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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Shaping of the Structure of Vinylidene Fluoride–Tetrafluoroethylene Copolymer Membranes

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Abstract—A ^{19}F NMR study revealed differences in the interaction of hard (phosphoric acid) and soft (acetic acid) precipitants with vinylidene fluoride–tetrafluoroethylene copolymer in dimethylformamide. Phase separation in solutions with additions of mixtures of phosphoric and acetic acids was examined.

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Processing of ternary systems polymer–solvent–precipitant by the phase inversion method is one of the most widely used procedures for preparing ultra- and microfiltration membranes [1, 2]. Generally, the pore structure of membranes in precipitation of a polymeric compound occurs by the mechanism of liquid phase separation and/or crystallization [3, 4]. For readily crystallizing polymers at phase inversion, the liquid and crystalline phase separation processes compete. As a rule, the morphology of the membrane formed is determined by only one, predominant type of phase separation [3].

Problems of membrane preparation from fluorinated polymers are actively discussed in the literature owing to a set of valuable properties of these materials [3–7]. The effect of crystallization processes in preparation of polyvinylidene fluoride (PVDF) membranes from PVDF solutions in DMF, containing water or 1-octanol as precipitant, was considered [3, 4, 7]. Buonomenna et al. [5] examined how the forming solution composition, preforming time, and precipitation bath hardness affect the sequence of liquid and crystalline phase separation processes in PVDF solutions.

We have shown previously [8] that solutions of vinylidene fluoride–tetrafluoroethylene copolymer (fluoroplastic-42, F-42) in DMF are characterized by different types of phase separation depending on the nature of the precipitant added. Addition of hard precipitants such as water or mineral acids initiates the liquid phase separation and leads to the formation of relatively highly permeable porous films. Soft precipitants (ethanol, isopropanol) cause gelatinization of the solutions because of partial crystallization of the polymer, which leads to the formation of virtually nonporous films.

In this study we examined the properties of solutions of F-42 with additions of hard and soft precipitants and the structure and permeability of membranes prepared from this copolymer.

EXPERIMENTAL

We studied the properties of solutions and membranes prepared from random F-42 copolymer of grade V [GOST (State Standard) 25428–82, Kirovo-Chepetsk Chemical Combine]. The molecular weight of the polymer, determined viscometrically in acetone according to [9] and calculated by the equation $[\eta] = 6.1 \times 10^{-5} M^{0.81}$, was 2.47×10^5. We used pure grade DMF as solvent. The copolymer concentration in all the solutions was the same, 10 wt %. As precipitants we used 85% phosphoric acid, glacial acetic acid, and their mixtures.

To study interactions in F-42 solutions, we used ^{19}F NMR. DMF-d_7 was taken as solvent. As precipitants we used deuterated acetic (CD_3COOD) and phosphoric (D_3PO_4) acids. The NMR spectra were recorded on an AVANCE-500 spectrometer (Germany) with an operating frequency for ^{19}F of 471 MHz in standard 5-

ml ampules. The ^{19}F chemical shifts were determined relative to fluorochloromethane. The spectra were recorded taking into account the relaxation of the corresponding atoms.

The precipitation numbers (PNs) (g dl^{-1}) of mixed precipitants were determined by titration of 100 ml of a 1% solution of F-42 in DMF to visible turbidization of the solution.

Solutions of F-42 were prepared at 80°C with continuous stirring. The ready solution was allowed to stand for 24 h at room temperature for cooling and degassing. The solution viscosity was determined by the falling ball method with a VN-2 Höppler viscometer at 25°C.

The light transmission of the solutions was measured with an M-101 automatic flow turbidity meter. The cell arranged in the device was connected to a U-2 liquid thermostat. The degree of supersaturation of solutions with precipitant additions was evaluated by the relative light transmission T/T_0, where T is the light transmission of the ternary solution and T_0, that of the binary solution with the same polymer concentration (taken as 100%).

Copolymer films were prepared by wet forming. A polymer solution was applied onto a reinforcing support [thermally bound polyester fabric, TU (Technical Specification) 8397-047-05283280], Komiteks Joint-Stock Company, Syktyvkar], with the subsequent immersion in the precipitation bath (water, 10°C). After completion of the phase separation, the membrane was washed to remove residual solvent and dried.

The main characteristics of the membranes obtained (filtration throughput *Q*, bubble point *R*) were determined using isopropyl alcohol by standard procedures [10]. The phase state of jellies was evaluated by X-ray phase analysis. The diffraction patterns were obtained with a DRON-3/0 X-ray diffractometer using CuK_α radiation in the continuous scanning mode of the scintillation counter (1 deg min^{-1}).

We found that, in contrast to PVDF solutions in which the polymer undergoes crystallization [7], solutions of F-42 in DMF are stable and their properties remain unchanged in the course of prolonged (for more than a year) storage. As we showed in [8], the character of phase separation in ternary solutions F-42–DMF–precipitant depends on the kind of the precipitant. For example, addition to a 10% F-42 solution of phosphoric acid (hard precipitant) in an amount exceeding 6 wt % initiates liquid phase separation. However, owing to high viscosity the system can remain for a long time in the supersaturated (metastable) state even on adding excess amounts (up to 9 wt %) of phosphoric acid. The time for which such systems exist in the supersaturated state and the optical and viscosity properties of the phases formed depend on the degree of solution supersaturation, which can be characterized by the relative light transmission. The lower the quantity T/T_0, the higher the degree of supersaturation and the faster the equilibrium in the system is attained. The phase equilibrium is attained gradually with time. First, a thin transparent layer of a liquid, separated by a clear phase boundary, is formed on the solution surface. Then the thickness of the upper layer continuously increases, which is accompanied by an increase in the viscosity of the lower layer. Finally, the lower layer loses fluidity and in the course of prolonged storage transforms into a jelly.

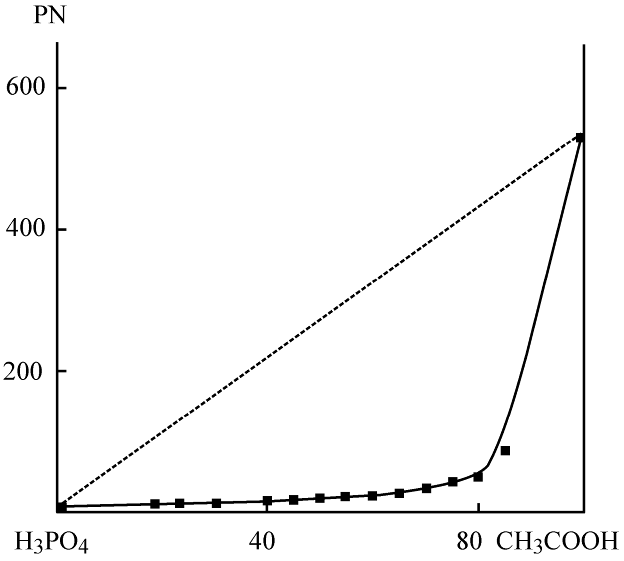

Fig. 1. Precipitation number PN as a function of the composition (%) of the mixed precipitant H_3PO_4–CH_3COOH.

With a soft precipitant (acetic acid), its concentration in a 10% solution of F-42 in DMF should be no less than 35 wt % to initiate the crystallization. Experimentally the crystallization is manifested as an increase in the viscosity of the visually transparent solutions with time, which is followed by their transition into a gelatinous state and full loss of the fluidity. In the course of storage of jellies, they undergo thickening and syneresis with the separation

Chemical shifts of CF_2 groups in the vinylidene fluoride–tetrafluoroethylene copolymer

Signal no.	Fragment	Chemical shift, ppm	Sequence
1	$\mathrm{CH_2{-}CF_2{-}CH_2{-}CF_2{-}CH_2{-}\mathbf{CF_2}{-}CH_2{-}CF_2{-}CH_2}$	–92.954	VV**V**VV
2	$\mathrm{CH_2{-}CF_2{-}CH_2{-}CF_2{-}CH_2{-}\mathbf{CF_2}{-}CH_2{-}CF_2{-}CF_2}$	–93.764	VV**V**VT
3	$\mathrm{CF_2{-}CF_2{-}CH_2{-}\mathbf{CF_2}{-}CH_2{-}CF_2{-}CF_2{-}CF_2}$	–95.861	T**V**VT
4	$\mathrm{CH_2{-}CF_2{-}CF_2{-}\mathbf{CF_2}{-}CH_2{-}CF_2{-}CH_2}$	–111.424	V**T**VV
5	$\mathrm{CH_2{-}CF_2{-}CF_2{-}\mathbf{CF_2}{-}CH_2{-}CF_2{-}CF_2}$	–112.377	V**T**VT
6	$\mathrm{CF_2{-}CH_2{-}CF_2{-}\mathbf{CF_2}{-}CH_2{-}CF_2{-}CH_2}$		V**T**VV[a]
7	$\mathrm{CF_2{-}CH_2{-}CF_2{-}\mathbf{CF_2}{-}CH_2{-}CF_2{-}CF_2}$		V**T**VT[a]
8	$\mathrm{CF_2{-}CH_2{-}CF_2{-}\mathbf{CF_2}{-}CH_2{-}CH_2{-}CF_2}$	–117.328	
9	$\mathrm{CF_2{-}CH_2{-}CF_2{-}CF_2{-}\mathbf{CF_2}{-}CF_2{-}CF_2{-}CH_2{-}CF_2}$	–122.043	VV**T**TV[a]
10	$\mathrm{CF_2{-}CF_2{-}CH_2{-}CF_2{-}\mathbf{CF_2}{-}CF_2{-}CF_2{-}CF_2{-}CH_2}$		TV**T**TV
11	$\mathrm{CH_2{-}CF_2{-}CH_2{-}CF_2{-}\mathbf{CF_2}{-}CF_2{-}CF_2{-}CF_2{-}CH_2}$	–124.384	VV**T**TV
12	$\mathrm{CF_2{-}CF_2{-}CH_2{-}CF_2{-}\mathbf{CF_2}{-}CF_2{-}CH_2{-}CF_2{-}CF_2}$	–125.611	TV**T**VT
13	$\mathrm{CF_2{-}CF_2{-}CH_2{-}CF_2{-}\mathbf{CF_2}{-}CF_2{-}CH_2{-}CF_2{-}CH_2}$	–126.370	TV**T**VV
14	$\mathrm{CH_2{-}CF_2{-}CH_2{-}CF_2{-}\mathbf{CF_2}{-}CF_2{-}CH_2{-}CF_2{-}CH_2}$	–127.101	VV**T**VV

[a] “Erroneous” linking.

of the low-molecular-weight phase. The optical density of solutions and jellies obtained on adding a soft precipitant indicates that the liquid phase separation does not occur. The limiting amount of acetic acid that can be introduced into a 10% solution of F-42 is 55–58 wt %.

Similar systems with gradual transition from amorphous to crystalline equilibrium were described in Papkov’s monograph [11], and their existence is due to different kinetics of the attainment of the amorphous and crystalline equilibria.

The probable cause of the occurrence of the phase separation by different mechanisms is different character of interactions of the precipitants with the polymer in the solution. To evaluate these interactions in the case of F-42 solutions, we used high-resolution ^{19}F NMR. The spectrum of a solution of F-42 in DMF is characterized by three intense groups of signals at 93–96, 109–112, and 125–127 ppm. All the signals in the spectrum belong to –CF_2– groups, because there are no other fluorine-containing groups in the copolymer. Hence, the observed set of signals can be attributed only to different environments of these groups. To elucidate the structure of F-42, we used an empirical additive scheme and the alternativeness principle [12].

The spectrum shows that the structure of the chain of this copolymer can be represented by a series of sequences consisting of tetrafluoroethylene (T) and vinylidene fluoride (V) units alternating in different orders. The assignment of signals to different fragments of the polymer chain is given in the table.

The ^{19}F NMR spectra of solutions with additions of hard and soft precipitants are similar to the spectrum of the solution containing no additives. Signals 3 and 9 are shifted on adding both kinds of precipitants. Signal 3 is shifted by 0.7 ppm on adding phosphoric acid and by 1.1 ppm on adding acetic acid, which is due to different nature of interaction of phosphoric and acetic acids with the copolymer in solution. The chemical shifts of the other signals remain essentially unchanged. These data suggest that both precipitants interact with the same fragments of the copolymer chain. These fragments are the sequences T**V**VT and VV**T**TV. Precipitant molecules interact with these fragments differently, which leads to changes in the conformation of polymer chains in solution and ultimately to different modes of phase separation.

Presumably, acetic acid is not a true precipitant (nonsolvent) for F-42 but rather acts as a diluent. In accordance with Mandelkern's rule [13] known in the practice of preparing crystallites from polymer solutions, the role of acetic acid consists in increasing the kinetic mobility of F-42 segments, which makes possible the occurrence of crystallization in media in which it was kinetically impossible. This is indicated by the following facts: (1) It is possible to introduce acetic acid into an F-42 solution in amounts exceeding 50 wt %; (2) Acetic acid, in contrast to phosphoric acid, wets the polymer; (3) The capability of the solution for gelatinization (polymer crystallization) depends both on the acetic acid concentration and on the polymer concentration in the solution. Thus, for the system under consideration, additions of soft precipitants apparently acts as diluent [13].

In the case of phosphoric acid, from the concentration dependences of the viscosity (an extremum in the excess viscosity isotherms) Fadeeva et al. [14] made a conclusion on formation of the compound $2H_3PO_4 \cdot DMF$. Apparently, formation of this compound drastically deteriorates the solvent quality for F-42 and causes a transition from bound coils to an aggregate of coils, with the subsequent amorphous phase separation [15].

To describe changes that occur in the system F-42–DMF–precipitant, it seemed appropriate to examine the joint effect of mixtures of hard and soft precipitants in various ratios on the phase equilibrium in solutions, and also the morphology and permeability of films obtained from these solutions.

The precipitation numbers of mixtures of acetic and phosphoric acids of various compositions with respect to 1% solution of F-42 in DMF depend on the component ratio in a nonadditive fashion (Fig. 1). Virtually in the entire range of compositions, the effect of the hard precipitant prevails over the effect of the soft precipitant, which is particularly clearly seen from insignificant increase in PN with an increase in the acetic acid content in the mixture to 40–50 wt %. Only at the acetic acid content exceeding 80 wt % the PN of the mixture starts to sharply increase.

It is known that the dependence of the hydraulic permeability of membranes on the precipitant content in the forming solution, as a rule, is jumpwise [16]. The same is true for the systems under consideration. Figure 2 shows as an example how the permeability to isopropanol and the bubble point of membranes

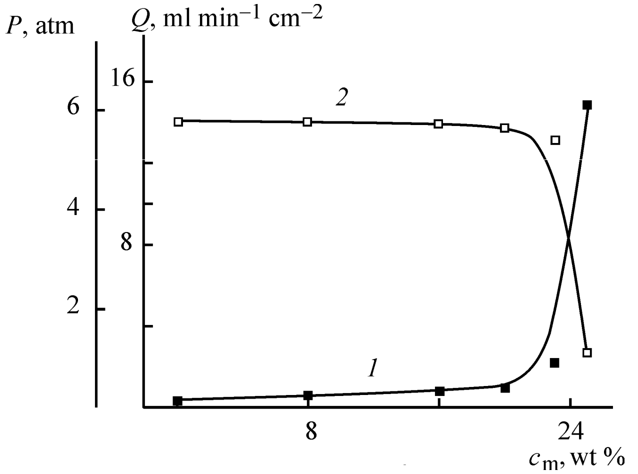

Fig. 2. (*1*) Throughput Q and (*2*) bubble point P of the membrane as a function of the content c_m of the mixed precipitant in the forming solution.

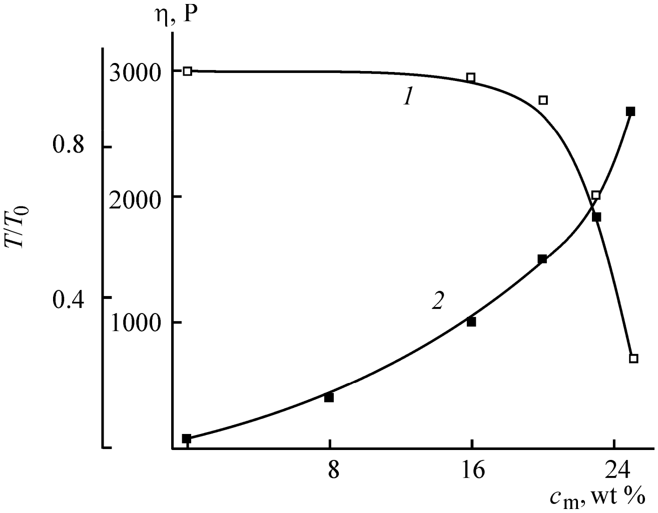

Fig. 3. (*1*) Light transmission T/T_0 and (*2*) relative viscosity η of forming solutions as functions of the content c_m of the mixed precipitant in the forming solution.

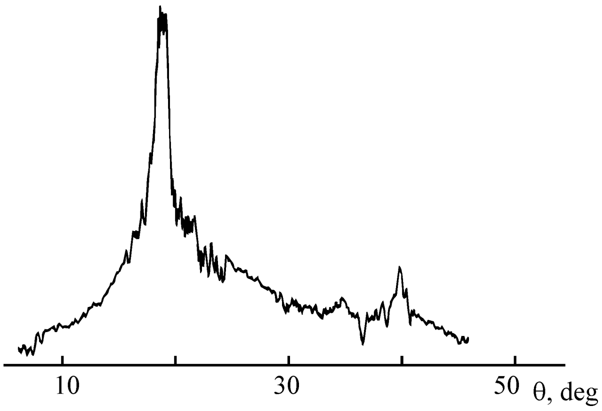

Fig. 4. Diffraction pattern of a jelly obtained upon storage of a solution containing 25% mixed precipitant with PN 32 g dl^{-1}. (2θ) Bragg angle.

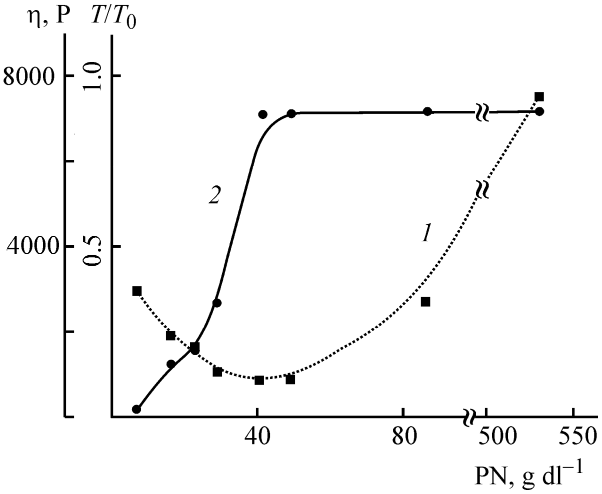

Fig. 5. (*1*) Light transmission T/T_0 and (*2*) viscosity η as functions of the PN of the mixed precipitant.

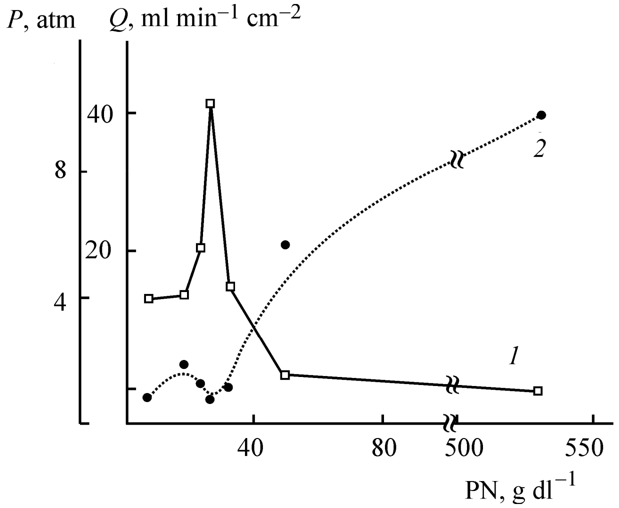

Fig. 6. (*1*) Throughput *Q* and (*2*) bubble point *P* of membranes as functions of PN of the mixed precipitant.

depend on the concentration of the precipitating mixture with PN 32 g dl^{-1}. As can be seen, in a fairly wide interval the membrane characteristics depend on the precipitant concentration insignificantly, and after reaching a certain critical concentration of the precipitant the membrane throughput sharply increases, which is accompanied by a decrease in the bubble point.

Figure 3 shows that, with an increase in the precipitant concentration, the solution viscosity monotonically increases. A bend in the dependence of

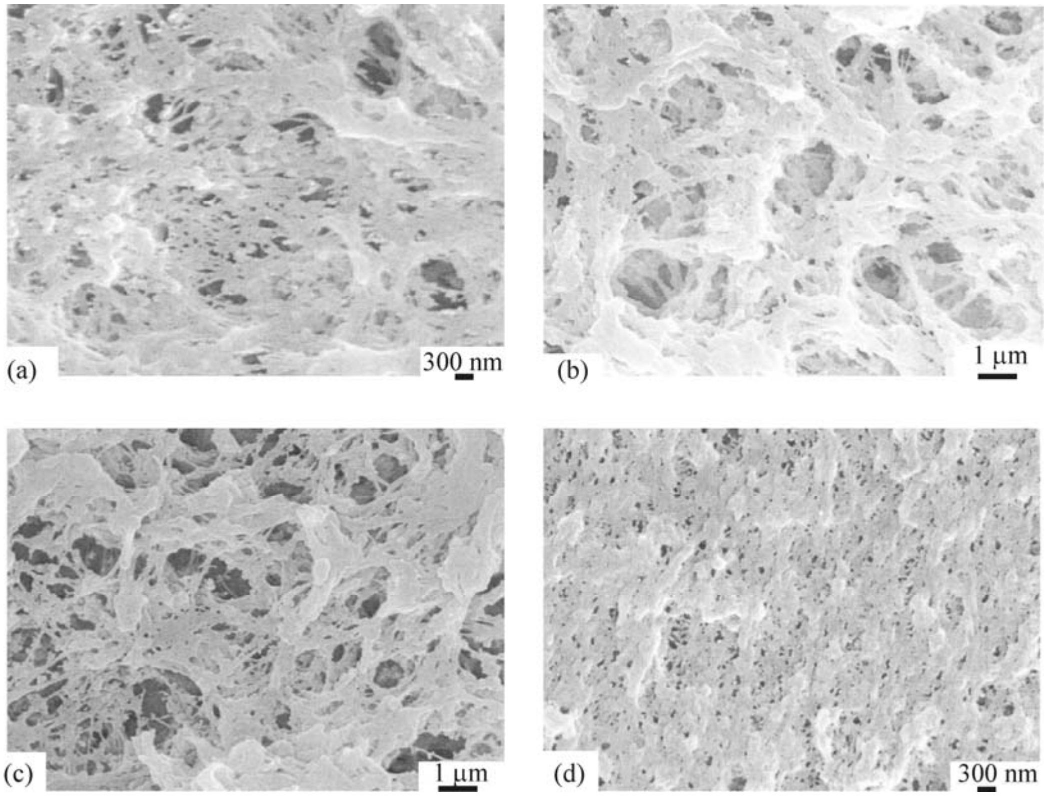

Fig. 7. Electron micrographs of the surfaces of the membranes prepared using mixed precipitants with different PNs. PN, g dl^{-1}: (a) 18, (b) 26, (c) 32, and (d) 49. Magnification: (a, d) 30000 and (b, c) 20000

the relative light transmission on the precipitant concentration suggests the occurrence of amorphous phase separation in the system at a mixed precipitant concentration of 23 wt %. Specifically the occurrence of the amorphous phase separation in the forming solution is responsible for a sharp increase in the pore size and in the hydraulic permeability of the films. When the precipitant concentration is increased to 25%, the solution undergoes gelatinization on the fourth day. Gelatinization is due to crystallization of the polymer, which is confirmed by the diffraction pattern of the jelly (Fig. 4). On adding the mixed precipitant in an amount of 26 wt %, the system becomes unstable and undergoes separation into two liquid phases on the next day.

The revealed relationships suggest that the crystalline and amorphous phase separation processes occur simultaneously, with the liquid phase separation being more pronounced for the mixed precipitant with PN 32 g dl^{-1}. With an increase in the PN of the mixed precipitant to 41 g dl^{-1}, the properties of the solutions remain largely similar. However, whereas with an increase in the mixed precipitant concentration in the solution to 25 wt % the light transmission decreases gradually, on adding more than 27 wt % mixed precipitant the solution undergoes gelatinization on the next day. For this mixed precipitant, the effect of the soft precipitant is more pronounced, despite the fact that the solutions obtained are characterized by low T/T_0 ratios suggesting the liquid phase separation.

Taking into account the jumpwise dependence of the film permeability on the mixed precipitant concentration, we examined the solution properties in the entire range of PNs for the compositions that occurred in the metastable state but, despite phase separation, exhibited certain kinetic stability sufficient for their processing into film materials. The content of the mixed precipitant in these formulations is, as a rule, 80–90 wt % of the maximum possible value.

We found that the PNs of mixed precipitants significantly affect the properties of solutions and membranes prepared from them. Figure 5 shows that, with an increase in PN from 6.8 to 30 g dl^{-1}, the solution viscosity increases and then flattens out. An increase in the viscosity still more complicates attainment of the hydrostatic equilibrium in the system. As a result, solutions with lower relative light transmission become kinetically stable. Introduction into the forming solution of mixed precipitants with PN in the range 6.8–32 g dl^{-1} in the critical concentration leads to its liquid phase separation. The dependence of the permeability of the films obtained on PN of mixed precipitants in this interval passes through a maximum (Fig. 6): The specific throughput of the films increases by a factor of 3, with a decrease in the bubble point. With a further increase in the weak precipitant content in the mixture ($PN \geq 40$), the quantity T/T_0 of the solutions increases, whereas the viscosity does not change noticeably. The throughput of films prepared from such solutions decreases, which is accompanied by an increase in the bubble point.

Comparative analysis of the surface morphology of films prepared using mixed precipitants with PN in the range 18–49 g dl^{-1} (range of sharp increase in the hydraulic permeability of films) shows (Fig. 7) that variation of the PN of the mixed precipitant leads to significant changes in the film structure. As compared to the sample shown in Fig. 7a, the surfaces of the films shown in Figs. 7b and 7c have a more developed and coarsely porous spongy structure, with a relatively broad pore-size distribution. Fine globular formations characteristic of the sample shown in Fig. 7a are absent. Further increase in the PN of the mixed precipitant to 49 leads to the formation of a different type of the structure. This is a relatively dense polymeric matrix with considerably finer pores and narrow pore-size distribution. Such changes in the surface structure of films with increasing PN of the mixed precipitant are associated with differences in the phase separation mode of the solutions: Amorphous phase separation is more pronounced in the range 18–32 g dl^{-1}, and crystalline phase separation, at higher PNs.

CONCLUSIONS

(1) Solutions of vinylidene difluoride–tetrafluoroethylene copolymer in dimethylformamide, containing a mixture of phosphoric and acetic acid, are a system with overlapping regions of liquid–liquid and liquid–crystal phase separation.

(2) By varying the ratio of the hard and soft precipitants, it is possible to vary the mode of the phase separation of the copolymer solutions and thus to control the structure and properties of the porous materials obtained.

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