polyacrylonitrile solutions with a concentration of (a) 0.001, (b) 1, and (c) 0.05%. The numbers of frames are given. The time was always measured from the time of the separation of cylinders by 5 mm (15.4 ms after the beginning of the experiment). Frames 1–6 and 8 correspond to the times of 0.8, 1.7, 2.5, 3.3, 4.2, 5, and 6.7 ms, respectively; frames 2, 16, 53, 110, 114, 121, and 125 correspond to the times of 1.7, 13.3, 44, 95, 100.8, and 104.2 ms, respectively; symbol N marks the region where the Rayleigh instability of the shell formed by the solvent begins; and frames 1 and 4–9 correspond to the times of 0.8, 3.3, 4.2, 5, 5.8, 6.7, and 7.5 ms, respectively.

filament of the polymer solution changes qualitatively (Fig. 2b). In the initial frames (2, 16), the contraction of the liquid filament is observed. Then, at a certain diameter, *an oriented fiber is formed and a solvent is separated on the surface of this fiber*, first, in the form of a cylindrical shell and, then, decaying through the mechanism of Rayleigh instability with the formation of separate drops. Frame 53 shows a magnified fragment of the jet marked by the symbol N, where the corrugation of the surface characteristic of the initial stage of instability is seen. After that, small droplets of the solvent, as beads on a string (frame 110), are joined into larger droplets and roll down over the fiber under the action of the gravitational force (frames 114, 121, and 125). This is due to elastic instability manifested in the phase separation of the solution with the formation of a fiber of a rubbery oriented polymer with unlimited “lifetime” (see [7]). Its deformations are completely similar to rubbery elastic deformations of a melt at high extension rates.

Finally, we consider an intermediate case—the instant of the transition from the Rayleigh instability

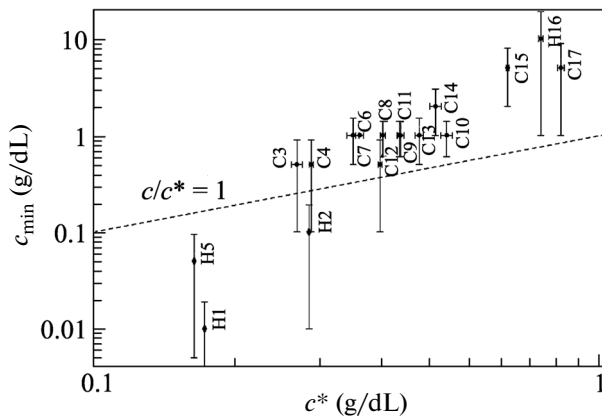


Fig. 3. (Minimum concentration of fiber formation vs. crossover concentration) correlation diagram.

of the liquid filament of the polymer solution to the formation of a thin elastic fiber with a finite lifetime. The corresponding series of frames is shown in Fig. 2c for the 0.05% solution. At this concentration, a thin filament connecting the halves of the stretched drop of the solution is formed (frames 5–8). The filament is gradually thinned and disappears from the field of view upon reaching the resolution of the camera (frame 9).

Thus, the developed method allows clearly identifying the instant of the transition from the Rayleigh instability to the formation of elastic “bridges” (filaments) by choosing experimentally the corresponding minimum concentration of the solution. In this case, the formulated problem is reduced to the determination of the minimum concentrations of the polymer in the solution at which the formation of the fiber begins. To this end, the deformation behavior of solutions of the series of polymers under study is considered and the set of the minimum concentrations at which the fiber formation begins is determined. The minimum concentration of the solution responsible for the fiber formation is determined by the method of the gradual narrowing of the concentration band bounded by Rayleigh instability from one side and the formation of fibers from the other side.

The experimental data obtained made it possible to plot the correlation diagram in the (minimum concentration of fiber formation vs. crossover concentration) coordinates for all polymers under study (Fig. 3).

The crossover concentration was determined as $c^* = 0.77/[\eta]$ [8]. At concentrations above $c/c^* \approx 1$, contacts appear between macromolecular coils and an entanglement network is formed. The line $c/c^* = 1$ is plotted on the plane of the states of the correlation diagram. As is seen, the concentration c_{\min} at which the transition occurs from capillary instability to the formation of the elastic filament is at $c/c^* > 1$ for all polymers except for three highest molecular mass polymers.

In this respect, solutions with concentrations above a certain threshold are completely similar to melts of polymers in the mechanism of the development of large strains. This is a necessary condition for the formation of the elastic jet/filament. However, in addition to large strains, the important sufficient condition of a high strain rate determined by the Weissenberg criterion should be satisfied [2].

Thus, the necessary condition for the transition from the capillary to elastic instability of jets of polymeric liquids is the formation of the entanglement network, which in turn allows the possibility of large elastic (rubbery elastic) strains of the solution at high extension rates.

At the same time, points on the correlation diagram for three polymers with the largest molecular masses and wide molecular mass distributions are in the region of dilute solutions. The effect of structuring possibly occurs in this case at very high degrees of dilution with the formation of supramolecular structures [9]. It can also be expected that the boundary of “dilute” solutions for polymers with a very large molecular mass is shifted under extension toward lower concentrations below the line $c/c^* = 1$ because interactions between macromolecules under extension can differ from those at a shear flow [10].

We are grateful to Dr. I.E. Nifant'ev and Dr. E.V. Chernikova (Moscow State University) for polyacrylonitrile samples kindly placed at our disposal. This work was supported by the Russian Science Foundation (agreement no. 4-23-00003, August 7, 2014).

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Translated by R. Tyapayev