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A Study of Cryostructuring of Polymer Systems. 46. Physicochemical Properties and Microstructure of Poly(vinyl alcohol) Cryogels Formed from Polymer Solutions in Mixtures of Dimethyl Sulfoxide with Low-Molecular-Mass Alcohols

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Abstract—Poly(vinyl alcohol) (PVA) cryogels (PVACGs) are obtained and studied. The PVACGs are formed by freezing–defrosting of polymer solutions in dimethyl sulfoxide (DMSO) or its mixtures with one of the first members of the series low-molecular-mass aliphatic alcohols (methanol, ethanol, *n*-propanol, and *n*-butanol). PVA content in these solutions is 100 g/L, while the concentration of an aliphatic alcohol is varied in a range of 0.44–2.55 mol/L depending on its nature. The polymer solutions are subjected to the cryogenic treatment at temperatures 30, 40, or 50°C lower than the crystallization temperature of DMSO (+18.4°C). The frozen samples are defrosted at a heating rate of 0.03°C/min. It is shown that, in a certain range of low-molecular-mass alcohol content in an initial system, its cryogenic treatment yields coarse-pored heterophase cryogels that have higher rigidity and heat endurance than those of DMSO–PVA cryogels. It has been shown that polymer cryoconcentration and phase separation play important roles in the formation of a cellular microstructure and an increase in the rigidity and heat endurance of PVACGs obtained in the presence of low-molecular-mass alcohols.

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INTRODUCTION

Macroporous noncovalent poly(vinyl alcohol) (PVA) cryogels (PVACGs), which result from cryogenic treatment (freezing–defrosting) of PVA solutions, are crystallization-type gel systems [1–3]. The physicochemical properties and porous structure of PVACGs depend on many factors. These are, primarily, the characteristics (molecular mass, content of unsaponified O-acyl groups and tacticity of polymer chains, etc.) of the gel-forming polymer (PVA), as well as its concentration in an initial solution and the regimes of the cryogenic treatment (freezing, incubation in frozen state, defrosting, and number of the treatment cycles) of the system [1–8]. Aqueous dispersion media are, most often, used for the preparation of initial PVA solutions, which are, subsequently, subjected to cryostructuring [1–3, 9–11]; however, PVACGs formed in organic media, in particular, dimethyl sulfoxide (DMSO) are also known [12–18]. The freezing temperature of DMSO is $T_0 \approx +18.4$°C [19]; therefore, when describing cryogenic-treatment regimes of such systems, it is convenient to use differential temperature $\Delta T = T_i - T_0$, where T_0 and T_i are the crystallization temperature of the pure solvent and the specific experimental temperature (expressed in Celsius degrees), respectively, rather than the absolute value of the temperature [20]. The possibility for the preparation of such cryogels was first revealed more than 30 years ago in work [12], in which it has been shown that 10–16% PVA solutions in DMSO undergo the sol–gel transition upon freezing at −20°C (38.4°C lower than the DMSO crystallization temperature, i.e., at $\Delta T = -38.4$°) followed by defrosting. At the same time, the physicochemical properties and microstructure of PVACGs formed from PVA solutions in DMSO are essentially different from those of cryogels obtained under analogous cryogenic treatment conditions from aqueous solutions with the same polymer concentrations [13–17]. In particular, the former PVACGs appear to have lower rigidity and heat endurance than the latter have [13, 15]. Since DMSO is a thermodynamically better solvent for highly deacetylated PVA than water is (the polymer has a higher affinity for DMSO) [21–23], the gelation efficiency is lower because of the competition between the polymer–solvent and polymer–polymer interactions. During the cryostructuring of PVA solutions, the latter interactions induce (due to hydrogen bonding between

hydroxyl groups of neighboring chains) the formation of microcrystallinity zones which play the role of physical sites of a supramolecular network in a PVACG [1, 2, 7, 8, 24]. Thus, variations in dispersion-medium affinity for the polymer make it possible to vary, to some extent, the properties of the resulting cryogels.

For example, it has been shown that the addition of any of the first four aliphatic alcohols in amounts smaller than those necessary for polymer coagulation to an aqueous PVA solution followed by the cryogenic treatment of a mixed solution resulted in the formation of PVACGs with the rigidity and heat endurance lower than those of PVACGs obtained in the absence of alcohols [25]. Therewith, the microstructure of the cryogels also greatly changed, with thin PVA fibers being formed in their bulk due to the dehydrating action of low-molecular-mass alcohols. Additives of polyhydric alcohols, such as ethylene glycol, diethylene glycol, and glycerol, had similar effects on the physicochemical properties and fusion temperature of PVACGs [26]. Hence, it could be expected that similar (at least, qualitatively) effects would take place upon the cryotropic gelation of PVA, when low-molecular-mass alcohols are incorporated into solutions of this polymer in DMSO. However, preliminary experiments have shown another character of the action of these alcohols on the properties of PVACGs resulting from the freezing of corresponding mixed solutions followed by their incubation in the frozen state and subsequent defrosting. Therefore, the goal of this work was to systematically study the effect of the composition of an initial organic solvent on the physicochemical characteristics and microstructure of PVACGs formed from polymer solutions in binary mixtures of DMSO and low-molecular-mass aliphatic alcohols.

EXPERIMENTAL

A preparation of PVA with a weight-average molecular mass of 86 kDa and 100% degree of deacylation (Acros Organics, United States) was used in the work as received.

Dimethyl sulfoxide (reagent grade) was purified by freezing two times. Aliphatic alcohols, methanol (MeOH), ethanol (EtOH), *n*-propanol (PrOH), and *n*-butanol (BuOH) (all produced by Khimmed, Russia) were purified by distillation. Mixed solvents were prepared using fractions of the alcohols with the following boiling temperatures: MeOH, 65.5°C; EtOH, 78.2°C; PrOH, 97.5°C; and BuOH, 117°C.

A PVA solution was prepared via the dispersion of dry polymer in a calculated volume of DMSO followed by swelling at room temperature for 15 h. Then, the swollen preparation was heated under continuous stirring in a water bath for 1 h until a homogeneous solution was obtained.

When preparing PVACGs in mixed organic solvents, the initial polymer solution in DMSO was thermostated at 20°C for 30 min; then, a calculated volume of an alcohol was added, with the mixture being intensely stirred, incubated for 20 min in an UNITRA ultrasonic bath (Unitra, Poland) to remove air bubbles, and dosed into molds for freezing. PVA concentration in these solutions was 100 g/L.

To measure the physicochemical characteristics, cryogel samples were prepared in dismountable duralumin containers with internal diameter and height of 15 and 10 mm, respectively. For determining the fusion temperatures of the cryogels, the samples were prepared in polyethylene test tubes (an internal diameter of 10 mm), with a metal ball with diameter and weight of 3.5 mm and 0.275 ± 0.050 g, respectively, being placed onto the bottom of the test tube. These procedures have been described in detail elsewhere [10, 11]. The test tubes and/or containers were placed into the chamber of a Julabo FP 45 HP precision programmed cryostat (Germany), where corresponding PVA solutions were subjected to cryogenic treatment. The samples were frozen at a ΔT value preset in a range from −30 to −50°C for 12 h and, then, defrosted at a heating rate of 0.03°C/min, which was controlled with the cryostat microprocessor.

Compression Young's moduli E of the PVACG samples were measured with a TA-Plus texture analyzer (Lloyd Instruments LTD., United Kingdom). The elasticity moduli were determined automatically using the software of the instrument from the linear regions of the stress–strain dependences at a uniaxial loading rate of 0.3 mm/min. The measurements were performed until 30% strain of a sample was reached.

PVACG fusion temperatures T_f were determined via a known procedure [10, 11] by placing a test tube with a cryogel, the lower part of which contained a metal ball, upside-down into a water bath equipped with a stirrer. The temperature was elevated at a rate of 0.4 ± 0.1°C/min. The temperature at which the ball passed through the layer of the fusing gel and fell onto the tube stopper was taken to be the sample's T_f.

The elasticity moduli and fusion temperatures of the cryogels were measured for three parallel samples, while the samples were prepared in at least three independent experiments. The data obtained were averaged.

The morphology of thin sections of the cryogels was studied using an Eclipse 55i optical microscope (Nikon, Japan) equipped with a digital system for image registration. PVACG samples formed from polymer solutions in DMSO or its mixtures with low-molecular-mass alcohols were, preliminarily, washed from organic solvents by exposing the cryogels for 2 weeks in excess distilled water, which was renewed every day. Then, thin sections (~10 μm) were cut perpendicularly to the cylindrical sample axis with an SM-1900 cryomicrotome (Leica, Germany). The sec-

tions were stained in an aqueous 1% Congo red solution and placed into a "pouring" medium according to [10, 11].

RESULTS AND DISCUSSION

The Influence of Low-Molecular-Mass Monohydric Alcohols Added into PVA Solutions in DMSO on the Physicochemical Properties of PVACGs

Since preparations of highly deacetylated PVA are insoluble in low-molecular-mass monohydric aliphatic alcohols, the incorporation of some amounts of these alcohols into a solution of the polymer in DMSO may induce various effects, such as gelation, coagulation, and precipitation of PVA. For example, additives of methanol, ethanol, or *n*-propanol in concentrations of ≥3.4 moles per liter of a mixed solvent induced fast gelation throughout the sample volume. Under the same experimental conditions, the limiting concentration of *n*-butanol was equal to nearly 2.55 mol/L. Therefore, in the subsequent experiments, the working concentrations of MeOH, EtOH, and PrOH were confined to 2.55 mol/L, while the highest concentration of BuOH was 1.70 mol/L, when no phase transformations were observed in a polymer solution at room temperature and, at least, until the onset of its freezing.

The diagrams presented in Fig. 1 show the dependences of (a) rigidity and (b) heat endurance of PVACG samples formed at $\Delta T = -30$°C from 100 g/L PVA solutions in DMSO in the absence and presence of the four low-molecular-mass aliphatic alcohols. Since, for the samples containing *n*-butanol, its limiting concentration (1.70 mol/L) was lower than that for samples containing methanol, ethanol, and *n*-propanol (2.55 mol/L), cryogels were additionally obtained on the basis of DMSO–BuOH–PVA solutions with "intermediate" alcohol contents of 0.44 and 1.31 mol/L (Fig. 1, *5*).

The data presented in Fig. 1 clearly show the influence (see the Introduction) of the type and amount of an added alcohol on the physicochemical parameters of PVA cryogels. For example, as has been previously shown, the values of the elasticity modulus and fusion temperature of a PVACG formed by freezing an aqueous solution with the same PVA concentration at a temperature 30°C lower than the solvent crystallization point are 8.27 ± 0.19 kPa and 73.7 ± 0.5°C, respectively [25]. At the same time, for the PVACG sample obtained in this work from a polymer solution in pure DMSO, the E and T_f values are equal to 7.57 ± 0.79 kPa and 44.8 ± 0.4°C, respectively, thereby being lower (in particular, T_f) than the parameters of the "aqueous" PVACG. The fusion temperature of noncovalent (physical) gels formed due to intermolecular hydrogen bonds is a function of their specific (calculated for unit volume) number [27]. Therefore, the comparison between the aforementioned values of T_f (the difference is nearly 29°C) shows a noticeably smaller number of hydrogen bonds in the structure of the PVACG formed in the medium of frozen DMSO. On the other hand, while an increase in the content of an added alcohol in an initial polymer solution led to a monotonic reduction in both the rigidity and heat endurance of the water–alcohol–PVA cryogels [25], the same characteristics of the DMSO–alcohol–PVA gels substantially increased (Fig. 1). This effect was most pronounced for the DMSO–BuOH–PVA systems (Fig. 1, *5*), and, at [BuOH] = 1.70 mol/L, the elasticity modulus increased by 15.5 times (from 7.6 to 117 kPa) (Fig. 1a) and the gel fusion temperature grew by 20.2°C (from 44.8 to 65°C) (Fig. 1b). The effects caused by the addition of methanol and ethanol (Fig. 1, *2*, *3*) to the initial polymer solution in DMSO were close to each other and markedly weaker than those in the cases of *n*-propanol (Fig. 1, *4*) and *n*-butanol (Fig. 1, *5*). The desolvating action of these alcohols on PVA increases upon the passage from BuOH to MeOH. Therefore, the data presented in Fig. 1 indicate that a rise in the efficiency of hydrogen bonding between the chains of PVA upon its cryotropic gelation in frozen DMSO–alcohol mixtures is facilitated by two factors. The first factor is a rise in the hydrophobicity of the medium due to an increase in the length of an alkyl substituent (R in Fig. 1) in a molecule of a low-molecular-mass alcohol (R–OH), and the second one is the desolvation of PVA chains due to a deterioration of the thermodynamic quality of a solvent with an increase in the fraction of an alcohol in the system.

The low-molecular-mass alcohols themselves have very low crystallization temperatures equal to −97.5°C (MeOH), −114.5°C (EtOH), −127.0°C (PrOH), and −90.0°C (BuOH) [19]. Therefore, when DMSO–alcohol–PVA solutions are frozen at $\Delta T = -30$°C (i.e., at −11.6°C) during the formation of PVACGs, the parameters of which are presented in Fig. 1, DMSO alone is crystallized. This causes a drastic increase in the concentrations of both PVA and an alcohol in the so-called "unfrozen liquid microphase" (ULMP) [1, 3, 7, 28], i.e., the regions that remain uncrystallized under these temperature conditions. Therefore, the content of a low-molecular-mass alcohol increases together with the content of the polymer in these regions. In this case, its fraction exceeds the critical concentration that causes the sol–gel transition already at a positive temperature. In our opinion, this must substantially intensify the gelation in the bulk of ULMP.

To confirm the general character of this mechanism for other regimes of the cryotropic gelation, we used the DMSO–MeOH–PVA systems with different contents of the low-molecular-mass alcohol as examples to study the effect of temperature on this process. The results obtained are presented in Fig. 2 as dependences of (a) E and (b) T_f on the temperature of freezing initial PVA solutions in DMSO in the absence

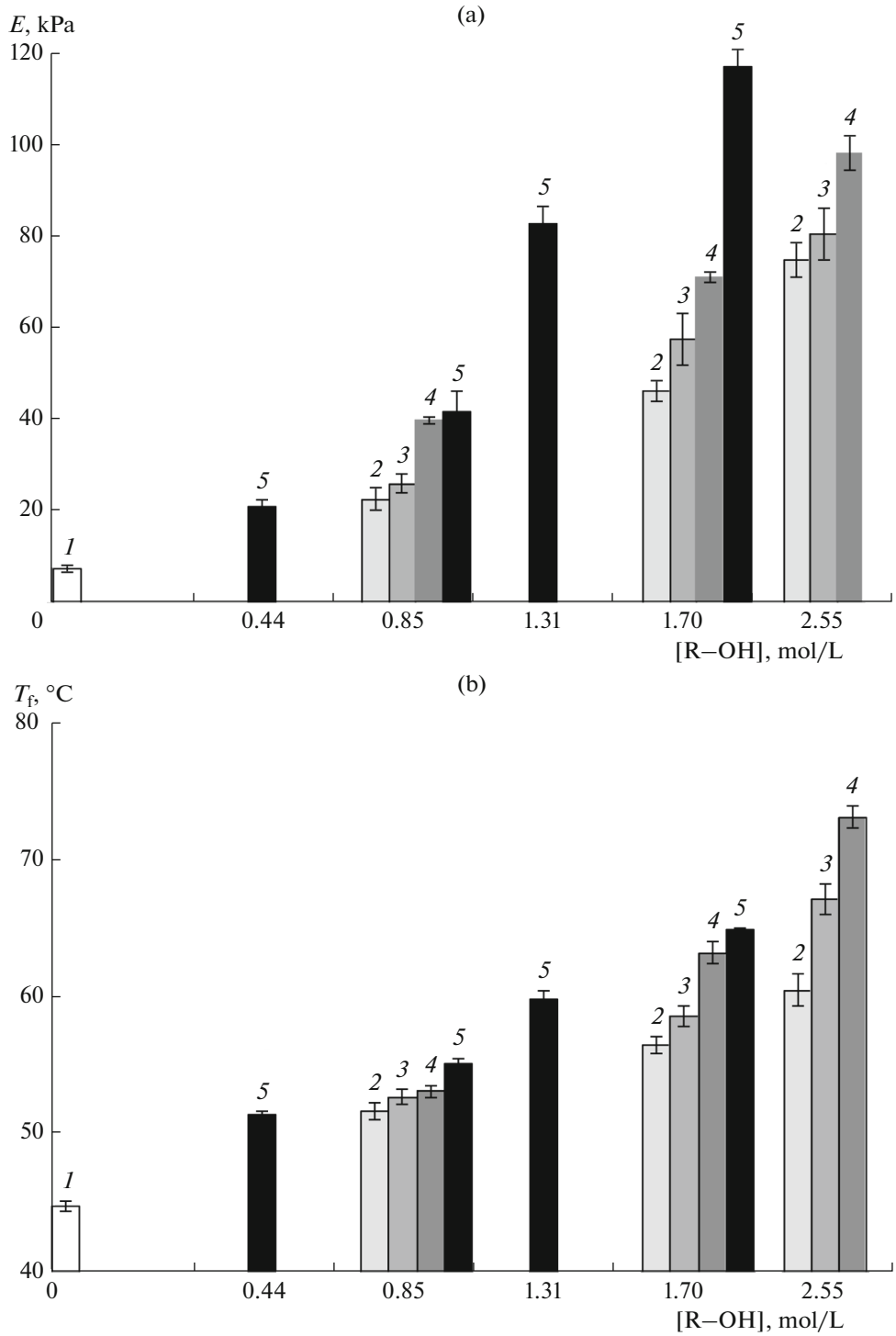

Fig. 1. Dependences of (a) elasticity modulus and (b) fusion temperature of PVACG samples on the concentration of an aliphatic alcohol in an initial polymer solution in DMSO: (*1*) no R–OH, (*2*) MeOH, (*3*) EtOH, (*4*) PrOH, and (*5*) BuOH; cryostructuring temperature is $\Delta T = -30$°C.

(Fig. 2, *1*) and presence of methanol in concentrations of (*2*) 0.85, (*3*) 1.70, and (*4*) 2.55 mol/L.

The comparison between the absolute values of the elasticity moduli of cryogels with equal MeOH concentrations formed by freezing of the initial solution at different temperatures within the aforementioned range shows (Fig. 2a) that PVACG samples obtained via cryogenic treatment at $\Delta T = -30$°C have somewhat lower rigidity. The difference between the samples frozen at temperatures 40 or 50°C lower than the

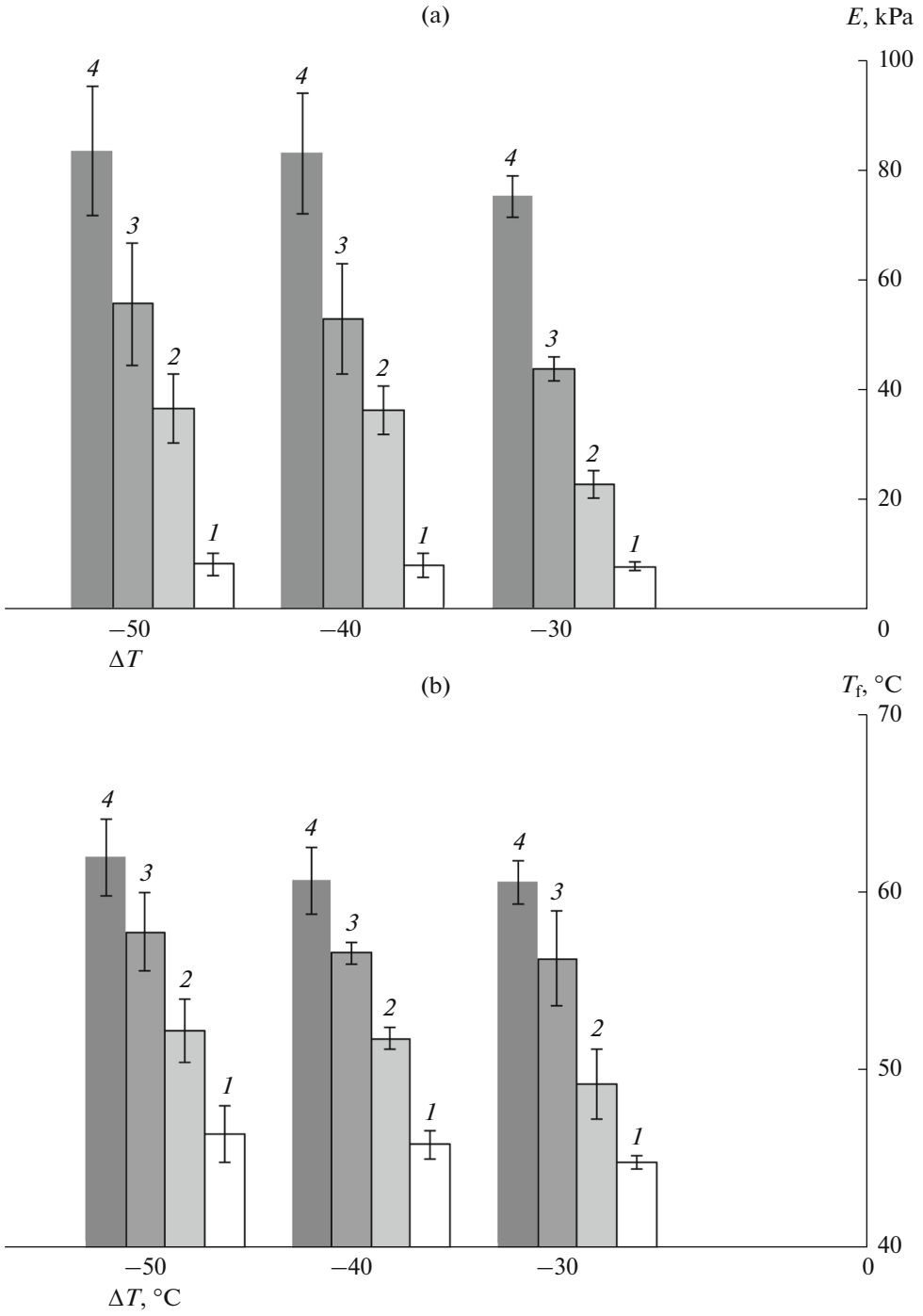

Fig. 2. Dependences of (a) elasticity modulus and (b) fusion temperature of PVACG samples on freezing temperature of initial DMSO–MeOH–PVA solutions at [MeOH] = (*1*) 0, (*2*) 0.85, (*3*) 1.70, and (*4*) 2.55 mol/L.

point of DMSO crystallization is insubstantial. At the same time, the general tendency in the effect of alcohol concentration on the physicochemical properties of these cryogels is the same for all the temperatures used of the cryogenic treatment; i.e., the rigidity of the resulting PVACGs substantially increases with the concentration of a low-molecular-mass alcohol in an initial PVA solution in DMSO. A similar conclusion may be made concerning the heat endurance of the cryogels (Fig. 2b); i.e., their fusion temperatures increase with the concentration of an added alcohol, while the magnitude of the effect for samples formed at $\Delta T = -30$, -40, or -50°C, weakly depends on the cryostructuring temperature. Hence, T_f, which is a

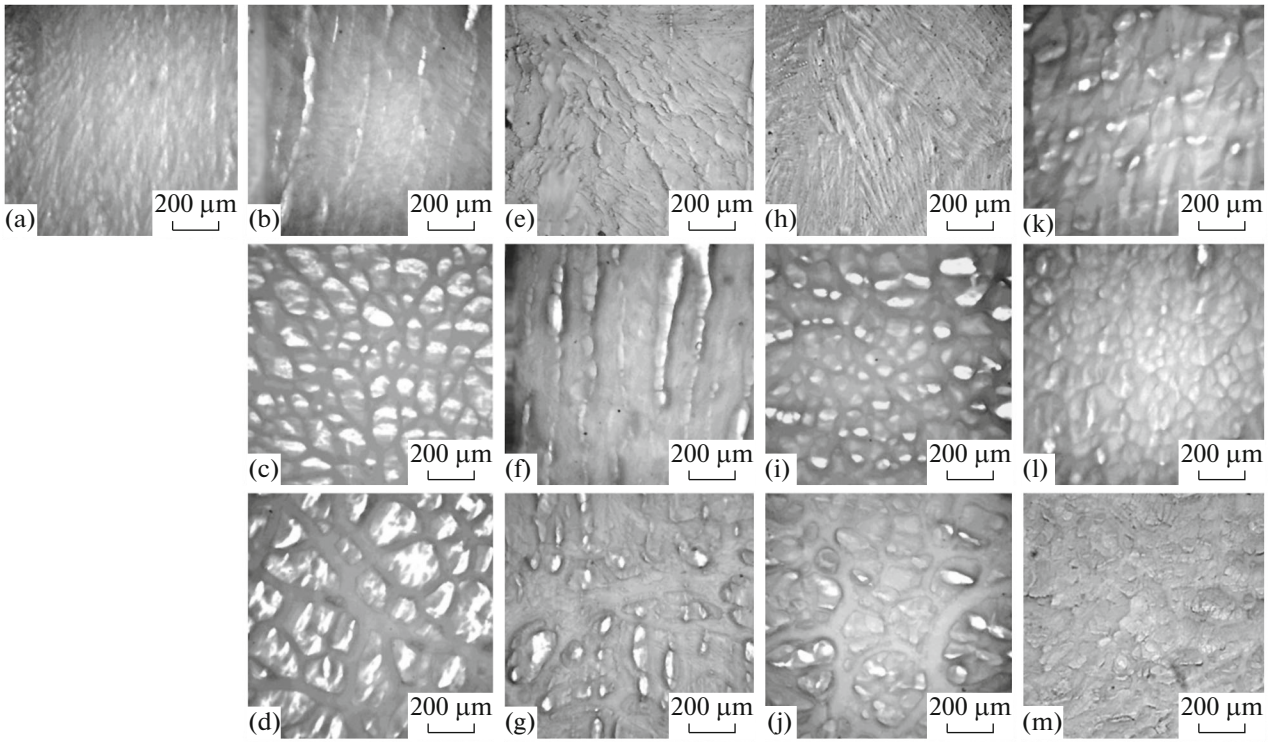

Fig. 3. Micrographs of thin sections of PVACG samples formed by freezing at $\Delta T = -30$°C of polymer solutions in DMSO (100 g/L) (a) without and with additives of low-molecular-mass alcohols: MeOH: (b) 0.85, (c) 1.70, and (d) 2.55 mol/L; EtOH: (e) 0.85, (f) 1.70, and (g) 2.55 mol/L; PrOH: (h) 0.85, (i) 1.70, and (j) 2.55 mol/L; and BuOH: (k) 0.44, (l) 0.85, and (m) 1.70 mol/L.

criterion of the amount of thermolabile intermolecular hydrogen bonds in the nodes of the three-dimensional networks of PVACGs formed in the media of frozen mixtures of DMSO and low-molecular-mass alcohols, is mainly determined by the concentration of an alcohol, which causes the gelation of such polymer systems. In turn, the integral mechanical properties (in our case, modulus E) of heterophase PVACGs depend on not only the rigidity of the gel phase (macropore walls), but also on the texture of the macroporous cryogels, because large pores are structural defects of the samples as a whole [1, 7, 10, 11, 14, 15]. Therefore, data on the porous morphology of such gel objects are commonly necessary in addition to information on their physicochemical properties.

The Microstructure of PVACGs Formed from Polymer Solutions in DMSO in the Presence of Low-Molecular-Mass Alcohols

The microstructure of PVA cryogels was studied by optical microscopy simlarly to in previous investigations of different PVACGs formed in aqueous media [10, 11, 25]. However, in the case of cryogels obtained in the medium of DMSO, the procedure of sample preparation had to be somewhat modified. The matter is that, first, in contrast to "aqueous" PVACGs, the studied cryogels are almost transparent because of the small difference between the refractive indices of DMSO-swollen macropore walls and the liquid contained in the micropores (therefore, they are indistinguishable in the microscope field of vision) and, second, the contrasting dye, Congo red, is very poorly sorbed by the polymer from DMSO; i.e., the macropore walls remain almost unstained in a thin section of a preparation. Therefore, PVACG samples formed from PVA solutions in DMSO in the absence and presence of low-molecular-mass alcohols were initially washed with water from the organic solvents (see Experimental) and, then, prepared by the common procedure of obtaining and contrasting thin sections. Their structure is shown in the micrographs presented in Fig. 3.

In the case of PVACGs obtained by freezing at $\Delta T = -30°$ of MeOH-, EtOH- and PrOH-containing solutions of PVA in DMSO, the samples contained R–OH in concentrations of 0.85 (Figs. 3b, 3e, 3h), 1.70 (Figs. 3c, 3f, 3i), and 2.55 mol/L (Figs. 3d, 3g, 3j), while, in the case of BuOH-containing PVACGs, alcohol concentrations in the samples were 0.44 (Fig. 3k), 0.85 (Fig. 3l), and 1.70 mol/L (Fig. 3m). In the latter case, initial solutions with higher butanol concentrations underwent gelation (see above) already at positive temperatures. Therefore, cryogels with

[BuOH] = 2.55 mol/L were not prepared. On the other hand, this alcohol began to affect the physicochemical characteristics of the cryogels at lower concentrations than the first three members of the series of aliphatic alcohols did (Fig. 1); therefore, Fig. 3k additionally shows the micrograph of a PVACG sample formed at [BuOH] = 0.44 mol/L.

The black-and-white image of the microstructure of the cryogel obtained from a PVA solution in DMSO (Fig. 3a) is characterized by heterogeneity and the alternation of intersecting "lamellar" dark (Congo-red-stained gel phase) and light (DMSO-filled macropores) regions. The cross-sectional sizes of the macropores lie in a range from ≈5 to ≈20 μm, thereby being several times larger than this parameter (1–2 μm) for water–PVA cryogels formed at the same polymer concentration and –30°C [10]. Our experience shows that DMSO crystals are, as a rule, larger than ice crystals formed at the same temperature related to the crystallization temperature of a pure solvent. Since, during the formation of cryogels, such as PVACGs, polycrystals of a frozen solvent play the role of a pore-forming agent [1, 6, 7, 10, 14, 15, 29], the aforementioned differences between the sizes of macropores in DMSO–PVA and water–PVA cryogels are quite evident.

The incorporation of any of the four used low-molecular-mass alcohols into the initial PVA solution in DMSO in a concentration of 0.85 mol/L (MeOH, EtOH, and PrOH) or, even, 0.44 mol/L (BuOH) caused noticeable changes in the cryogel microstructure (Figs. 3b, 3e, 3h, 3k, respectively). As compared with PVACGs of DMSO-PVA composition (i.e., those free of the alcohols), the general texture of the samples changed, and some amount of larger pores arose with cross-sectional sizes of up to 20 (Fig. 3b) or nearly 50 μm (Fig. 3k). A further increase in the concentration of an aliphatic alcohol led to still greater transformations of the microstructure of the corresponding cryogels.

Therewith, some common tendencies and differences in the action of low-molecular-mass alcohols should be noted. For example, as the content of any of the alcohols grows, increasing amounts of large oval pores are observed in the cryogels (Figs. 3c, 3f, 3i, 3l). At [R–OH] = 2.55 mol/L, their diameter is as large as 200 (Fig. 3d) and even 350–400 μm (Figs. 3g, 3j), thereby indicating a phase separation yielding a gel phase with a high concentration of the polymer (macropore walls stained with Congo red) and a bulky liquid phase enriched with an unfrozen low-molecular-mass alcohol. At the qualitative level, this process may be considered to be a "forced" syneresis caused by the effects of cryoconcentration. In addition, micrographs in Figs. 3b, 3e, 3h, and 3f show that the transition from the anisodiametric shape of macropores formed by DMSO polycrystals in an additive-free cryogel to the roundish shape of large pores resulting from the forced syneresis proceeds through some intermediate elongated pores with a cross-sectional sizes larger than that seen in Fig. 3a. In the case of PVACG obtained in the presence of ethanol (1.70 mol/L), some of these elongated pores have the shape of a necklace, because of ellipsoidal elements present in them (Fig. 3f). The type of an added aliphatic low-molecular-mass alcohol, i.e., alkyl radical length, which determines its relative hydrophobicity, also has an effect on the porous morphology of a PVACG obtained in an organic solvent. Seemingly, the higher the hydrophobicity of an alcohol the lower its content in a system at which the critical concentration of the phase separation in a corresponding polymer solution being frozen is reached. For cryogels formed in the presence of BuOH, this effect has already been mentioned above when discussing their physicochemical properties. At the same time, the comparison of the microstructure of PVACGs containing the least hydrophobic aliphatic alcohol, MeOH, with the cryogels containing EtOH, PrOH, or BuOH indicates the desolvating effect of methanol, because the gel phase of the macropore walls in samples formed in the presence of MeOH (Figs. 3c, 3d) is markedly denser. Hence, it may be supposed that there is a competitive influence of the desolvating (for PVA) effect of an aliphatic alcohol and its hydrophobicity on the morphology of pores in DMSO–ROH–PVA cryogels.

The analysis of the total array of the data obtained on the mechanical and structural characteristics of PVACGs formed from polymer solutions in DMSO with additives of low-molecular-mass aliphatic alcohols leads to the following question. Why, in spite of the fact that an increase in the concentration of any of these alcohols leads to a substantial enlargement of pores in the cryogels (Fig. 3), i.e., to the enhancement of the imperfectness of the materials as a whole, does their rigidity regularly increase (Figs. 1a, 2a)? We suggest that this, at first sight, apparent contradiction may be explained by the following set of factors.

First, the phase separation in a system being frozen drastically increases the concentration of the gel-forming polymer in the phase enriched with it, while, the higher its concentration is, the more rigid the resulting physical gels in general [30, 31] and PVACGs in particular [1–3, 9, 29, 32–35] are. It is of interest that PVACGs with a cellular morphology very similar to that presented in the micrographs depicted in Figs. 3g and 3k were also formed from aqueous solutions of PVA/gum arabic mixtures, in which liquid-phase separation resulted from the thermodynamic incompatibility of the two polymers in a common solvent caused by an increase in their concentrations upon freezing of the majority of water [36]. Therewith, a rise in the content of non-gel-forming gum arabic in an initial mixed solution caused an increase in the elasticity modulus of the resulting heterophase cryogels, as has also been observed for the DMSO–ROH–PVA cryogels.

Second, the consequences of the changes in the conformation of coils of PVA macromolecules due to the deterioration of the thermodynamic quality of the solvent upon the addition of an alcohol must be taken into account. As has been mentioned above, DMSO is a thermodynamically good solvent for PVA, and its macromolecules occur in its medium in the conformation of swollen loose random coils [37]. At a rather high concentration of the polymer in a solution, the coils are overlapped to yield a network of fluctuation entanglements [38]. The incorporation of a nonsolvent into the system causes a certain contraction of the coils, thereby enhancing the polymer–polymer intermolecular interactions in the zones of the topological entanglements. These conformational transformations may result in different phenomena, such as a dramatic increase in the viscosity of a liquid system, liquid-phase separation, gelation, or, in the limiting case, coagulation/precipitation of the polymer. As follows from the micrographs depicted in Fig. 3, when an initial solution of PVA in a DMSO + ROH mixed solvent is subjected to the cryogenic treatment, the process "stops" after the phase separation and the formation of a cryogel in the bulk of the phase strongly enriched with the polymer, which predetermines the high rigidity of the resulting PVACG. In the case of PVA cryogels prepared in an aqueous medium with the addition of the same low-molecular-mass alcohols, the polymer is desolvated more intensely, because the affinity of water for PVA is lower than that of DMSO. This, as has been mentioned in the Introduction, causes the microcoagulation of the polymer and decreases its concentration in the zone of gelation. As a result, the rigidity and heat endurance of the cryogels obtained in a water–alcohol medium decrease as compared with those of PVACGs with the same polymer concentration but free of low-molecular-mass alcohol additives [25].

CONCLUSIONS

The study of the effect of the composition and nature of an organic solvent on the physicochemical characteristics and microstructure of PVA cryogels formed from polymer solutions in DMSO mixed with one of the first four members of the series of aliphatic alcohols has shown that, in a certain range of alcohol concentrations, coarse-pore heterophase cryogels are formed that have higher rigidity and heat endurance than do DMSO–PVA cryogels. At present, various PVACGs are applied mainly as materials for biotechnology and biomedicine [1–6, 39], and the peculiarities revealed in the properties and microstructure of PVA cryogels formed in organic media may underlie the development of gel materials possessing new practically valuable characteristics.

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