Pis'ma v ZhETF, vol. 111, iss. 1, pp. 50 – 51 © 2020 January 10

Capillary-induced phase separation in ultrathin jets of rigid-chain polymer solutions

A. V. Subbotin[+*1)], *A. N. Semenov*[×]

[+] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russia*

[*] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia*

[×] *Institut Charles Sadron, CNRS-UPR 22, Universite de Strasbourg, 23 rue du Loess, BP 84047, 67034 Strasbourg Cedex 2, France*

Submitted 23 October 2019
Resubmitted 20 November 2019
Accepted 21 November 2019

DOI: 10.31857/S0370274X20010105

Capillary thinning and break-up of liquid jets is one of the long-standing important problems attracting wide scientific and industrial interest [1]. The problem is particularly challenging in the case of polymer liquids [2–4]. Last decades the essential progress has been attained in study of Newtonian jets [5, 6]. However experiments reveal that Newtonian and polymer liquid threads show qualitatively different types of behavior [7]. In particular the jets formed by solutions of flexible polymers can show formation of blistering patterns where solvent droplets set on micro- or nano-fibers [8–10]. The nature of these patterns is insufficiently explored. One of the approaches elucidating this phenomenon was based on the opportunity for polymer molecules to migrate in the thinner regions due to the stress-concentration coupling effect [11]. Another molecular model, which has been proposed recently, puts forward the idea of a flow induced phase separation in dilute polymer solutions under extension [12, 13]. It predicts a polymer/solvent demixing due to the flow-induced orientation of polymer chains acting to reverse their effective interactions from repulsive to attractive. As a result the elongated chains tend to micro-separate and form a network of fibrils tending to compress laterally by squeezing the solvent out to the jet surface.

Most of the above results cover solutions of flexible chains. Meanwhile solutions of stiff polymers such as polypeptides, DNA, cellulose, aromatic polyamide copolymers etc. are particularly interesting for applications. Our study is focused on capillary thinning of solutions of rigid rods in the regime of ultrathin jet when its diameter is smaller than the rod length and the rods are highly oriented along the jet axis. Such regime arises at the terminal stage of capillary thinning.

[1)] e-mail: subbotin@ips.ac.ru

We examined two qualitatively different mechanisms of polymer liquid jet instability arisen on long and short length-scales. For length-scales exceeding the rod length the surface tension-driven thinning develops in a conventional way (Plateau–Rayleigh mechanism [1]) which ultimately should result in breaking up of the jet. By contrast, we show that at shorter length-scales the rods get effectively trapped inside the jet core whereas the solvent drains to the surface and forms annular droplets there, Fig. 1. The latter process of capillary phase separation occurs much faster and can prevent the jet from breaking up. This mechanism works both with non-volatile solvents and with no specific attraction between oriented polymer chains and differs from the mechanism of phase separation which is connected with a reduction of the steric repulsion of the stretched chains [12, 13]. Moreover, the described mechanism may be also at work in solutions of semiflexible polymers if the chains are highly stretched due to extension. Thereby the discovered capillary-driven phase separation effect can provide a universal mechanism of fiber formation in solutions of stretched polymers.

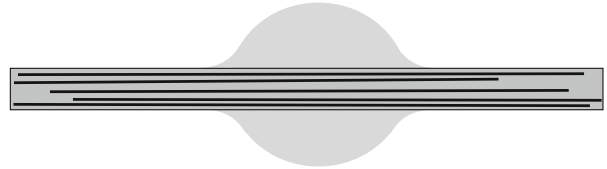

Fig. 1. (Color online) Illustration of annular droplet of solvent on the polymer solution jet

Experimental observation and identification of the predicted solvent/polymer demixing mechanism is a challenging problem. A thin quasi-uniform jet can be easily produced, for example, by stretching a liquid droplet. One option is to use solutions of DNA. These

chains can be very long and form nano-thick fibers in solutions [14]. The most appropriate system to verify our results must involve very long rods. Such macromolecular rods (with length $\geq 1-10$ microns) are known, examples are given by protein polymers (F-actin, microtubules) and other self-assembling supramolecular structures (like tri-arylamine fibers) [15–19].

A. V. Subbotin acknowledges financial support from the Russian Science Foundation (Grant # 17-79-30108). A. N. Semenov acknowledges a partial support from the International Research Training Group (IRTG) "Soft Matter Science: Concepts for the Design of Functional Materials".

Full text of the paper is published in JETP Letters journal. DOI: 10.1134/S0021364020010051

1. J. Eggers and E. Villermaux, Rep. Prog. Phys. **71**, 036601 (2008).
2. G. H. McKinley, *Visco-elasto-capillary thinning and break-up of complex fluids*, in Rheological Review (The British Society of Rheology, Aberystwyth, 2005), p. 1.
3. A. Ya. Malkin, A. Arinstein, and V. G. Kulichikhin, Prog. Polym. Sci. **39**, 959 (2014).
4. V. G. Kulichikhin, I. Yu. Skvortsov, A. V. Subbotin, S. V. Kotomin, and A. Ya. Malkin, Polymers **10**, 856 (2018).
5. J. R. Castrejón-Pita, A. A. Castrejón-Pita, S. S. Thete, K. Sambath, I. M. Hutchings, J. Hinch, J. R. Lister, and O. A. Basaran, PNAS **112**, 4582 (2015).
6. Y. Li and J. E. Sprittles, J. Fluid Mech. **797**, 29 (2016).
7. A. V. Bazilevskii, S. I. Voronkov, V. M. Entov, and A. N. Rozhkov, Sov. Phys. Dokl. **26**, 333 (1981).
8. R. Sattler, S. Gier, J. Eggers, and C. Wagner, Phys. Fluids **24**, 023101 (2012).
9. A. V. Semakov, I. Yu. Skvortsov, V. G. Kulichikhin, and A. Ya. Malkin, JETP Lett. **101**, 690 (2015).
10. A. Ya. Malkin, A. V. Semakov, I. Yu. Skvortsov, P. Zatonskikh, V. G. Kulichikhin, A. V. Subbotin, and A. N. Semenov, Macromolecules **50**, 8231 (2017).
11. J. Eggers, Phys. Fluids **26**, 033106 (2014).
12. A. V. Subbotin and A. N. Semenov, J. Polym. Sci.: Part B: Phys. Ed. **54**, 1066 (2016).
13. A. N. Semenov and A. V. Subbotin, J. Polym. Sci.: Part B: Phys. Ed. **55**, 623 (2017).
14. X. Fang and D. H. Reneker, J. Macromol. Sci.: Part B: Phys. **36**, 169 (1997).
15. F. Gittes, B. Mickey, J. Nettleton, and J. Howard, J. Cell Biol. **120**, 923 (1993).
16. F. Oosawa and S. Asakura, *Thermodynamics of the Polymerization of Protein*, Acad. Press, San Diego (1975).
17. J. van Mameren, K. C. Vermeulen, F. Gittes, and C. F. Schmidt, J. Phys. Chem. B **113**, 3837 (2009).
18. E. Moulin, F. Niess, M. Maaloum, E. Buhler, I. Nyrkova, and N. Giuseppone, Angew. Chem. Int. Ed. **49**, 6974 (2010).
19. I. Nyrkova, E. Moulin, J. J. Armao IV, M. Maaloum, B. Heinrich, M. Rawiso, F. Niess, J.-J. Cid, N. Jouault, E. Buhler, A. N. Semenov, and N. Giuseppone, ACS Nano **8**, 10111 (2014).