

# Ultrafiltration Membranes Based on Various Acrylonitrile Copolymers

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Received July 5, 2019; revised July 25, 2019; accepted August 9, 2019

**Abstract**—The structure and properties of ultrafiltration membranes synthesized from bicomponent solutions in *N,N*-dimethylformamide using five commercial acrylonitrile copolymers of various compositions and molecular masses have been studied. The molecular mass characteristics of the copolymers ( $M_w$ ,  $M_w/M_n$ ) have been determined; the viscosity properties of dilute and concentrated solutions have been studied. It has been shown that depending on the chemical composition and molecular mass of the copolymer, the concentration dependence of the water flux is different: for copolymers with a molecular mass of  $M_w$  of 76000–81000 g/mol, with an increase in the copolymer concentration in solution from 12 to 16%, the water flux of the membranes decreases from 300–500 to 40–150 L/(m<sup>2</sup> h) depending on the copolymer composition. For samples with a higher molecular mass ( $M_w = 99000$  and 107000 g/mol), the water flux of the membranes hardly depends on the copolymer concentration in the casting solution; it is 150 and 75 L/(m<sup>2</sup> h), respectively. The rejection factor of the membranes with a molecular mass of 40000 g/mol for polyvinylpyrrolidone increases with increasing copolymer concentration in the casting solution regardless of the chemical composition and molecular mass of the copolymer. Scanning electron microscopy studies of the membrane structure have shown that membranes synthesized from copolymers with a higher molecular mass have a denser structure and a thicker selective layer than the respective parameters of membranes synthesized from acrylonitrile copolymers with a lower molecular mass, which are characterized by the presence of large macrovoids in the membrane matrix. These differences in the membrane structure are attributed to different viscosities of the casting solutions at identical copolymer concentrations.

**Keywords:** polyacrylonitrile, ultrafiltration, flat membranes, acrylonitrile copolymer, permeability

**DOI:** 10.1134/S2517751619060015

## INTRODUCTION

Polyacrylonitrile (PAN) is commonly used to synthesize membranes for filtering liquid media. Advantages of PAN are stability in a medium of nonpolar and low-polar organic solvents, such as hydrocarbons, alcohols, and esters [1]; hydrophilicity; relatively high chemical and thermal stability, in particular, resistance to active chlorine [2]; and low cost [3, 4]. Polyacrylonitrile-based micro- and ultrafiltration (UF) membranes are most commonly used in biotechnology, medicine, the textile industry, and wastewater treatment [5–10].

Conventionally, PAN membranes are synthesized by the wet-phase inversion method [11]. There are reports on the use of dimethylformamide (DMF), dimethylacetamide (DMAA), and dimethyl sulfoxide (DMSO) [12] as solvents for PAN in membrane synthesis. The morphology, average pore size, effective porosity, and, accordingly, transport properties of UF

membranes are determined by a number of parameters: the casting solution composition, the solvent used to prepare the solution, the polymer concentration, the type and concentration of the blowing agent [13–16], the composition and temperature of the coagulation bath [17, 18], etc. Low-molecular-mass additives (blowing agents) to casting solutions are used to obtain a required complex of the operational properties of the membranes [16]. These additives are water [19], inorganic salts [20, 21], low-molecular-mass organic compounds [13, 14], surfactants [22], polymers [23], etc.

Variations in the casting parameters provided the formation of flat PAN-based UF membranes with different morphologies of the pore structure and a given pore diameter (2–70 nm) [2]. These membranes exhibit high transport characteristics: the water flux achieves 2 m<sup>3</sup>/(m<sup>2</sup> h bar) [2], while the nitrogen gas permeability is 120 m<sup>3</sup>/(m<sup>2</sup> h bar) [24]. Polyacrylonitrile hollow fiber membranes are intensively used in

**Table 1.** Characteristics of acrylonitrile copolymers

Sample	Membrane-forming copolymer	Manufacturer	$M_w$ , * g/mol	$M_w/M_n$ *	$\eta_{sp}$ *
I	Poly(acrylonitrile- <i>co</i> -methyl acrylate) (92 : 8)	Orgsteklo Research Institute for Synthetic Fiber with Pilot Plant, Russia	107000	2.31	1.41
II	Poly(acrylonitrile- <i>co</i> -methylacrylate- <i>co</i> -2-acrylamide-2-methylpropanesulfonic acid) (91 : 8 : 1)	Naftan, Belarus	61000	1.72	0.78
III	Poly(acrylonitrile- <i>co</i> -itaconic acid) (99 : 1)	European Carbon Fibers (ECF, former EPG), Germany	99000	2.56	1.29
IV	Poly(acrylonitrile- <i>co</i> -methyl acrylate) (93.6 : 6.4)	Haihang industry Co., Ltd (China)	76000	2.88	0.76
V	Poly(acrylonitrile- <i>co</i> -methyl acrylate) (91.5 : 8.5)	Haihang industry Co., Ltd (China)	81000	2.35	0.96

\* Data of the authors.

ultra- [25] and nanofiltration processes [5, 26] and in hydrophilic pervaporation [27].

The complex of physicochemical properties of PAN provides the common use of PAN-based membranes as substrates for synthesizing high-performance composite membranes for various purposes [28–30]. Thus, composite gas separation membranes with thin layers of PolyActive brand polymers (carbon dioxide permeability of  $>5 \text{ m}^3/(\text{m}^2 \text{ h bar})$  [31]) or polymers of intrinsic microporosity (carbon dioxide permeability of  $20 \text{ m}^3/(\text{m}^2 \text{ h bar})$  [32]) have been developed for  $\text{CO}_2$  extraction problems and chemically resistant composite membranes have been synthesized for the separation of aromatic/saturated hydrocarbons by the organophilic pervaporation method (toluene flux of up to  $15 \text{ kg}/(\text{m}^2 \text{ h})$  [33]). For the separation of organic media, nanofiltration composite membranes resistant to organic solvents (acetone permeability of up to  $14 \text{ kg}/(\text{m}^2 \text{ h bar})$  [34]) have been developed; PAN membranes modified with hydrazine hydrate exhibit a high resistance to alkaline media [35]; the exposure of membranes to IR radiation makes PAN insoluble in organic solvents [36, 37]. Earlier, it was shown that a correct choice of a porous substrate and an optimization of the substrate synthesis are particularly important for designing high-performance gas separation membranes [38].

This study is focused on the structure and properties of flat UF membranes synthesized from acrylonitrile (AN) copolymers with different compositions and molecular masses. The formulation of the problem is attributed to the fact that AN homopolymers with different molecular masses are typically used as a membrane-forming polymer [4, 6, 7, 12, 39–41]. At the same time, AN copolymers used to produce chemical fibers are available on the market. An advantage of AN copolymers is the better dyeability of chemical fibers, which is important for the textile industry.

There are hardly any reports on systematic studies of the use of AN copolymers in membrane synthesis. This study will make it possible to identify promising copolymers for the subsequent production of porous membrane substrates with optimum mechanical and transport properties.

## EXPERIMENTAL

In this study, commercial AN copolymers used for the production of chemical fibers were used (Table 1).

The molecular mass characteristics of the used copolymers (weight average molecular mass  $M_w$ , number average molecular mass  $M_n$ , degree of polydispersity  $M_w/M_n$ ) were studied by gel permeation chromatography on a PolymerLabs GPC-120 chromatograph. Analysis was conducted in a DMF medium containing 0.1 wt % LiBr at  $50^\circ\text{C}$  and a flow rate of 1 mL/min. Two PLgel 5- $\mu\text{m}$  MIXED-C columns were used for separation. A polymer solution in an eluent with a polymer concentration of 0.7–1 mg/mL was prepared for analysis. Molecular mass was calculated in accordance with the poly(methyl methacrylate) (PMMA) standards ( $M_{\text{PMMA}} = 8 \times 10^2 - 3 \times 10^7$ ); for PAN, the molecular mass was recalculated using Mark–Kuhn–Hauwink coefficients known from the literature ( $K_{\text{PAN}} = 39.4 \times 10^{-4}$ ,  $\alpha_{\text{PAN}} = 0.75$ ,  $K_{\text{PMMA}} = 17.7 \times 10^{-4}$ ,  $\alpha_{\text{PMMA}} = 0.62$ ):

$$\log M_{\text{PAN}} = \frac{1 + \alpha_{\text{PMMA}}}{1 + \alpha_{\text{PAN}}} \log M_{\text{PMMA}} + \frac{1}{1 + \alpha_{\text{PAN}}} \log \frac{K_{\text{PMMA}}}{K_{\text{PAN}}} \quad (1)$$

The specific viscosity of 0.5 wt % solutions of copolymers in DMF was determined using a capillary viscometer with an inner diameter of the capillary of 0.56 mm at  $25^\circ\text{C}$ .

Casting solutions of the copolymers were prepared using DMF (reagent grade, Khimmed, Russia). The copolymer concentration was varied in a range of 12–17%. The choice of concentration limits was based on the ratio of the balance of the molecular mass of the copolymer, the copolymer concentration in the casting solution, and the viscosity of the casting solution [39–41]. The solution was stirred at a temperature of 100°C for 3–4 h and degassed for 12 h.

The dynamic viscosity of the prepared casting solutions was determined using a Brookfield RV DV-III Ultra Programmable Rheometer rotational viscometer at 25°C.

To synthesize membranes, casting solutions were cast in the form of a thin layer onto glass using a die with a gap thickness of 160  $\mu\text{m}$  and then precipitated in distilled water. The resulting membranes were washed in distilled water for at least 17 h.

The transport properties of the membranes were studied in cells under stirring at an operating pressure of 0.1 MPa and 20°C. The flux of the membranes ( $J$ , L/(m<sup>2</sup> h)) was calculated by the formula

$$J = \frac{V}{St}, \quad (2)$$

where  $V$  is the filtrate volume, L;  $S$  is the membrane area, m<sup>2</sup>; and  $t$  is the filtration time, h.

The separation properties of the membranes were determined in terms of rejection factor  $R$  (%):

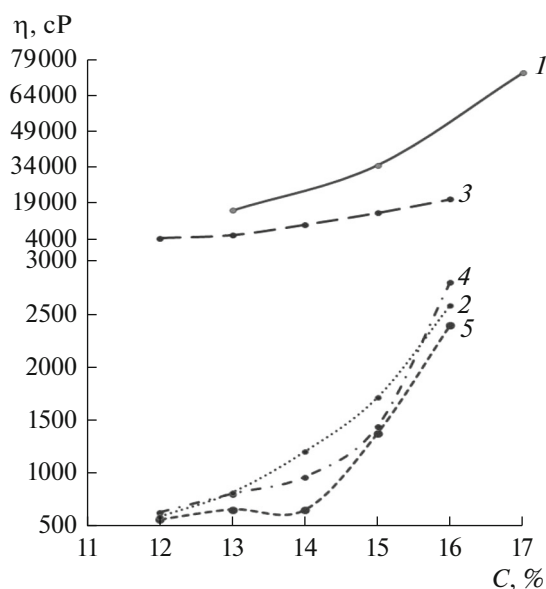
$$R = \left(1 - \frac{c_p}{c_0}\right) \times 100\%, \quad (3)$$

where  $c_0$  and  $c_p$  is the solute concentration in the feed solution and the permeate, respectively. The model solution was an aqueous solution of polyvinylpyrrolidone (PVP K-30, Fluka,  $M_w = 40000$  g/mol, a solution concentration of 3 g/L). The PVP concentration in solutions was determined using an ITR-2 Rayleigh interferometer.

The geometric parameters and structural morphology of the membranes synthesized from the different AN copolymers were studied by scanning electron microscopy (SEM) on a Hitachi Tabletop TM 3030 Plus microscope equipped with a highly sensitive low-vacuum secondary electron detector (Hitachi High Technologies Corporation, Japan). Cleavages of the samples were obtained in a liquid nitrogen atmosphere; a layer of gold was deposited on the resulting cleavages using a DSR-1 spraying gun (NSC, Iran). The thickness of the gold film layer was varied in a range of 50–100 Å.

## RESULTS AND DISCUSSION

Table 1 shows results of determination of the molecular mass characteristics and specific viscosity of the copolymers in DMF. Depending on the manufacturer and composition of the copolymers, the

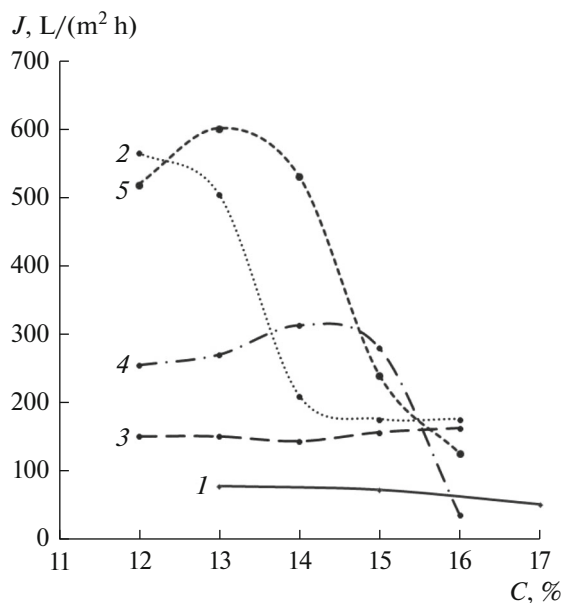


**Fig. 1.** Dependence of the viscosity of acrylonitrile copolymer solutions on the copolymer concentration at  $T = 25^\circ\text{C}$ . Curve numbers correspond to copolymer numbers in Table 1.

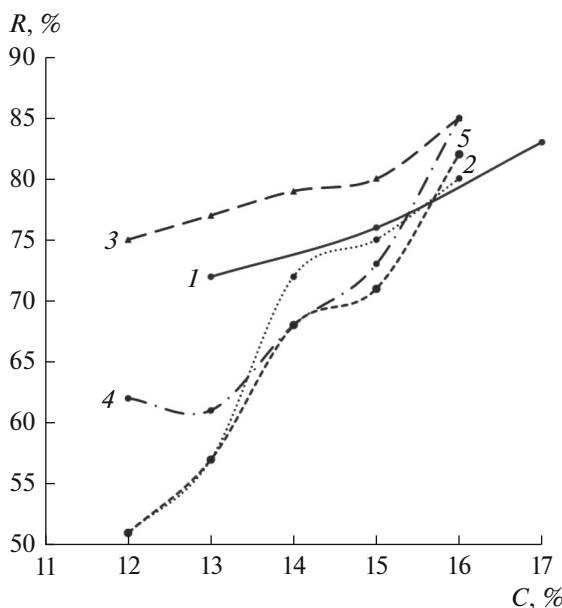
weight average molecular masses  $M_w$  differ by a factor of 1.4–1.7. The degree of polydispersity ( $M_w/M_n$ ) is approximately the same for all the samples (2.31–2.88), except for copolymer II, which has the lowest  $M_w/M_n$  of 1.72. The specific viscosity of the copolymers increases with increasing molecular mass, except for samples II and IV. The molecular mass of sample IV is higher, although the specific viscosity of it is slightly lower than that of sample II; this finding can be attributed to the different chemical compositions of the copolymers and their different affinities for the solvent (DMF), which are responsible for their different conformations in solution.

The results of determination of the dynamic viscosity of concentrated copolymer solutions in DMF are shown in Fig. 1. The viscosity of the casting solutions increases with increasing copolymer concentration; this finding is consistent with the published data [42, 43]. It is evident from Fig. 1 that solutions with high-molecular-mass copolymers (samples I and III) are characterized by significantly higher viscosity values. It should be noted that the solution viscosity abruptly decreases upon switching from samples with a molecular mass of 99000–107000 (samples I and III) to samples with  $M_w = 76000$ –81000 (samples II, IV, and V). Thus, at a relatively small difference in molecular mass for copolymers III and V ( $M_w = 99000$  and 81000, respectively), the viscosities of 14–16 wt % solutions differ more than tenfold.

The water flux and rejection factor of membranes synthesized from solutions of different concentrations are shown in Figs. 2 and 3. Analysis of the data shown



**Fig. 2.** Dependence of the water flux of the membranes on the copolymer concentration in the casting solution. Curve numbers correspond to copolymer numbers in Table 1.



**Fig. 3.** Dependence of the rejection factor of the membranes for PVP K-30 on the copolymer concentration in the casting solution. Curve numbers correspond to copolymer numbers in Table 1.

in Fig. 2 revealed significant differences in both the pattern of the change in the permeability and the absolute values of flux across the membranes synthesized from the different copolymers. Thus, the highest water flux (more than 500 L/(m<sup>2</sup> h)) is exhibited by the films synthesized from 12–13 wt % solutions of

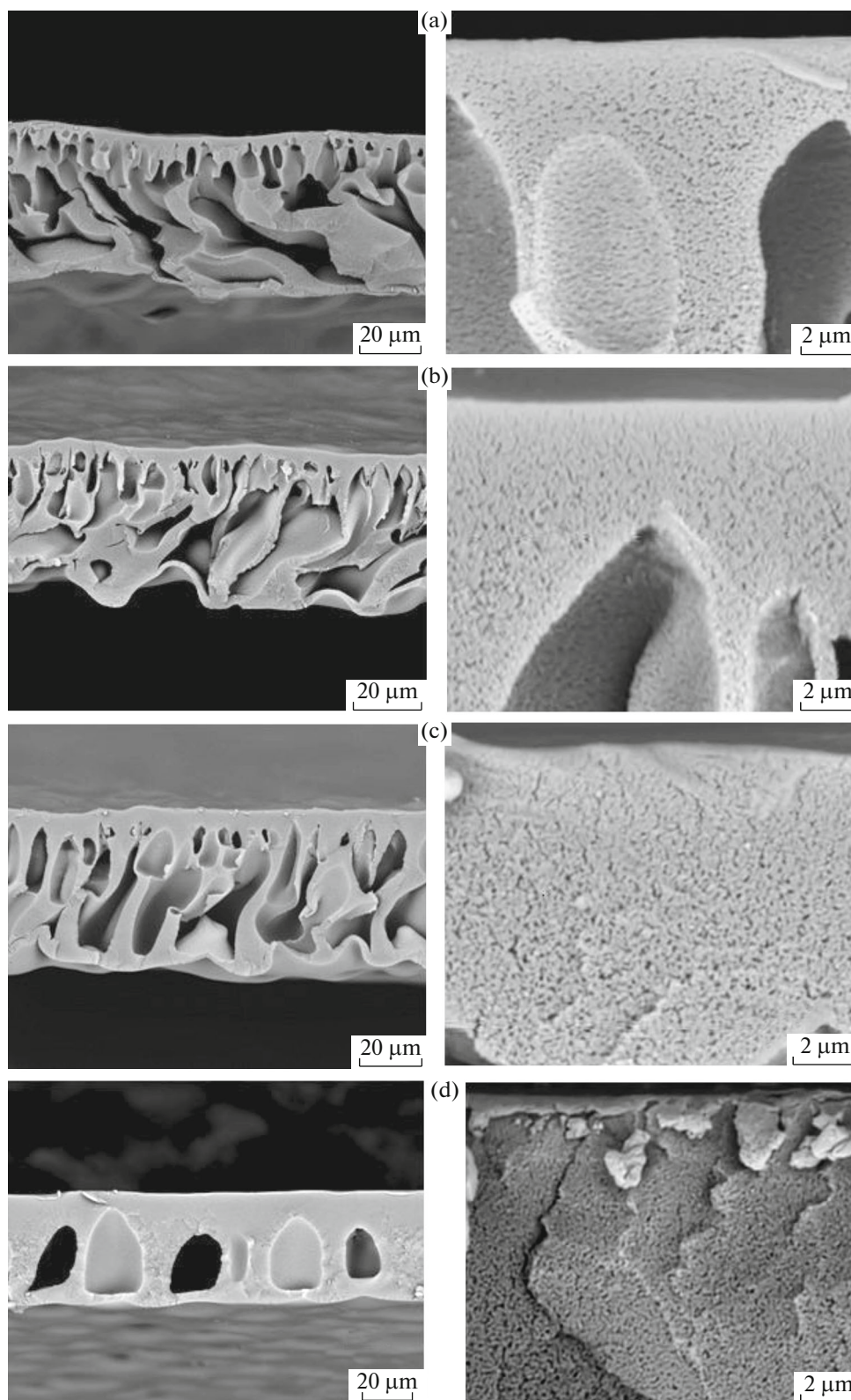
copolymers II and V. With an increase in the copolymer concentration in the casting solution to 16 wt %, the water permeability of the films decreases to 176 and 126 L/(m<sup>2</sup> h) in the case of copolymers II and V, respectively.

With respect to the behavior of the concentration dependence of the water permeability of the membranes, the studied copolymers can be divided into two groups. For samples II and V, the behavior of the concentration dependence of water permeability is quite predictable; that is, with an increase in the copolymer concentration in solution, the water flux of the membranes decreases. A slight decrease in the membrane permeability at a copolymer concentration in the casting solution of 12 wt % can be attributed to the partial degradation of fragments of the polymer spatial framework of the gel and their fusion into a single unit owing to the gel fluidity under the action of high internal stresses. For samples I and III, which have a higher molecular mass, the water flux of the membranes is 75 and 150 L/(m<sup>2</sup> h), respectively; it hardly depends on the copolymer concentration in the casting solution. The twofold difference in the water flux of the membranes is apparently associated with differences in both the molecular mass and chemical composition of the copolymers. The membranes based on copolymer IV hold an intermediate position.

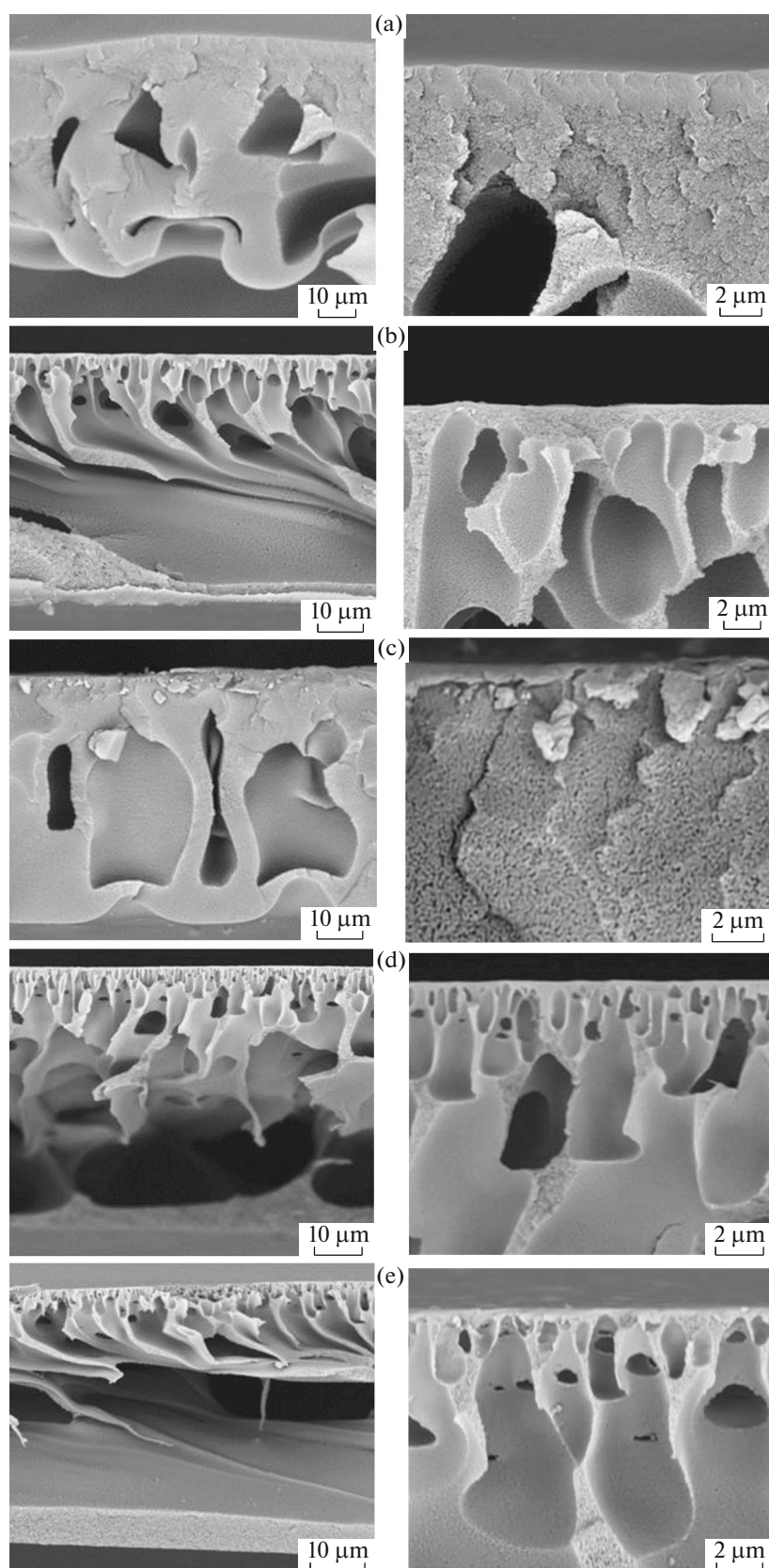
Analysis of the curves of the dependence of the rejection factor of the membranes for PVP K-30 on the AN copolymer concentration in the casting solution (Fig. 3) showed that the selective properties of the membranes are improved with an increase in the copolymer concentration in the casting solution regardless of the chemical composition and molecular mass of the copolymer. The largest increase in the rejection factor with increasing copolymer concentration is characteristic of membranes synthesized from the copolymers of the first group: the rejection factor increases from 51 to 80% in the case of sample II, from 51 to 82% in the case of sample V, and from 63 to 85% for copolymer IV. For copolymers I and III, for which the water flux of the membranes does not depend on the copolymer concentration in the solution, the rejection factor increases from 72–75 to 82–85%. The maximum rejection factor is found for the membranes synthesized from 16% solutions of copolymers III and IV. It is evident from Fig. 2 that for copolymer IV, with an increase in the concentration from 15 to 16%, the water flux abruptly decreases (from 250 to 37 L/(m<sup>2</sup> h)); this decrease can be attributed to the formation of a denser selective layer, which contributes to an increase in the rejection factor for PVP K-30 from 72 to 85%.

It was found that the dependence of the transport properties of the membranes on the AN copolymer concentration in solution correlates with the results of the SEM studies of the membrane structure using the example of membranes based on copolymer III (Fig. 4). The micrographs of cleaved cross sections of mem-





**Fig. 4.** Scanning electron microscopy micrographs of the membranes synthesized from solutions of copolymer III in DMF. Solution concentration: (a) 12, (b) 13, (c) 14, and (d) 15%.



**Fig. 5.** Scanning electron microscopy micrographs of the cleaved cross section of the membranes synthesized from 16% solutions of copolymers (a) I, (b) II, (c) III, (d) IV, and (e) V in DMF.

branes synthesized from 12–15% solutions of copolymer III clearly show an asymmetric structure with a dense surface layer and a porous substructure, which is typical of immersion membranes. With an increase in the copolymer concentration in solution, the polymer framework becomes denser; that is, the number of elongated macrovoids decreases; at a copolymer III content of 15 wt %, a foam-like matrix comprising large individual voids is formed.

To compare the structure, SEM micrographs of flat membranes synthesized from 16% solutions of various AN copolymers in DMF are shown in Fig. 4. It is evident from the figure that the membranes synthesized from solutions of copolymers with a higher molecular mass (samples I and III) and, therefore, with a higher viscosity of the casting solution have a more pronounced spongy structure and a thicker dense selective layer. The membranes synthesized from solutions of copolymers with a lower molecular mass are characterized by a pronounced selective layer resting upon a large-pore substructure; the substructure comprises, in addition to finger-shaped vacuoles, large voids, which can adversely affect the mechanical properties of the films.

## CONCLUSIONS

Thus, even slight changes in the chemical composition and molecular mass of the membrane-forming copolymer can significantly change the structure and transport properties of the resulting membranes; the effect of the molecular mass of the membrane-forming copolymer is dominant.

The subsequent task is to synthesize composite membranes; therefore, an important aspect is an optimum ratio of transport and selective characteristics of the used membrane substrates synthesized from AN copolymers. To provide the formation of ultrafine selective layers on the surface, the membrane substrates should have the smallest pore size in order to prevent the penetration of the polymer solution deep into the pores, where it can block them. In this context, promising membranes are those that have the best selective properties, i.e., the highest rejection factor for PVP K-30. On the other hand, these membrane substrates should exhibit high transport properties to minimize the resistance to gas transport; that is, they should exhibit the highest possible water flux. Another important aspect is the mechanical strength and structure of the resulting hollow fiber membranes, which depends on the viscosity of the casting solution of the AN copolymer. With allowance for these aspects, a promising material for the formation of membrane substrates is a poly(acrylonitrile-*co*-itaconic acid) copolymer (99 : 1), i.e., sample III.

## ACKNOWLEDGMENTS

The authors thank D.S. Bakhtin for SEM studies of the membranes.

## FUNDING

The reported study was funded by RFBR according to the research project no. 18-58-00033 Bel\_a and BRFFR according to the research project no. X18P-083.

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*Translated by M. Timoshinina*