

Cryostructuring of Polymer Systems. XXVI. Heterophase Organic–Inorganic Cryogels Prepared via Freezing–Thawing of Aqueous Solutions of Poly(vinyl alcohol) with Added Tetramethoxysilane

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ABSTRACT: Composite heterophase organic–inorganic hybrid cryogels of poly(vinyl alcohol) (PVA) containing silica constituents were prepared and studied. Such constituents were formed in the course of hydrolytic polycondensation (sol–gel process) of tetramethoxysilane (TMOS) introduced in to the aqueous polymer solution prior to its freeze–thaw treatment. It was shown that moderate (over the range of -15 to -30°C) freezing, then frozen storage, and subsequent thawing of the water/PVA/TMOS systems resulted in the formation of macroporous composite cryogels filled with dispersed silica particles (discrete phase). The continuous phase of such gel materials represents the supramolecu-

lar PVA network, which is supposed to be additionally cured with the silicon-containing oligomeric cross agents formed from TMOS in the course of hydrolytic polycondensation. The incorporated silica components influenced the morphology of cryogels. The effects of significant increase in gel strength and heat resistance with increasing TMOS concentration in the initial feed and with thawing rate decreasing have also been observed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2689–2702, 2007

Key words: PVA; TMOS; composite cryogels; freezing–thawing; organic–inorganic hybrids

INTRODUCTION

It is known that macroporous noncovalent (physical) cryogels on the basis of such synthetic and natural polyol polymers, as poly(vinyl alcohol) (PVA),^{1–4} starch^{5–7} and its components (amylopectin and amylose),^{8,9} maltodextrin,¹⁰ polygalactomannans,^{11–14} β -glucan,^{15–16} etc., are formed in consequence of the cryogenic treatment (freezing, frozen storage, thawing) of aqueous solutions or sols of the listed macromolecular precursors. At that, the driving force of intermolecular interactions which gives rise to the formation of microcrystallinity zones is the hydrogen bonding between the OH-groups of neighboring chains. Such microcrystallites perform as junction knots in the 3D polymeric network.^{17–20}

The most studied among similar freeze–thaw-induced noncovalent gel systems are the PVA cryogels (cryoPVAGs) that also attract considerable attention regarding their practical use, in particular, as materials of biomedical application (e.g., as gel bases

of artificial cartilages or certain soft tissues)^{1,3,21,22} and in biotechnology (e.g., as matrices for the immobilization of biomolecules and cells).^{2,4,23,24}

In this respect, of special interest are the cryoPVAGs formed not only from PVA solutions without any foreign additives, but the complex and composite cryoPVAGs containing extra soluble or nonsoluble (fillers) components, capable of changing significantly the properties of cryoPVAGs.^{2,4,21,22}

Thereupon, the aim of this work was the preparation and study of novel organic–inorganic heterophase cryoPVAGs, when tetramethoxysilane (TMOS) was introduced in to the aqueous polymer solution prior to its freezing. TMOS is known to transform to polysilicic acid and then to silica structures during hydrolysis in aqueous media.^{25–27} Simultaneous “embedding” of organic and inorganic polymers into the common gel matrix results in arising of new additional properties for the end materials, as it was shown for diverse (but not for cryogels) gel systems (see, for instance, Refs. 28–31). In this case, the increased mechanical strength and heat resistance of similar multicomponent matrices (they are called by a term “hybrid gels”) are usually attributed to the interaction of inorganic and organic components on the molecular or nanoparticulate levels.³² Thus, the addi-

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tion of a tetra-alkoxysilane (e.g., TMOS) in the aqueous solution of some poly(*N*-vinylamides), likewise poly(*N*-vinylpyrrolidone) or poly(*N*-vinylcaprolactame), causes the formation of rubber-elastic hybrid hydrogels,^{33,34} whereas in the absence of such silanes the solutions do not gel at all. The addition of the same amounts of TMOS simply in water results (after completion of the sol-gel reaction) in dispersion of silica particles. Hence, the “collage” of so distinct components, as aqueous solution of a poly(*N*-vinylamine) and tetraalkoxysilane, which undergoes the hydrolytic polycondensation in such aqueous medium, is able to impart new quality (gel state) to final polymer system. Therefore, one can expect that introduction of finely dispersed Si-bearing matter (silica and intermediate products of TMOS hydrolysis) into polymeric matrix during the cryotropic gel-formation has to effect the properties of resulting cryogels. As far as ordinary (i.e., without foreign additives) cryoPVAGs were extensively explored; those systems were selected for the comparative study with hybrid cryoPVAGs (H-cryoPVAGs). As a direction of possible practical application of such hybrid gel materials, we are also planning to consider further their potential as matrices for the immobilization of enzymes.

EXPERIMENTAL

Materials

PVA with molecular weight of 86 kDa and deacetylation degree of 99–100% (Acros Organics, Belgium) was used in the work for the preparation of cryoPVAGs and H-cryoPVAGs.

TMOS (Merck, Germany) was purified by distillation at atmospheric pressure taking the fraction with $T_{bp} = 121\text{--}122^\circ\text{C}$ and $n_D^{20} = 1.3680$.

The dye Congo red (Aldrich Chemical Co.), gelatin (photo quality), phenol (chemically pure, >99% of basic substance), glycerol (pure for analysis), methanol (chemically pure, >99% of basic substance) (all Reachim Co., Russia) were used without further purification. All aqueous solutions were prepared using deionized water.

Methods

PVA solutions were made in a following way. The definite amount of PVA was suspended in the required volume of water so to reach the PVA content of 120 g/L. The mixture was stored 15 h at room temperature for polymer to swell. Then the suspension was heated for 1 h under stirring on a boiling water bath for PVA complete dissolution. The sample was weighed before and after heating, and the amount of evaporated water was compensated. The obtained solution was filtered, then thermostated at 20°C for

30 min before making compositions with TMOS. The latter one was introduced in amounts corresponding to 0.14, 0.28, 0.42, 0.56, and 0.70 mol per 1 base-mole of the polymer. Then water was added to make up final PVA concentration 93.4 ± 0.2 g/L in each sample, and the composition was stirred for 7 min prior to freezing.

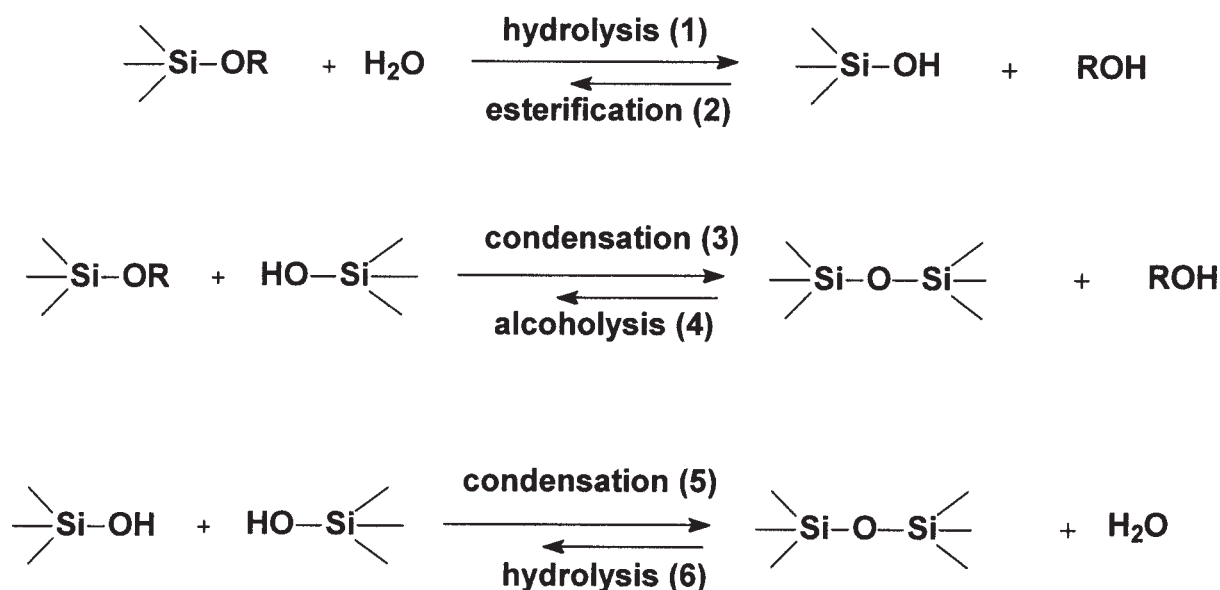
The samples of cryoPVAGs and H-cryoPVAGs for measurements of their physico-mechanical characteristics were formed in sectional duralumin molds (inner diameter 15 mm, height 10 mm). For the determination of fusion temperature, cryogels were prepared in transparent polyethylene test tubes (inner diameter 10 mm). The test tubes were filled with 5 mL of liquid composition, and a stainless steel ball with the diameter of 3.5 mm and weight of 0.275 ± 0.005 g was placed on the bottom of each test tube. The containers and the test tubes were placed into the chamber of precision programmable cryostat FP 45 HP (Julabo, Germany), where the samples were frozen and kept at certain subzero temperature for 12 h. Further the temperature was risen to +20°C with the rate controlled by the cryostat microprocessor.

Apparent instantaneous shear modulus (G_0) characterizing elastic properties of the material and shear modulus for the 30-min-loading (G_{30} , reflects the plastic behavior of a material) were determined according to the technique earlier described in detail and used for the characterization of rheological behavior of diverse nonfilled and filled (composite) cryoPVAGs.^{35–38} The measurements were carried out at $(21 \pm 1)^\circ\text{C}$ by the penetration of spherical punch (5 mm in dia.) into a gel sample at constant load of 4.9×10^{-3} N. To avoid drying, the samples were covered with thin layer of silicone oil. After the tests, the attained deformations of cryogels were small and did not exceed 5%; no macroscopic squeezing of moisture was detected for all the gel samples thus examined.

Gel fusion temperatures (T_f) were determined as follows. The tightly stoppered polyethylene tube, where cryogel with metal ball at the bottom has been formed, was placed upside down into a water bath. The temperature was increased with the rate of $(0.4 \pm 0.1)^\circ\text{C}/\text{min}$. The gel fusion point was determined as the temperature when the ball fell down the stopper of the test tube after passing through the fusing gel.

Shear moduli and cryogel fusion temperatures were measured for four parallel samples, where the samples were obtained in 3–5 independent experiments. The results obtained were averaged.

The cryogels' morphology was studied by means of optical microscope Axiolab Pol (Carl Zeiss Jena, Germany) equipped with video-recording system (Sony, Japan). Thin (6–8 μm) sections of cryoPVAGs and H-cryoPVAGs were prepared using cryomicrotome Shandon Cryotome (Thermo Electric Corp., UK). Each section was placed on the microscope glass, which



Scheme 1 Chemical reaction occurring upon the hydrolytic polycondensation of tetraalkoxysilanes in aqueous media.^{26,27}

was then immersed for 10 s into 1% aqueous solution of Congo red for staining. The excess of the dye was rinsed by water and the excess of water was removed with filter paper. Then the section was poured with one drop of "fixing medium" (solution of 1 g of gelatin in 12 mL of 50% aqueous glycerol and 0.2 g of phenol as a bacteriostatic agent) and sealed with a cover glass. Prior to studies, the samples were stored at 4°C in a closed vessel.

The dimensions of SiO₂ particles (number average and weight average diameters— D_n and D_w , respectively) entrapped in the H-cryoPVAG matrices were determined by means of optical microscopy. For calculation, the following formulas were used:

$$D_n = \left(\frac{\sum (N_i D_i^3)}{\sum N_i} \right)^{1/3}, \quad D_w = \left(\frac{\sum (N_i D_i^6)}{\sum (N_i D_i^3)} \right)^{1/3};$$

$$\text{where } \sum N_i = 100 \pm 5.$$

The polydispersity index was determined as $k = D_w/D_n$. Using the data obtained, respective distribution diagrams were plotted.

RESULTS AND DISCUSSION

Selection of experimental conditions for the preparation of organic-inorganic hybrid cryoPVAGs

Structure, physicochemical, and thermal properties of cryoPVAGs are determined by the combination of many factors, including characteristics of the gel-forming polymer (i.e., molecular weight, content of OH-groups, chain tacticity), its concentration in initial

solution, the presence of foreign solutes or dispersed fillers, and, certainly, by the conditions of cryogenic treatment.¹⁻⁴ To clarify the effects of the added TMOS and products of its hydrolysis on the properties of resulting cryogels, it was, first of all, necessary to establish optimal conditions for the preparation of cryoPVAGs and H-cryoPVAGs with reproducible characteristics (G_0 , G_{30} , and T_f). Besides, it was also required to explore the influence of methanol additives on cryogel properties, inasmuch as methanol is liberated in the course of TMOS hydrolytic polycondensation (reactions (1) and (3) in Scheme 1), and this alcohol is well-known to be the precipitant for PVA.

These experiments (their results are summarized in the Table I) revealed some peculiarities of the influence of freezing temperature and methanol additives on the characteristics of respective cryoPVAGs. Freezing of PVA solutions over the temperature range of -18 to -30°C with subsequent thawing with the rate of 0.03°C/min resulted in the formation of cryoPVAGs possessing both high rigidity and fusion temperature. Therefore, such conditions were implemented for testing the "methanol effects."

It was found that addition of increasing amount of methanol in the composition, which was used for the preparation of cryoPVAGs, gave rise to considerable decrease in gel strength and heat resistance of corresponding samples. Thus, the presence of even small (~ 2%) amount of added CH₃OH in the initial polymer solution has diminished the values of both shear moduli (G_0 and G_{30}) of the resulting cryogel by about one third and decreased T_f by ~ 4°C as compared with the equiconcentrated cryoPVAG without methanol additives. The fivefold higher amount of CH₃OH (~ 11%) in the initial system gave rise to formation of

TABLE I
Properties of PVA Cryogels Prepared from the Aqueous and Water–Methanol Solutions of the Polymer^a

Methanol concentration in PVA solution, % (w/w)	Freezing temperature (°C)	Properties of cryoPVAGs		
		G_0 (kPa)	G_{30} (kPa)	T_f (°C)
–	–15	3.8 ± 0.3	2.8 ± 0.1	72.0 ± 0.3
–	–18	7.0 ± 1.6	5.3 ± 1.3	^b
–	–20	6.9 ± 0.9	5.1 ± 0.9	72.5 ± 0.2
–	–30	6.8 ± 0.6	4.6 ± 0.7	72.9 ± 0.3
2.10	–20	4.6 ± 0.9	3.8 ± 0.8	68.4 ± 0.4
4.45		2.9 ± 0.3	2.3 ± 0.1	66.9 ± 0.3
6.60		2.1 ± 0.2	2.0 ± 0.1	65.8 ± 0.3
8.45		1.9 ± 0.2	1.7 ± 0.3	62.9 ± 0.2
11.2		1.5 ± 0.2	1.4 ± 0.1	62.3 ± 0.3

^a PVA concentration in the initial system: 93.4 ± 0.2 g/L, freezing time: 12 h, thawing rate: $0.03^\circ\text{C}/\text{min}$.

^b No data.

low fusible ($T_f \sim 62^\circ\text{C}$) and 3.9- to 4.9-times weaker cryogels. It is noteworthy that the addition of methanol somewhat stronger influenced on elastic rather than plastic characteristics of cryoPVAGs. For instance, the increase in methanol concentration in initial PVA solution from 2.1 to 11.2% yielded the decrease in the G_0 values (in comparison with cryogel without methanol additives) by 32.6% and 77.9%, respectively, whereas G_{30} values decreased by 26.9% and 73.7%. It also has to be noted that even the highest methanol concentration used in our experiments was still lower than the methanol concentration causing the precipitation of PVA from aqueous solutions at a room temperature. However, owing to the cryoconcentrating effects (an increase in solute concentration as far as ice is crystallizing) the actual methanol concentration in the still unfrozen part of the system (so-called unfrozen liquid microphase (ULMP)^{1,4,39}) could exceed the concentration required for PVA precipitating. Such an effect could deteriorate the efficiency of PVA cryotropic gel-formation, as it follows from the data of Table I (diminished gel strength and heat resistance of CH_3OH -containing cryogels). Very similar effects, i.e., the decrease in rigidity and fusion temperature of cryoPVAGs, were observed upon addition of diol alcohol—ethylene glycol and triol alcohol—glycerol in PVA solution prior to its freeze–thaw treatment,⁴⁰ and NMR studies confirmed the cryoconcentrating phenomena for such alcohols in ULMP.⁴¹ So, all these data testify that low molecular weight alcohols, which are water-miscible nonsolvents (precipitants) for PVA, are capable of causing the adverse effects on the formation of cryoPVAGs.

In this context it was of significance to compare the structural peculiarities of cryoPVAGs formed in the absence and in the presence of methanol. Figure 1 shows the micrographs of fine sections of the equiconcentrated (by polymer) cryogels prepared in experiments, when CH_3OH concentrations were as follows:

0 [Fig. 1(a)], 2.1 [Fig. 1(b)] and 11.2% [Fig. 1(c)]. On the black and white photos, the dark area is the gel phase stained with Congo red (see Experimental) and light areas are the macropores filled with water.

If the cryoPVAGs prepared from the binary solution water/polymer had relatively uniform distribution of oval macropores in gel matter (diameters of these macropores were mainly from 1 to 5 μm [Fig. 1(a)], the formation of cryogels from the ternary systems water/polymer/methanol led to considerable heterogenization of macroporous material, as well as to marked changes of both the structure of its gel phase and size of the pores. Noticeable modification of the morphology of the cryogels was observed even at low (2.1%) methanol concentration in the initial system: the pore walls became denser (their more intense staining testifies this fact) and attained a “fibrous” texture [Fig. 1(b)], but in respect to the material as a whole this resulted in its loosening owing to the increase in the space of macropores. This apparently was the main reason for decrease in the integral rigidity of such cryoPVAG (Table I). At the same time, a decrease in the fusion temperature of cryoPVAG formed in the presence of methanol additives indicated that despite the mentioned higher density of the gel framework, the structure of the junction knots of the supramolecular physical network is, obviously, less perfect (the knots are the microcrystallinity zones, which dissociate at heating up to T_f).² Most probably this was because of the changes in hydrophilic/lipophilic balance of the medium of gel-formation, i.e., of ULMP, where because of worsening the thermodynamic quality of the solvent certain collapse of PVA coils took place. Further increase in CH_3OH content in the feed (e.g., till $\sim 11\%$) caused even stronger changes of microstructure of corresponding cryoPVAG. The gel phase became more diffuse, and the boundaries of macropores became vague [Fig. 1(c)]. At that, the cryogel’s rigidity and heat resistance

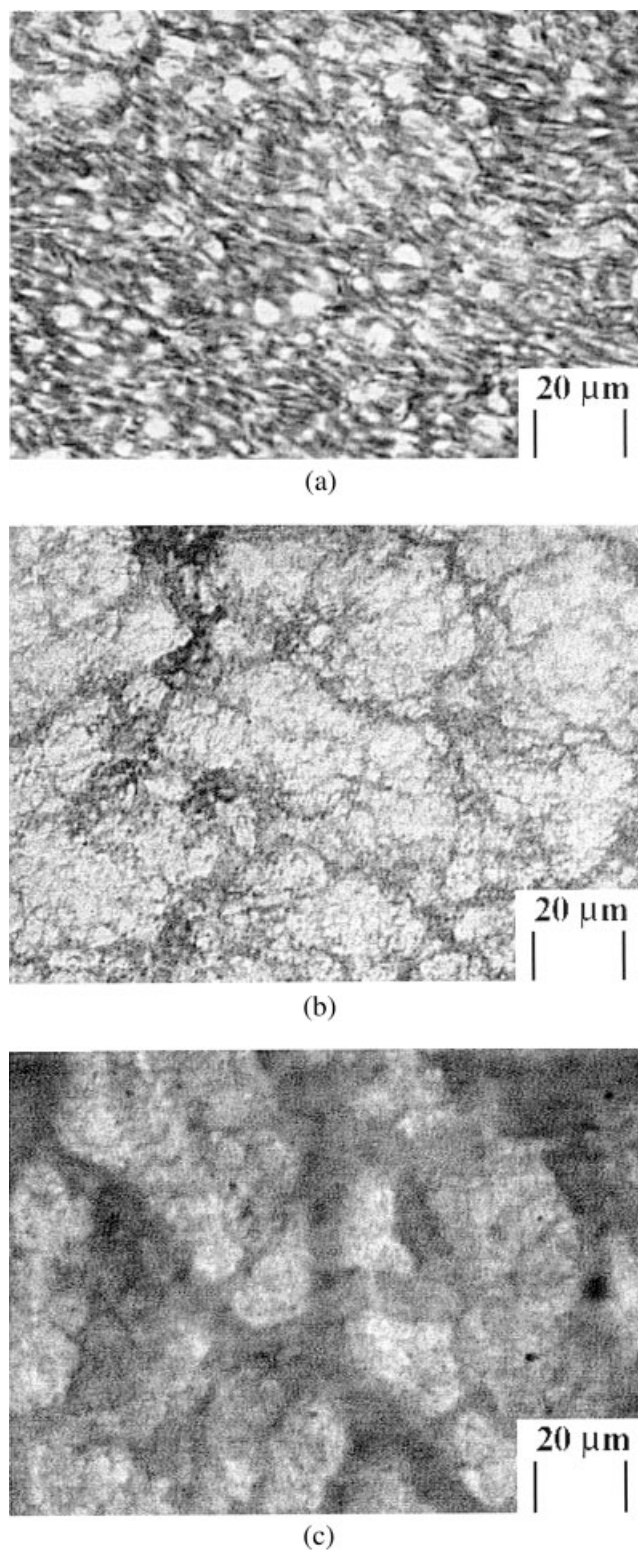


Figure 1 Optical microscopy micrographs of thin sections of cryoPVAGs prepared from the initial systems water/PVA (a) or water/PVA/methanol (b, 2.1% CH₃OH; c, 11.2% CH₃OH). Conditions of cryostructuring: PVA concentration in the initial system 93.4 ± 0.2 g/L, freezing at -20°C for 12 h, thawing with the rate of $0.03^{\circ}\text{C}/\text{min}$.

decreased considerably (Table I). One can suppose that in the course of formation of such materials, the high enough methanol concentration in ULMP was able to bring about not only the compression of PVA macromolecular coils, but also led to the microcoagulation of the polymer in its concentrated solution. As a result, all these factors could hinder (including sterically) the intermolecular interactions, which are “usually” responsible for the formation of 3D network of cryoPVAGs.

Thus, taking in to consideration the experimental data discussed above (Table I and Fig. 1), as well as the fact that after introducing TMOS in to the system water/PVA, the formation of silica-like structures is accompanied by the liberation of methanol; one can expect definite changes in the morphology of resulting hybrid cryogels and, apparently, decrease in their rigidity and fusion temperature in comparison with the same parameters of common (i.e., without foreign additives) cryoPVAGs. However, the measurements of physicomechanical and thermal characteristics of H-cryoPVAGs produced via the cryogenic treatment of initial triple systems containing varied amount of TMOS revealed an opposite trend.

Properties and structure of hybrid organic–inorganic cryoPVAGs

TMOS is unstable in the presence of water, and reactions of hydrolytic polycondensation start to proceed immediately after the silane is introduced in PVA aqueous solution, that is, after mixing of reagents the system water/PVA/TMOS is chemically changed with time. Therefore, all the procedures for preparing the initial samples and their freezing were standardized throughout our studies regarding the temperature and time of the preparation protocol (see “Experimental”). So, as a result of the cryogenic treatment

TABLE II
Properties of Hybrid Cryogels Prepared via the Freeze–Thaw Treatment^a of the Systems Water/PVA/TMOS

Initial ratios [TMOS] : [PVA] (mol/base-mol)	Characteristics of H-cryoPVAGs		
	G_0 (kPa)	G_{30} (kPa)	T_f ($^{\circ}\text{C}$)
^b	6.9 ± 0.9	5.1 ± 0.9	72.5 ± 0.2
0.14 : 1	10.0 ± 3.1	8.2 ± 2.2	95.0 ± 1.5
0.28 : 1	13.1 ± 3.4	11.3 ± 3.2	^c
0.42 : 1	16.5 ± 4.9	14.3 ± 3.9	^c
0.56 : 1	19.8 ± 6.1	17.4 ± 5.0	^c
0.70 : 1	24.0 ± 7.5	20.4 ± 6.6	^c

^a PVA concentration in the initial water/PVA/TMOS system: 93.4 ± 0.2 g/L, freezing temperature: -20°C , freezing time: 12 h, thawing rate: $0.03^{\circ}\text{C}/\text{min}$.

^b PVA cryogel formed without TMOS additives.

^c The samples did not melt upon heating till $\sim 100^{\circ}\text{C}$; a disturbance of their integrity and partial fragmentation took place.

under the conditions chosen and discussed in the previous section for producing of cryogels based on water/PVA and water/PVA/methanol systems, the goal objects of present study, namely organic–inorganic H-cryoPVAGs, were prepared. The values of G_0 , G_{30} , and T_f measured for these novel PVA-based cryogels are summarized in Table II.

The following peculiarities inherent in such hybrid gels were revealed:

Firstly, the experimental error of the physico-mechanical tests for the H-cryoPVAGs was considerably increased as compared with the systems without TMOS additives (from 8 to 18% up to nearly 30%). This evidently was because of introducing chemically-active TMOS in to the initial feed. TMOS additives caused the structural and phase heterogenization of final cryogels (see below), thus markedly influencing the reproducibility of rheological tests.

Secondly, in spite of the “softening” effect of liberating methanol on the strength of cryoPVAGs, the formation of silica-like structures resulted in very pronounced increase in rigidity of H-cryoPVAGs. For instance, if at 11.2%-content of methanol the G_0 and G_{30} values of respective cryoPVAG were decreased by 77 and 74% (Table I), in the case of H-cryoPVAG prepared with TMOS in an amount corresponding to the same amount of liberated methanol, namely, [TMOS]:[PVA] = 0.7 : 1 (here and below in the text such ratio is given in moles of TMOS per one base-mole of PVA), the values of the moduli were increased by 249 and 298% (Table II). However, also taking into account the “negative constituent” of the effect of methanol appearing upon the TMOS hydrolytic polycondensation, the “corrected” total values of such an increasing effect should be 326 and 372%, respectively. Note also that simply methanol additives somewhat stronger influenced, as it was already pointed out, on the elastic properties of cryogels, whereas for the hybrid systems their G_{30} values (characterizing the plastic behavior of the gel samples) were predominantly increased.

Thirdly, the fusion temperatures of H-cryoPVAGs grew so considerably, as we were able to measure the T_f values only for the cryogel samples prepared with the lowest amount of TMOS ([TMOS] : [PVA] = 0.14 : 1). At the higher initial TMOS concentrations the final hybrid cryogels did not melt until the boiling temperature of their liquid constituent (water–methanol mixture) was reached. This, in turn, did not cause the fusion of the samples with the formation of highly viscous sol, but gave rise to the disturbance of the integrity of specimens and their fragmentation. Possible reasons for such a heat resistance of H-cryoPVAGs will be touched below after discussion of the data on the structure of hybrid cryogels.

The microphotographs of thin sections of H-cryoPVAGs obtained by freezing–thawing method (after the

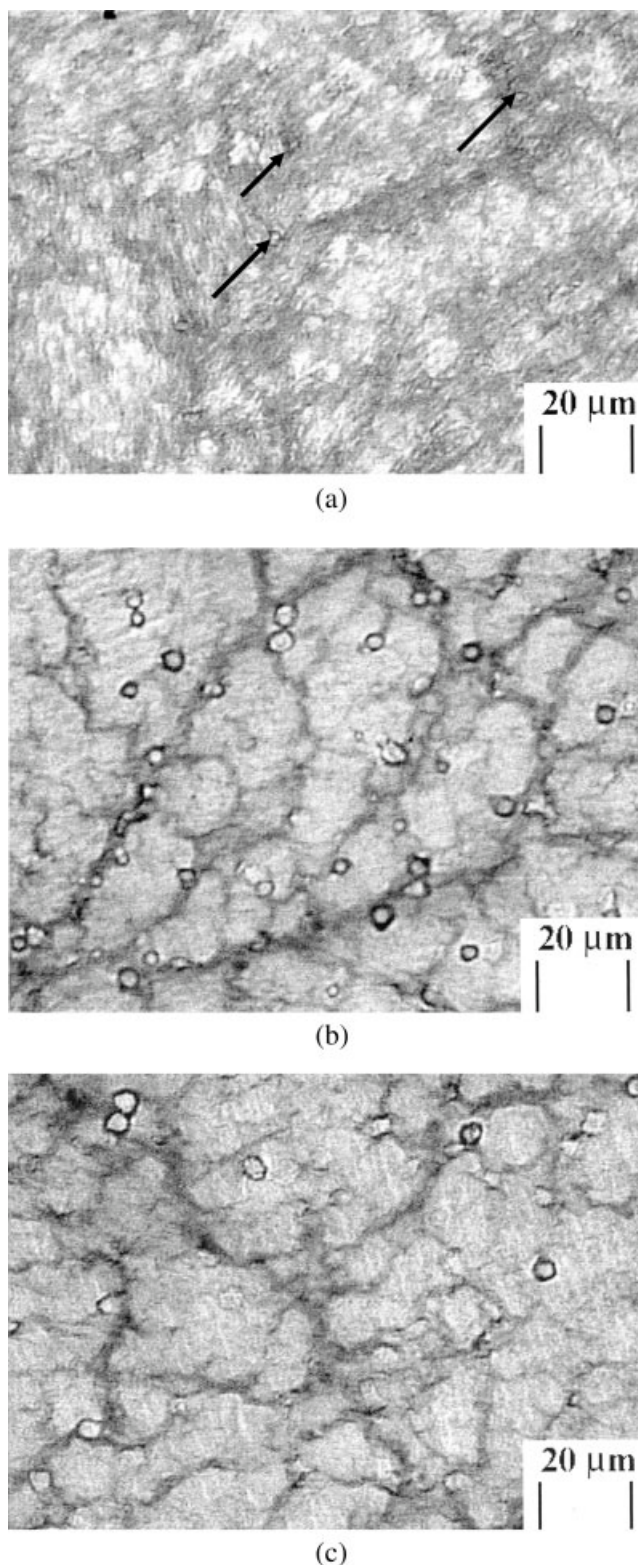


Figure 2 Optical microscopy micrographs of thin sections of composite H-cryoPVAGs prepared from the initial systems water/PVA/TMOS with various concentration of organosilicon compound: [TMOS] : [PVA] = 0.28 : 1, (a); 0.56 : 1, (b); and 0.70 : 1 (c). Conditions of cryostructuring are the same as indicated in the legend of Figure 1.

addition of different amount of TMOS in PVA solution) are shown on Figure 2. It turned out that the morphology of each sample, as a whole, and of its structural elements, in particular, depended on the concentration of organosilicon additive. First of all, when comparing the micrographs in Figure 2 with those in Figure 1, one can see the appearance of small dispersed filler particles in the bulk of H-cryoPVAG. Such semi-transparent (surrounded by a dark "halo") particles of the discrete phase had average diameters from 1 to 5 μm [in Fig. 2(a), where the particles are few and small enough, they are indicated by arrows]. It was found that the particles of dispersed silica prepared by TMOS dropping in pure water then looked analogous, when observed in a microscope. Therefore, one can guess that silica structures, which were generated from TMOS in the course of its hydrolytic polycondensation (Scheme 1), at least partially formed independent discrete phase entrapped in continuous phase of macroporous gel matrix, thus giving rise to the filled polymeric material, i.e., composite PVA cryogel.

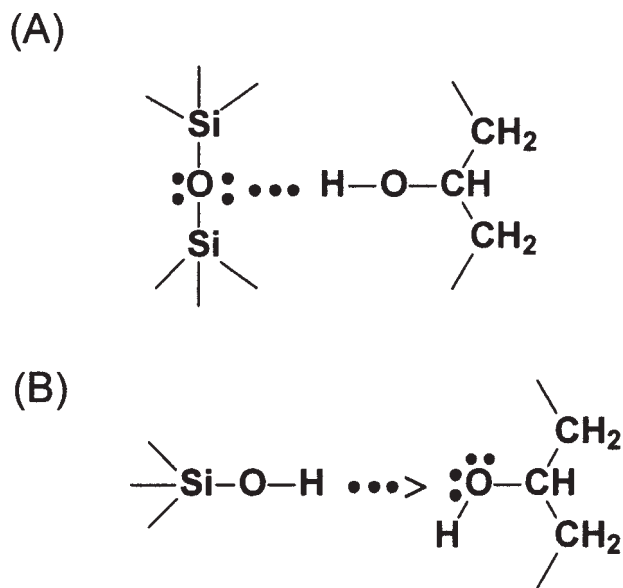
At the same time, the methanol, being secreted upon such cryotropic gel-formation, transformed the structure of continuous phase. Thus, similar to the micrograph in Figure 1(b), in the images of Figure 2(b,c) one can see the condensed fibrous structure of the material with the considerably larger pores as compared to cryoPVAG prepared without any additives [Fig. 1(a)]. It is noteworthy that even at the highest used concentration of organosilicon component in the initial feed, i.e., at $[\text{TMOS}] : [\text{PVA}] = 0.7 : 1$ corresponding to the 11.2%-concentration of liberating methanol, the morphology of the gel phase of respective H-cryoPVAG [Fig. 2(c)] differed from the cryoPVAG prepared with the addition of the same amount of methanol [Fig. 1(b)]. The micrograph in Figure 2(c) most of all resembled that in Figure 1(b) related to cryoPVAG prepared at the minimum (2.1%) concentration of added methanol. This important fact testifies that some of the products of TMOS hydrolytic polycondensation, commencing from certain stages of gel-formation, hindered from the methanol-induced further changes of the morphology of gel phase, namely, prevented its transition to the structure shown in Figure 1(c). Moreover, if also will take into account the above-mentioned effect of strong increase in heat resistance of H-cryoPVAGs even at low concentration of TMOS in the initial feed (Table II); the nature of such structural features requires special discussion.

First, it was reported elsewhere³⁸ that fusion temperatures of composite cryoPVAGs obtained by freezing-thawing of suspensions (silica particles mixed with PVA solution) only slightly (by 1–2°C) differed from the T_f values of nonfilled cryo-PVAGs. This means that simply additives of dispersed silica particles have small effect on the thermal properties of the continuous gel phase. However, the rigidity of the

filled cryogels is increased considerably. Thus, silica particles acted as active fillers, mainly influencing the physicomechanical properties of such composite cryogels. Therefore, strong increase in T_f in the case of H-cryoPVAGs can not be attributed to the formation of TMOS-originated discrete silica phase in the bulk of continuous phase (Fig. 2).

Second, as far as the particles of the inorganic filler were virtually unable to affect on the heat resistance of H-cryoPVAGs, and *in situ* liberating methanol should considerably bring down the T_f values (Table I) and loosen the gel phase structure [Fig. 1(c)], it might be some other factors hindering those processes. It is soundly to suppose that some of the still soluble "intermediate" products of TMOS hydrolytic polycondensation could interact (either react) with PVA macromolecules and thus to be incorporated into the network of the polymer gel. One of the arguments in favor of this assumption is the fact that no particles of discrete silica were detected in the micrographs of thin section of H-cryoPVAG formed at the lowest used TMOS concentration ($[\text{TMOS}] : [\text{PVA}] = 0.14 : 1$), whereas the gel strength and T_f of such samples were already considerably increased (Table II). The formation of the particles of inorganic discrete phase was observed only at a higher initial TMOS concentration. Apparently, this was the consequence of two competing processes: (i) the interaction of still soluble "intermediate" products of TMOS hydrolytic polycondensation with PVA macromolecules leading to the formation of quasi-homogeneous polycomplexes and (ii) the 3D TMOS hydrolytic polycondensation giving rise to the growth of silica particles. The former process had, apparently, somewhat greater rate.

In the third place, evidently just the incorporation of the above-discussed "intermediate" silicon-containing products (they perform as crosslinking agents) in the polymeric phase of H-cryoPVAGs was responsible for the "inhibition" of unfavorable influence of methanol. Unfortunately, the exact nature of such crosslinking compounds is not so far identified, although it is known^{42,43} that at low conversion of the reactions of tetraalkoxysilanes' hydrolytic polycondensation among the products there are linear, branched, and cyclic oligoalkoxysilaxanols, which are soluble in aqueous alcohols (ULMP of the studied systems is quite such a system). Therefore it is natural to assume the processes of binding (most probably cooperative) of those compounds with OH-groups of PVA via the hydrogen bonds. Oligoalkoxysilaxanols like the $\text{H}[\text{—O—Si}(\text{Alk—O})_2\text{—}]_x\text{OH}$ (or those with partially saponificated pendant groups), which were found out among the products of hydrolytic polycondensation,⁴² can be the examples of similar Si-containing cross agents. Such an assumption does not contradict the chemistry of these systems, so it can be con-



Scheme 2 The structures of possible hydrogen bonds between the fragments of oligomethoxysilaxanols and OH-groups in PVA (see the text for explanations).

sidered as a working hypothesis capable of explaining the experimental data obtained.

Principally, there are two possible types of hydrogen bonds that can be formed in these systems (Scheme 2):

- "normal type"—in between the H-atom of PVA hydroxyl group and siloxane oxygen atom (more exactly its lone electron pair),
- "highly polarized" hydrogen bond—in between the unshared electron pair of the oxygen atom of PVA hydroxyl group (acting as a weak base) and the silanol group of a siloxanole (exhibiting weak acidic properties).

The first type (A) of such hydrogen bonds has to be thermosensitive and dissociate at moderate heating in a similar way to the hydrogen bonds in the junction knots of physical gels like the gelatin ones⁴⁴ or cryoPVAGs.^{45,46} At the same time, the second type (B) of H-bonds forthcoming by its nature to ionic bonds has to be significantly more thermostable and, therefore, from our viewpoint, just this type of H-bonding can be responsible for the enhanced heat resistance of H-cryoPVAGs (Table II).

In addition, one can not exclude direct reaction of TMOS, either intermediate methoxysilaxanols with OH-groups of PVA via the mechanism of *trans*-esterification. However, the intermolecular covalent Si—O—C-bonds formed in this case are the hydrolytically unstable and should be cleaved in the presence of gross excess of water in the system of interest.

As for the dispersed silica particles themselves being entrapped in H-cryoPAAGs, their size charac-

teristics were evaluated. The average diameter of the particles and their size distribution for the filled cryogels, whose morphology is shown in Figure 2(b,c), are presented in Figure 3. It was found that increase in the initial TMOS concentration from [TMOS] : [PVA] = 0.56 : 1 to [TMOS] : [PVA] = 0.7 : 1 gave rise to increase in the mean diameter of silica particles and in broadening of their size distribution (the polydispersity index k was risen from 1.155 to 1.225). In other words, the higher the amount of TMOS introduced in the initial PVA aqueous solution, the higher the possibilities for the growth of particles of inorganic discrete phase in these systems in the course of their cryotropic gelation.

Summing up the above considered data on the cryogels formed from the feed of water/PVA/TMOS composition, we can draw the conclusion that such cryogels include at least two types of silicon-containing components: the particles of dispersed silica filler and, presumably, oligomeric substances performing as

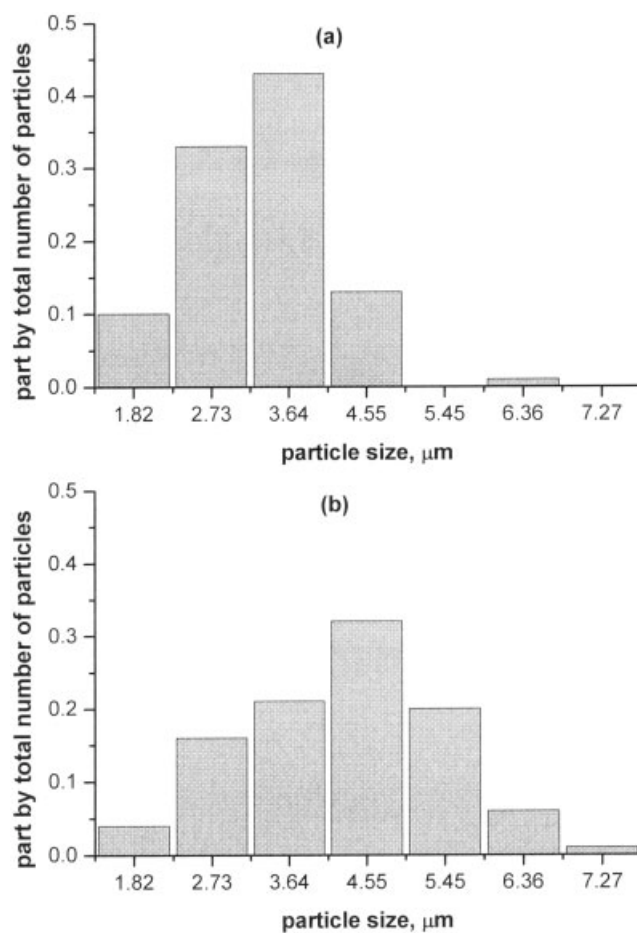


Figure 3 Size distribution of the particles of discrete phase in composite H-cryoPVAGs prepared from the initial systems water/PVA/TMOS with [TMOS] : [PVA] = 0.56 : 1 (a) ($D_n = 3.49 \mu\text{m}$, $D_w = 4.03 \mu\text{m}$, $k = D_w/D_n = 1.155$) and 0.70 : 1 (b) ($D_n = 4.58 \mu\text{m}$, $D_w = 5.61 \mu\text{m}$, $k = D_w/D_n = 1.225$). Conditions of cryostructuring are the same as indicated in the legend of Figure 1.

TABLE III
Physicomechanical Properties of CryoPVAGs and Composite H-CryoPVAGs Prepared at Different Freezing Temperatures^a

Freezing temperature (°C)	Characteristics of cryogels												
	G ₀ values ^b (kPa)						G ₃₀ values ^c (kPa)						
	d		0.14:1		0.28:1		0.42:1		0.56:1		0.70:1		0.84:1
-15	3.8 ± 0.3	3.9 ± 0.9	4.1 ± 1.1	4.2 ± 1.5	4.4 ± 0.5	4.5 ± 0.9	2.8 ± 0.1	2.9 ± 0.9	3.1 ± 0.6	3.2 ± 1.0	3.4 ± 0.7	3.6 ± 0.5	3.6 ± 0.5
-18	7.0 ± 1.6	7.2 ± 3.0	7.6 ± 2.8	9.6 ± 3.1	10.7 ± 3.2	13.2 ± 3.6	5.2 ± 1.3	6.1 ± 1.5	6.6 ± 1.7	7.7 ± 2.1	9.9 ± 2.9	12.4 ± 3.0	12.4 ± 3.0
-20	6.9 ± 0.9	10.0 ± 3.1	13.1 ± 3.4	16.5 ± 4.9	19.8 ± 6.1	24.0 ± 7.5	5.1 ± 0.1	8.2 ± 2.2	11.3 ± 3.2	14.3 ± 3.9	17.4 ± 5.0	20.4 ± 6.6	20.4 ± 6.6
-30	6.8 ± 0.6	11.9 ± 0.2	17.2 ± 3.3	22.0 ± 1.6	26.5 ± 0.8	31.3 ± 9.0	4.6 ± 0.7	8.7 ± 1.2	13.1 ± 3.1	16.9 ± 5.1	21.4 ± 0.6	25.7 ± 7.7	25.7 ± 7.7

^a PVA concentration in the initial water/PVA/TMOS system: 93.4 ± 0.2 g/L, freezing time: 12 h, thawing rate: 0.03°C/min.

^b G₀ values (kPa) for cryogels prepared from the water/PVA/TMOS mixtures at initial ratio [TMOS]:[PVA] (mol/base-mole).

^c G₃₀ values (kPa) for cryogels prepared from the water/PVA/TMOS mixtures at initial ratio [TMOS]:[PVA] (mol/base-mole).

^d The data for PVA cryogels formed under the same conditions, but without TMOS additives.

TABLE IV
Physicomechanical Properties of CryoPVAGs and Composite H-CryoPVAGs Prepared When the Frozen Samples Were Defrosted with Different Thawing Rates^a

Freezing temperature (°C)	Thawing rate (°C/min)	Characteristics of cryogels											
		G ₀ values ^b (kPa)						G ₃₀ values ^c (kPa)					
		d		0.14:1		0.28:1		0.42:1		0.56:1		0.70:1	
-20	0.3	3.4 ± 0.2	6.0 ± 1.1	8.8 ± 1.0	12.0 ± 1.5	15.2 ± 1.5	18.8 ± 2.7	2.8 ± 0.1	4.0 ± 1.2	5.5 ± 0.1	6.9 ± 0.2	8.5 ± 2.3	10.1 ± 2.3
	0.03	6.9 ± 0.9	10.0 ± 3.1	13.1 ± 3.4	16.5 ± 4.9	19.8 ± 6.1	24.0 ± 7.5	5.1 ± 0.1	8.2 ± 2.2	11.3 ± 3.2	14.3 ± 3.9	17.4 ± 5.0	20.4 ± 6.6
	0.003	11.2 ± 2.5	13.7 ± 3.3	16.5 ± 4.5	20.5 ± 6.1	24.3 ± 5.6	29.4 ± 1.9	5.9 ± 1.3	9.2 ± 1.4	12.0 ± 2.2	15.0 ± 4.0	19.8 ± 6.4	23.1 ± 6.7
-30	0.3	3.3 ± 0.5	8.4 ± 3.1	13.5 ± 0.9	18.0 ± 5.6	22.4 ± 6.5	27.1 ± 6.6	2.6 ± 0.3	5.3 ± 0.7	11.1 ± 3.3	15.9 ± 3.7	16.9 ± 4.1	18.4 ± 4.6
	0.03	6.8 ± 0.6	11.9 ± 0.2	17.2 ± 3.5	22.0 ± 1.6	26.5 ± 0.8	31.3 ± 9.8	4.6 ± 0.7	8.7 ± 1.2	13.1 ± 3.1	16.9 ± 5.1	21.4 ± 0.6	25.7 ± 5.9

^a PVA concentration in the initial water/PVA/TMOS system: 93.4 ± 0.2 g/L, freezing time: 12 h.

^b G₀ values (kPa) for cryogels prepared from the water/PVA/TMOS mixtures at initial ratio [TMOS]: [PVA] (mol/base-mole).

^c G₃₀ values (kPa) for cryogels prepared from the water/PVA/TMOS mixtures at initial ratio [TMOS]: [PVA] (mol/base-mole).

^d The data for PVA cryogels formed under the same conditions, but without TMOS additives.

crosslinking agents. Therefore, such materials could be defined as *hybrid composites* to distinguish them from the virtually homophase (or with the heterogeneity on a nanoscale level⁴³) organic–inorganic hybrid gels formed upon the hydrolytic polycondensation of tetraalkoxysilanes in aqueous solutions of poly(*N*-vinylpyrrolidone)³³ or poly(*N*-vinylcaprolactame).³⁴

Influence of cryotropic gel-formation conditions on the properties of composite H-cryoPVAGs

The influence of the conditions of cryogenic treatment of aqueous PVA solutions on the properties of resulting traditional nonfilled cryoPVAGs was studied rather comprehensively.^{1–4,23,35,36} It is known that when the only freeze–thaw cycle is applied, the most important process's factors are the temperature regime and, especially, the profile of thawing.^{2,4,46} Therefore, in the present study, the role of these parameters was investigated in relation to composite H-cryoPVAGs. Table III contains the data on the physico-mechanical characteristics of hybrid composites formed at various freezing temperatures and defrosted with the same rate of 0.03°C/min, and Table IV gives the experimental results for the samples frozen at equal temperature (either at –20°C, or at –30°C), but thawed off with different rates.

These results show that over the studied ranges of TMOS, initial concentration and freezing temperature (–15 to 30°C) and the rigidity of composite samples monotonically (i.e., without the extreme points) increased with decrease in the temperature of cryogenic process (Table III). Thus, the G_0 value for the H-cryoPVAG prepared from the feed with [TMOS] : [PVA] = 0.14 : 1 and frozen at –30°C exceeded by a factor of 3.1 times the G_0 value of the equiconcentrated cryogel sample frozen at –15°C, and the corresponding G_{30} values differed by a factor of three times. In the case of cryogels formed from the feed with [TMOS]:[PVA] = 0.7 : 1 the ratios of these moduli were ~ 7 and 7.1 times, respectively. Accordingly, such a trend was equally manifested in respect of both elastic and plastic properties of the composite organic–inorganic cryogels under discussion. At that, the bigger amount of TMOS introduced into the initial reagents mixture, the more pronounced the effect of increase in rigidity of H-cryoPVAGs with lowering the freezing temperature (over the range studied in our work). Obviously, this testified that the increase in initial TMOS concentration caused not only the “strengthening” effect due to the rise of a portion of dispersed filler in the composite cryogels, but also that the cryoconcentrating effects (the lower the temperature, the less the volume of UFLP and the higher the solutes concentration there)^{2,4} very markedly promoted the processes of H-bonding between the sili-

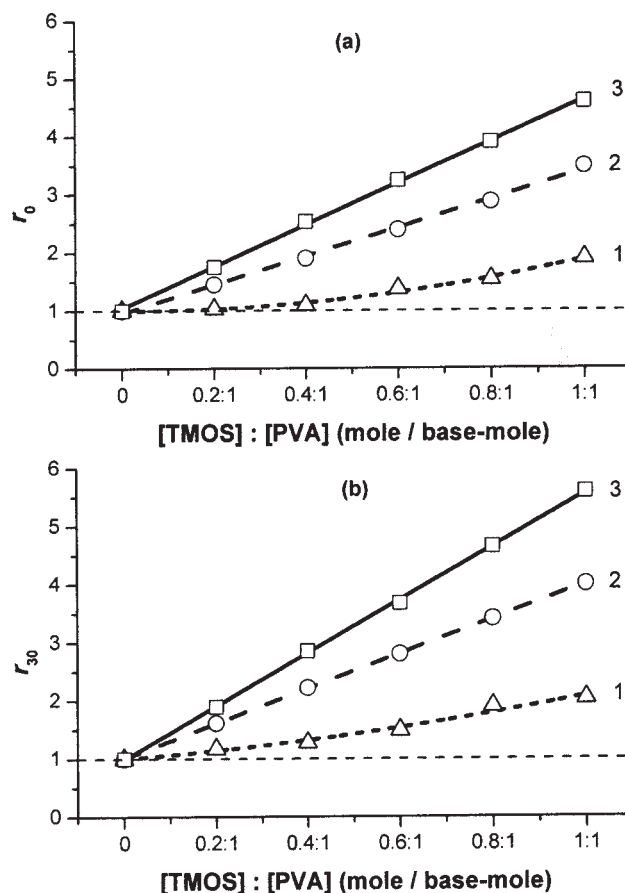


Figure 4 Dependences of normalized r_0 (a) and r_{30} (b) values on the initial [TMOS]/[PVA] ratio for H-PVAGs prepared at freezing temperatures of –18°C (1), –20°C (2) and –30°C (3). Conditions of cryostructuring: PVA concentration in the initial water/PVA/TMOS system: 93.4 ± 0.2 g/L; freezing time: 12 h; thawing rate: 0.03°C/min; every r parameter was computed assuming as the unity the lowest G value for respective (identical initial [TMOS]/[PVA] ratio) cryogel prepared at –15°C.

con-containing crosslinking substances (Scheme 2) and the supramolecular network of PVA cryogel.

If to normalize the measured values of G_0 and G_{30} with respect to the lowest shear module, namely, assuming the G value of the H-cryoPVAG sample prepared at –15°C (Table III) as the unity, the discussed trend becomes even more obvious. The plots for such normalized data are depicted in Figure 4, where the dependences of reduced magnitudes (r_0 and r_{30} , correspondingly) on the [TMOS]:[PVA] ratios are given. One can see not only the total effect of the freezing temperature, but also somewhat stronger influence of that factor on the r_{30} values [a more steep slope of the lines in Figure 4(b) as compared with those in Fig. 4(a)]. Most likely, this fact points to a decrease in flexibility of polymer chains because of their “fixation” by the silicon-containing crosslinking agents.

It is of interest that the rigidity of cryoPVAGs prepared without addition of TMOS and frozen at one of

the temperatures over the range of -18 to -30°C was changed only by 5–15%, whereas strengthening of composite H-cryoPVAGs was increased by a factor of several times. Besides, the differences in the r values for samples formed at these temperatures of cryostructuring increased progressively with the concentration of TMOS [Fig. 4(a,b)]. So, it enables to infer that cryoconcentration of substances in ULMP with lowering the temperatures of cryogenic process facilitated significantly the binding phenomena of organosilicon cross agents with PVA (Scheme 2).

The next important parameter influencing the properties of cryoPVAGs is the thawing rate. It is well known that decreasing the rate of thawing of the moderately frozen solutions of polyol polymers (capable of forming physical (noncovalent) cryogels) results in the stronger and more heat resistant specimens.^{2,4,8–10,12,36,47} Usually such effect of the defrosting dynamics is explained by a very high viscosity of ULMP; therefore, rather long time is required for realizing the large enough amount of stable intermolecular contacts.^{2,4,48} In the case of cryoPVAGs with the highest efficiency, these processes proceed in the vicinity of -2 to -3°C .⁴⁶ This means that the lower the thawing rate, the longer time the system resides within such "optimal" region of negative temperatures.

The data presented in Table IV indicate that slow thawing of the samples, which were frozen at various temperatures upon the preparation of cryoPVAGs without TMOS additives, resulted in considerable increase in gel strength. In particular, the normalized (regarding the respective lowest shear modulus) r_0 and r_{30} values for cryoPVAGs prepared by freezing at -20°C and then thawed with the rates of either 0.3, or 0.03 or $0.003^{\circ}\text{C}/\text{min}$ have varied as follows: 1, 2.03, 3.29 and, respectively, 1, 1.82, 2.11. That is, the effect was stronger pronounced concerning r_0 rather than r_{30} . It means that the decrease in thawing rate mainly facilitated the growth of elasticity of cryoPVAGs. On the contrary, for the composite H-cryoPVAGs the tendency was somewhat another. Although, likewise the case of cryoPVAGs, the absolute values of G_0 and G_{30} for H-cryoPVAGs also increased with slowing the thawing rate (Table IV), the trends of variation in the r_0 and r_{30} reduced values differed from cryoPVAGs. Thus, composite samples prepared from the feed with maximum TMOS concentration ($[\text{TMOS}] : [\text{PVA}] = 0.7 : 1$), frozen at -20°C , and thawed with the rates of 0.3, 0.03 or $0.003^{\circ}\text{C}/\text{min}$ had values r_0 and r_{30} equal to, correspondingly, 1, 1.28, 1.56 and 1, 2.03, and 2.31. That is, here the effect was stronger pronounced for r_{30} . This evidently means that in the case of H-cryoPVAGs, a decrease in thawing rate right now greater influenced on the plastic behavior of such gel matrices. In other words, entrapment of the particles of inorganic discrete phase into the matrix of PVA cryogel and simultaneous crosslinking of the polymeric

network of continuous phase by the silicon-containing oligomers not only increased the rigidity of final gel materials, but also changed their elasticity/plasticity balance.

In this respect, it is of interest to analyze the data in Figure 5 demonstrating the effects of thawing rate on the r_0 and r_{30} values normalized relatively to the corresponding lowest shear modulus for cryoPVAG samples defrosted with every particular rate. One can see [Fig. 5(a)] that increasing the initial TMOS concentration exerted strong influence on the elastic properties of H-cryoPVAGs in the case of fast thawing, whereas at slow defrosting this effect was not so manifested. For example, H-cryoPVAGs formed from the feed with $[\text{TMOS}] : [\text{PVA}] = 0.7 : 1$, frozen at -20°C and thawed off with the rates of 0.3, 0.03 or $0.003^{\circ}\text{C}/\text{min}$ had r_0 values equal to 5.53, 3.48 and 2.63, respectively. This demonstrates a very strong influence of the thawing conditions on the "intensity" of elasticity growth,

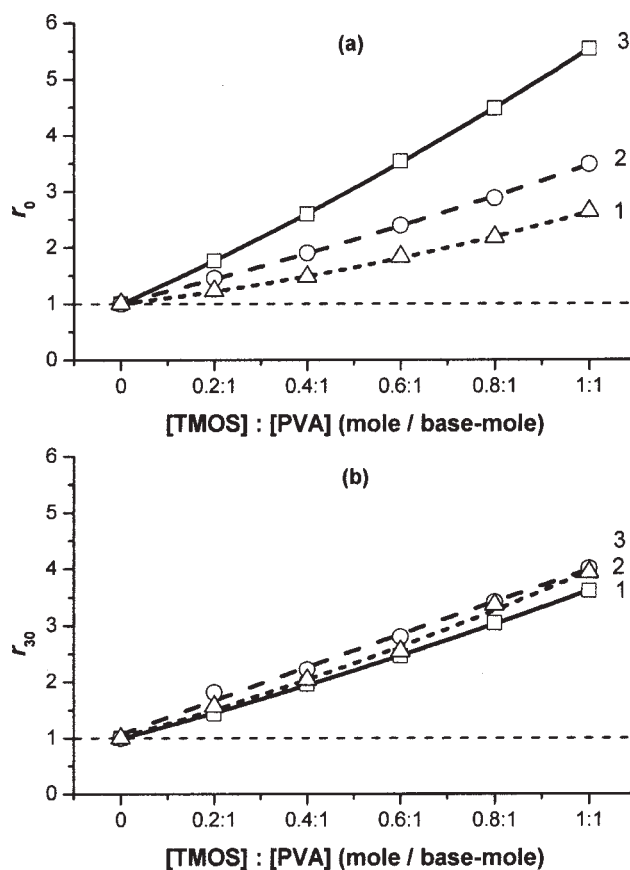


Figure 5 Dependences of normalized r_0 (a) and r_{30} (b) values on the initial $[\text{TMOS}]/[\text{PVA}]$ ratio for H-PVAGs prepared, when frozen ($-20^{\circ}\text{C}/12$ h) samples were thawed out with the rates of $0.3^{\circ}\text{C}/\text{min}$ (1), $0.03^{\circ}\text{C}/\text{min}$ (2), and $0.003^{\circ}\text{C}/\text{min}$ (3). Conditions of cryostructuring: PVA concentration in the initial water/PVA/TMOS system 93.4 ± 0.2 g/L; freezing at -20°C for 12 h; every r parameter was computed assuming as the unity the lowest G value for respective (the same thawing rate) cryogel prepared without TMOS additives.

which was induced by filling and, in parallel, cross-linking of such composite cryogels. At the same time, it turned out that variation of plastic characteristics of H-cryoPVAGs with increase in initial TMOS concentration did not virtually depend on the thawing rate within the studied its interval [Fig. 5(b)].

Therefore, the following two questions can be formulated:

- i. Why, as a matter of fact, the thawing rate of frozen system water/PVA/TMOS influenced the physicochemical properties of final composite H-cryo-PVAGs? Indeed, if the fixation of polymeric chains with organosilicon cross agents occurs in ULMP, such an influence has not to be observed in a similar way to synthesis of covalently-linked cryogels,⁴ when the 3D network is formed during prolonged incubation of the system in a moderately frozen state. Therefore, the rate of subsequent thawing does not practically affect the properties of the resulting chemically-linked cryogel.
- ii. The second question: what is the reason for different influence of thawing rate on the elastic and plastic characteristics of composite H-cryoPVAGs with increasing TMOS concentration in the initial systems? In other words, what is the reason for the differences between the plots in Figure 5(a,b)?

To answer these questions, let us consider the following facts.

Firstly, it is known that the formation of 3D network of traditional cryoPVAGs, i.e., those prepared by the freeze-thaw treatment of aqueous PVA solutions, occurs quite in the course of thawing of frozen samples.^{2,4,36,48,49} On the other hand, if the thawing process is carried out with a high enough rate (around 5–10°C/min and faster), the cryogel is not formed at all, because a rather slow sol-gel transition requires long time, as the gel-formation proceeds in the ULMP possessing very high viscosity. Besides, at high thawing rates, the water from the melting ice progressively dilutes ULMP, and the polymer concentration quickly becomes lower than the critical gelation concentration. At the thawing rate equal to, for instance, 3°C/min, the system under defrosting “passes through” the interval of negative temperatures from –3°C to 0°C for only 1 min, i.e., for a very short while. At the thawing rate of 0.3°C/min this time is 10 min, at the thawing rate of 0.03°C/min it is 1 h 40 min, and at the thawing rate of 0.003°C/min nearly 17 h. Quite such an elongation is known to result in the higher efficiency of PVA cryotropic gelation (the increase in yield of the gel-formation process is observed).⁴⁸

Secondly, upon the entrapment of preliminary prepared (rather than formed *in situ* from the TMOS) silica particles in the matrix of PVA cryogel no “additional” (plus to the influence of thawing rate) effects were detected: decreasing the thawing rate has increased the rigidity of both filled and nonfilled samples at the same extent.³⁸ Hence, different slopes of the curves in Figure 5(a) were not the consequence of the presence of dispersed filler in the gel matrix. These differences testified to the apparent interrelation in between the thawing regimes and the already discussed crosslinking reactions caused by the silicon-containing oligomeric products of TMOS hydrolytic polycondensation.

Then, in the third place, it can be inferred that the processes of formation of physical network of PVA cryogel occur in parallel (but with different rates) with binding of organosilicon cross reagents and PVA macromolecules (as well as their associates and network elements) exactly when such complex multicomponent reaction system is thawed off. Otherwise, if the crosslinking agents will “complete their work” at essential extent yet in the course of freezing or incubation the system frozen, no noticeable influence of the thawing rate should be observed. Apparently therefore, that is because of simultaneous action of the two processes (the formation of physical network of the cryogel and its “fixation” by the silicon-containing crosslinking species), the cross agents play a dominating role at relatively fast thawing rates (e.g., 0.3°C/min). This is because, rising of noncovalent intermolecular contacts polymer–polymer and the formation of physical junction knots of the network (the microcrystallinity zones) do not have time to occur till a significant degree. Just in this case, the higher the TMOS concentration, the stronger the effect of the crosslinking molecules in respect to increase in rigidity of composite H-cryoPVAGs (Table IV) and in rise of respective r_0 values [Fig. 5(a), line 1]. On the contrary, at slower thawing (in our experiments at 0.03 and, especially, 0.003°C/min) the processes of the formation of physical network have already enough time to proceed significantly deeper. As a result, the influence of organosilicon cross agents is descended, as the main contribution to the integral mechanical properties of the final material is right now determined by the physical junction knots of the polymer network, i.e., by the microcrystalites (by their amount and average length of ordered segments) formed during the prolonged residing the system within the temperature zone of the most favorable for PVA cryotropic gelation (see above).

As for the difference in the character of r_0 and r_{30} depends on the initial TMOS concentration [Fig. 5(a,b)], we believe that such a difference was because of the already discussed influence of Si-containing cross agents on the flexibility of PVA chains. Since this

property is responsible for the plastic behavior of the samples, a decrease in chain flexibility caused by crosslinking should result in the decrease in plasticity of the gel material on the whole. Inasmuch as the variation of the thawing rate by two orders of magnitude (from 0.3 to 0.003°C/min) did not have effect on corresponding dependences of r_{30} on TMOS concentration [Fig. 5(b)], it could be inferred that the rate of crosslinking processes that occurred with the participation of soluble products of TMOS hydrolytic polycondensation has exceeded the rate of the formation of physical junction knots (the microcrystallinity zones) in the cryoPVAGs. That is why, even a slow thawing (i.e., prolonged residence of the yet frozen system over the temperature range being optimal for PVA microcrystallization) was unable to influence considerably the segmental motion of the polymer chains blocked by the crosslinks. Another argument in favor of the higher rates of the cross agent/PVA binding as compared to the PVA-PVA interactions can be the structure (b) shown in Scheme 2, as the formation of highly polarized hydrogen bonds between hydroxyl and silanol groups (i.e., the formation of H-bonds approximated to the properties of ionic bonds) is a fast process likewise the ionic reactions, in general.

CONCLUSIONS

This article describes a novel type of polymer gel-heterophase (composite) hybrid organic-inorganic cryoPVAGs, which is formed as a result of freezing-thawing of aqueous PVA solutions with additives of TMOS. The main structural features of these gel materials are their macroporosity and the presence of the particles of dispersed silica filler. The latter ones are entrapped in the matrix of the continuous phase, which, in turn, is the supramolecular PVA physical network, which is supposed to be additionally fixed by the silicon-containing crosslinking oligomeric products of TMOS hydrolytic polycondensation. Such organic-inorganic cryogels are, simultaneously, the composite materials (because of the presence of discrete phase) and the hybrid systems (as the gel-forming polymer and Si-containing moieties belong to the content of gel phase). The complex multicomponent and heterophase structure of composite H-cryoPVAGs differs them cardinally from the known apparently homophase hybrid hydrogels formed upon the addition of tetraalkoxysilanes (including TMOS) in to the aqueous solution of poly(*N*-vinylamides),^{33,34} and also from the composite cryoPVAGs merely filled with dispersed silica,³⁸ in which continuous phase does not differ chemically from that in nonfilled cryoPVAGs. Because of combining in the same material of the properties inherent in filled cryoPVAGs and of the hybrid organo-inorganic nature of the addition-

ally linked continuous phase, composite H-cryoPVAGs acquire a set of novel qualities. Namely, rigidity and heat resistance of these gels are substantially increased. Such effects for polymer cryogels, in general, and for cryoPVAGs, in particular, were unknown earlier and revealed for the first time.

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