
MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Nanofibers Based on an Aliphatic Copolyamide, Prepared by Electroforming

I. P. Dobrovol'skaya^a, P. V. Popryadukhin^a, V. E. Yudin^a, K. Balik^b,
Z. Weishauptova^b, and M. Zaloudkova^b

^a Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

^b Institute of Rock Structure and Mechanics ASCR, Prague, Czech Republic

Received February 25, 2011

Abstract—The rheological properties and stability of solutions of poly- ϵ -caprolactam–polyhexamethylenedipamide copolymer in an alcohol–water solvent were studied. The properties of fibers prepared from the copolymer solution by electroforming were examined.

DOI: 10.1134/S1070427211100211

Electroforming allows preparation of polymer fibers from 50 to 4500 nm in diameter. The solution or melt of a polymer undergoes polarization in a high-intensity electric field with the formation of microjets, which are deposited in the form of nanofibers [1, 2]. This procedure is used for preparing nanofibers of polyethylene, polypropylene, polyvinyl alcohol, polyethylene oxide, polyvinylpyrrolidone, polyamides, polymethyl methacrylate, polylactide, cellulose derivatives, and other polymers. Materials based on nanofibers are characterized by low density, high porosity, and permeability to water and gases [2–4].

Preparation of fibers by electroforming from a solution of an aliphatic polyamide is described in a patent [5]. In this process, concentrated (88%) formic acid was used as solvent, which considerably complicates the electroforming process and is environmentally unfavorable.

Aliphatic copolyamides are of interest for preparing nanofibers by electroforming, because they are soluble in alcohol–water mixtures. These polymers are used for preparing porous film materials by coagulation of the polymer in aqueous or aqueous-alcoholic precipitation bath [2].

It is known that the poly- ϵ -caprolactam–polyhexamethylenedipamide copolymer (CPA) exhibits

the best film- and fiber-forming properties [5]. In addition, it is bioinert and contains no residual solvent or other harmful impurities, which allows this CPA to be used for preparing medical materials and matrices for cell technologies. The solvent is alcohol–water mixture, which makes the forming process environmentally safe. Materials based on this polymer preserve the service characteristics in aqueous media for a long time. They are used as filtration materials for fine purification of liquid and gaseous media [5].

Data on preparation of nanofibers from aliphatic copolyamides by electroforming are lacking. Data on the rheological properties of aliphatic copolyamides in alcohol–water solvents and on correlation of these properties with the fiber structure are insufficient.

In this study we examined the rheological properties of CPA solutions in an alcohol–water solvent, the phase state of these solutions, and the structure of nanofibers prepared by electroforming.

EXPERIMENTAL

The investigation objects were solutions of poly- ϵ -caprolactam–polyhexamethylenedipamide copolymer (PA 6/66, Anid Limited Liability Company) in alcohol–water solvents. The concentration of CPA solutions

was 10–30 wt %, and the composition of ethanol/water mixtures varied from 45/55 to 97/3 vol %. Solutions were prepared at 70°C by stirring for 2 h, after which they were filtered and degassed by keeping for 2 h at a pressure of 0.1 atm. The onset of phase segregation was determined from the cloud point of the solution, and the transition to the solid state, from the loss of the solution fluidity.

Electroforming of the fibers was performed on a laboratory installation of the Institute of Macromolecular Compounds, Russian Academy of Sciences, schematically shown in Fig. 1. A solution was fed with an injector pump through a die electrode into an electric field of the intensity $E = 1.5 \times 10^4$ – 4.0×10^5 V m⁻¹ at the interelectrode distance of 0.1–0.5 m. The fibers were deposited on an electrode in the form of a Teflon-coated metal plate.

Rheological measurements were performed with an MCR 301 rheometer (Anton Paar) at 20°C using the cylinder-in-cylinder procedure both in the mode of shear flow at shear rates of 1–4000 s⁻¹ and in the dynamic mode at circular frequencies of 0.5–100 rad s⁻¹ and strain of 10–1%.

Microscopic examination was performed with a Quanta 450 electron microscope. Prior to measurements, the specimen surface was coated with carbon.

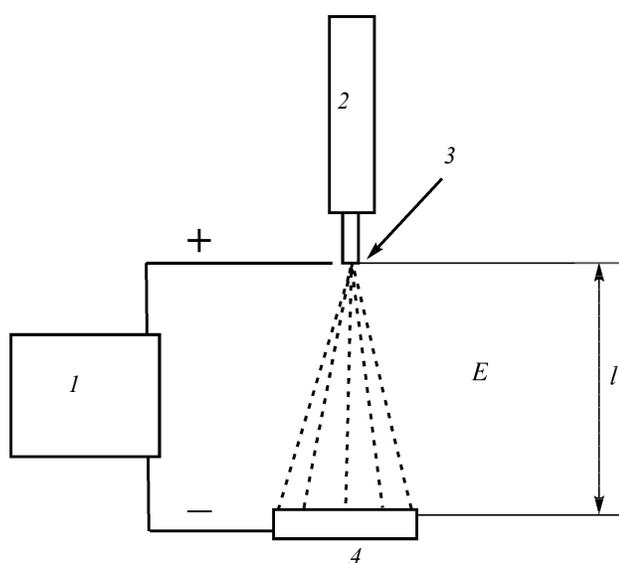


Fig. 1. Schematic of an installation for fiber electroforming: (1) high-voltage unit, (2) dosing unit, (3) die electrode, (4) depositing electrode, (E) electric field intensity, and (l) interelectrode distance.

For the fiber preparation technology, an important parameter is the solution stability. Namely, its properties should not change during the periods of solution preparation, filtration, and degassing and of the fiber forming proper. Therefore, the goal of our study was plotting of liquid–solid phase diagrams for CPA solutions in relation to the solvent composition (ethanol–water ratio) and polymer concentration in the solution.

Figure 2 shows the phase diagram of 15 wt % CPA solutions. As can be seen, the dependences of the time at which the solution starts to undergo phase segregation (liquidus line) and time of the solution transition to the solid state (solidus line) on the ethanol content of the solvent are nonmonotonic. The ethanol concentration in the alcohol–water mixture at which the solid phase does not separate out for a long time and the solution does not pass into the solid state is 75–85% (Fig. 2). Therefore, as solvent for preparing CPA solutions we chose a mixture with the ethanol/water ratio of 80/20.

The second important parameter affecting the solution stability is the polymer concentration. Figure 3 shows the phase diagram of CPA solutions of various concentrations. It follows from these data that, with an increase in the polymer concentration, the solutions become less stable and the time of the phase segregation and transition of the solution into the gel state decreases. With an

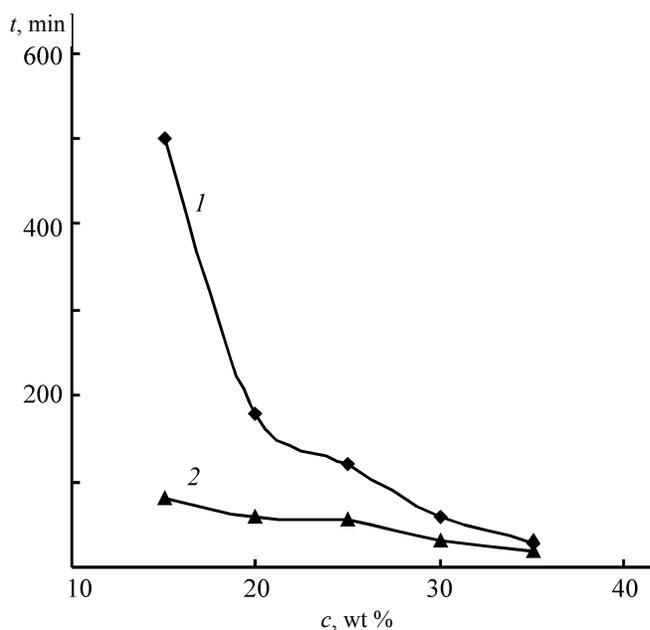


Fig. 2. Phase diagram of 15 wt % CPA solutions: (t) time of keeping the solution at 20°C and (c) ethanol content of the alcohol–water mixture. Line: (1) liquidus and (2) solidus; the same for Fig. 3.

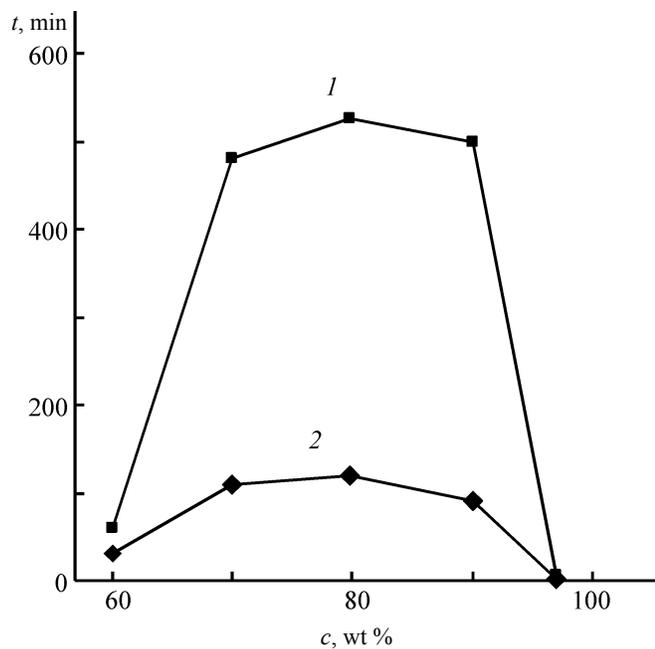


Fig. 3. Phase diagram of CPA solutions in 80/20 ethanol/water solvent: (*t*) time of keeping the solution at 20°C and (*c*) CPA solution concentration.

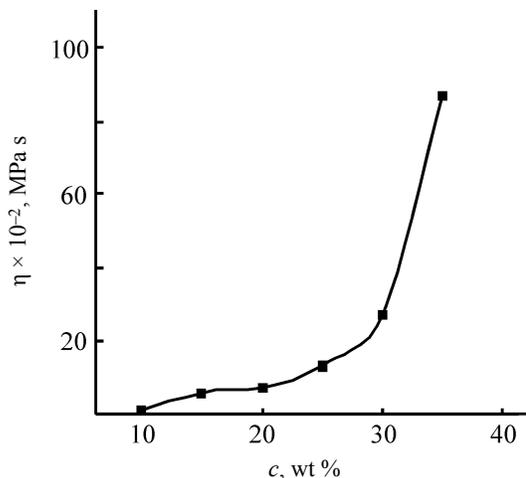


Fig. 4. Viscosity of CPA solution $\eta \times 10^{-2}$ as a function of concentration *c*.

increase in the concentration of CPA solutions, their viscosity increases (Fig. 4), especially for solutions of the concentration exceeding 25 wt %.

It should be noted that the stability of the solutions

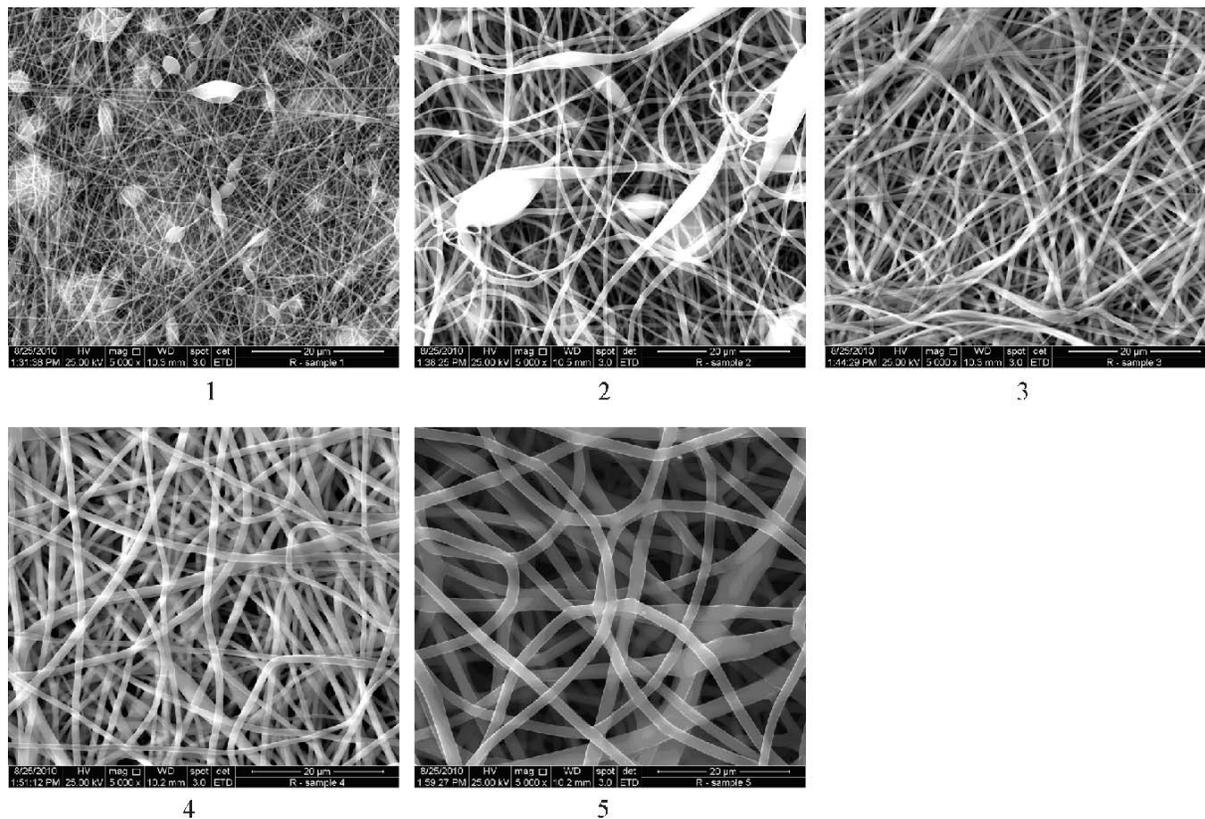


Fig. 5. Electron micrographs of CPA fibers prepared from solutions of various concentrations. Concentration, wt %: (1) 10, (2) 15, (3) 20, (4) 25, and (5) 30.

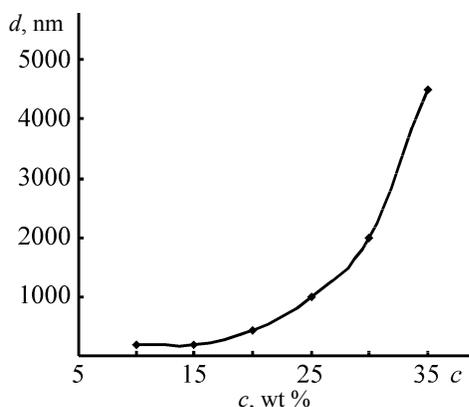


Fig. 6. Fiber diameter d as a function of CPA solution concentration c .

was studied at 20°C. Therefore, the phase segregation times obtained are minimal. With an increase in the temperature of forming, filtration, or degassing, the time of precipitation of the solid phase from the solution increases.

Thus, the properties required for fiber forming are exhibited by CPA solutions in 80/20 ethanol/water mixture at the polymer concentration not exceeding 25 wt %.

From CPA solutions of various concentrations, we prepared fibers by electroforming. The electron micrographs of the fibers are shown in Fig. 5. As can be seen, forming from 10–15 wt % solutions yields fibers with a relatively large amount of defects in the form of elongated droplets. Presumably, CPA solutions of relatively low concentration do not exhibit the dielectric characteristics required for polarization of the polymer in the electric field and formation of microjets forming fibers with a diameter of tens or hundreds of nanometers, depositing on the electrode. The second possible cause of such defects in fiber forming from solutions of relatively low concentration is incomplete removal of the solvent from the polymer solution in the course of the polymer deposition. At the polymer concentration exceeding 15 wt %, the fibers are uniform in diameter, with no defects. A similar structure of fibrous materials obtained

by electroforming is observed with polyvinyl alcohol, polyethylene oxide, chitosan, and other polymers [6, 7].

Based on the results of electron-microscopic examination, we calculated the mean diameter of fibers prepared from solutions with various CPA concentrations. We found that, with an increase in the solution concentration, the fiber diameter increased (Fig. 6). The smallest fiber diameter is observed in forming from a 10 wt % solution, about 200 nm. With an increase in the solution concentration over 20%, the fiber diameter increases considerably, up to 4500 nm.

CONCLUSIONS

- (1) Fibers with the diameter in the range 200–4500 nm were prepared by electroforming from solutions of poly- ϵ -caprolactam–polyhexamethylenedipamide copolymer in an alcohol–water solvent.
- (2) The optimal ethanol/water ratio in the solvent, ensuring the phase stability of the solution, is 80/20.
- (3) The most stable solutions having the optimal rheological characteristics contain 15–20 wt % copolymer.
- (4) The diameter of nanofibers prepared by electroforming increases with an increase in the solution concentration and ranges from 200 to 4500 nm.

REFERENCES

1. Schiffman, J.D. and Schauer, C.L., *Polym. Rev.*, 2008, vol. 48, pp. 317–325.
2. Mulder, M., *Basic Principles of Membrane Technology*, Dordrecht: Kluwer Academic, 1996, 2nd ed.
3. RF Patent 2039535.
4. US Patent 6790528.
5. Nachinkin, O.I., *Polimernye mikrofil'try* (Polymeric Microfilters), Moscow: Khimiya, 1985.
6. Lee, H.W., Karim, M.R., Park, J.H., et al., *J. Appl. Polym. Sci.*, 2009, vol. 111, pp. 132–139.
7. Jia, Y.-T., Gong, J., Gu, X.-H., et al., *Carbohydrate Polym.*, 2007, vol. 67, pp. 403–412.