Study of Cryostructuration of Polymer Systems. XV. Freeze–Thaw-Induced Formation of Cryoprecipitate Matter from Low-Concentrated Aqueous Solutions of Poly(vinyl alcohol)

LILIJA G. DAMSHKALN, IRINA A. SIMENEL, VLADIMIR I. LOZINSKY

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov st.28, 117813 Moscow, Russia

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ABSTRACT: Freeze–thaw treatment of low-concentrated ($<C^*$) aqueous solutions of poly(vinyl alcohol) (PVA) results in the formation of a cryoprecipitate fraction. It is shown that the efficiency of such a process (the yield of PVA cryoprecipitation) depends on the initial polymer concentration in the solution to be frozen and the conditions of a cryogenic influence. The key factor is defrostation dynamics: The slower the thawing rate, the higher the cryoprecipitation yield. The iodine-staining method is employed for the quantitative analysis of PVA concentrations in the solutions under study and the necessity of the use of reduced (0–2°C) temperatures throughout such a PVA quantification is demonstrated. Observation of the kinetics of the freeze–thaw-induced formation of cryoprecipitate matter reveals the extreme character of the temperature dependence of the efficacy of PVA macromolecule aggregation, the extreme point being situated in the vicinity of −2°C. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1978–1986, 1999

Key words: poly(vinyl alcohol) (PVA); low-concentrated water solutions; freeze–thaw-induced precipitation; thermal stability of PVA–iodine complexes

INTRODUCTION

It is well known that aqueous solutions of poly(vinyl alcohol) (PVA) undergo physical changes as a result of their freezing, frozen storage, and subsequent thawing. Such cryogenic treatment of concentrated PVA solutions gives rise to gel formation (causes the formation of the so-called PVA cryogels[1]), whereas solutions of low polymer concentration are capable of separating of the PVA-rich microgel phase from the initially (before freezing) homogeneous samples after the defrostation of the respective frozen specimens.[2–5] While various peculiarities of the cryotropic gelation of concentrated PVA solutions were thoroughly investigated (for review, see refs. 1, 6, and 7), only limited data were obtained in the early studies accomplished around 30 years ago in respect to the freezing–thawing influence on dilute and semidilute PVA solutions. Thus, Labudzińska and Ziabicki,[2,3] and somewhat later Peppas,[4] using a light-scattering technique, observed the promoting effect of cryogenic treatment on the association of macromolecules in such systems. The freeze–thaw-induced variations of the viscosity characteristics of similar solutions and the formation of the cryoprecipitate fraction was described by Khukhrachik and Baramboim.[5] At the same time, more detailed knowledge on the freeze-induced aggregation of PVA macromolecules in dilute and semidilute solutions of the polymer is required, not only for information on

Correspondence to: V. I. Lozinsky.

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the freeze/thaw stability/instability of these low-concentrated systems, but also for better understanding of the fine mechanisms of the early stages of the formation of PVA cryogels. This is due to that the processes of the initial association of individual chains to each other, then the aggregation of the associates (clusters), and, further, their involvement in formation of the microgel phase undoubtedly participate in the subsequent "constructing" of a supermolecular network of such heterogeneous gel materials as PVA cryogels. Therefore, the goal of the given investigation was to study the basic characteristic features of the freeze–thaw behavior of low-concentrated aqueous PVA solutions with impact on the dynamics of the cryogenically induced formation of a polymer-rich cryoprecipitate fraction.

EXPERIMENTAL

Materials

PVA, 100% hydrolyzed, average MW 115,000 (Aldrich Chemical Co., Milwaukee, WI) was used in the work without additional purification. This PVA batch had a viscosity-average molecular weight of 138,000 ± 2100 as was determined by capillary viscometry with a Ubbelohde-type viscometer (25°C, water, $[\eta] = 5.95 \times 10^{-4} M_{\eta}^{0.63}$).[8] The crystalline iodine and potassium iodide employed for the determination of the PVA concentration were purchased from Reakhim (Russia); they were a "chemically pure" grade. All solutions were prepared with deionized water.

Methods

Initial solutions of the polymer (PVA concentration in the range of 0.1–1.0 g/dL) were prepared by the suspending a weighed amount of the dry polymer powder in the required volume of deionized water and storing these mixtures overnight at room temperature to swell the polymer, followed by their dissolution by heating the samples in a boiling water bath for 90 min with stirring. The loss of the liquid due to evaporation was determined by weighing the samples and then was compensated by the addition of the required amount of pure water. The solutions thus obtained were filtered through a sintered glass filter for the removal of possible insoluble admixtures, and the filtrate was, after cooling to room temperature, used in the experiments.

Cryogenic treatment of the samples was accomplished as follows: Five-milliliter portions of the freshly prepared PVA solutions were poured into glass vials of 15-mL capacity, closed with plastic stoppers, and immersed into the liquid coolant (ethanol) of the chamber of a precision cryostat FP 45 HP (Julabo, Germany), where the preassigned negative temperature was already maintained. After the incubation of the samples under these conditions for the desired time, the defrostation with the thawing rates of 0.03 and 0.3°C/min was carried out using the microprocessor-controlled facilities of the cryostat. A faster defrostation of the samples was accomplished by immersion of the frozen specimens into the water thermostat at 40°C. In this case, as was determined in the preliminary tests, the thawing rate was of the order 3°C/min, and the thawing proceeded for no more than 6 min. In the subsequent discussion, these three thawing regimes will be termed "slow," "moderate," and "fast" defrostation. The thawed-out samples usually represented themselves as opaque heterogeneous systems with cryoprecipitate small particles (microgel fraction) suspended within the liquid bulk. These samples were then processed at a temperature which did not exceed 20°C. The insoluble matter was separated by centrifugation at 3500 rpm for 15 min with a K 23 D centrifuge (MLW, former GDR), and the aliquots of the transparent supernatant were taken for quantification of the PVA content. The yield of the cryoprecipitation process was calculated as $[(C_0 - C_t)/C_0] \times 100\%$, where C_0 is the initial PVA concentration in the solution before the cryogenic treatment, and C_t, the polymer concentration in the supernatant of a sample taken for analysis after frozen storage for a particular time t.

Concentrations of PVA in the solutions under study were determined essentially in accordance with the iodine-staining method described by Imai and Matsumoto.[9] Certain modifications in the procedure, which were necessary to implement, are discussed below. Concentrations of I_2 and KI in the reagent solution were 2×10^{-3} and 8×10^{-3} mol/L, correspondingly. Photometric measurements were performed with a UV-VISspectrophotometer Model 557 (Hitachi, Japan).

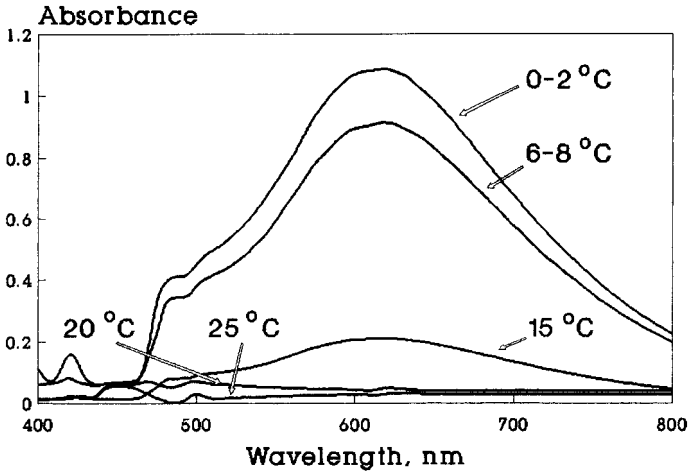

Figure 1 Absorption spectra of the solutions of PVA/iodine complexes stored for 24 h at various temperatures (indicated by the arrows toward the curves).

RESULTS AND DISCUSSION

Determination of PVA Concentration in the Solutions Under Study

To obtain the quantitative pattern of the features of PVA cryoprecipitation depending on the conditions of cryogenic treatment, the residual amount of soluble polymer in the supernatants after separation of the liquid and insoluble phases by centrifugation of the thawed-out heterogeneous suspensions were measured (see Experimental). For this aim, we tried to utilize the iodine-staining method known for decades.[9–12] In this case, the aliquot of the PVA solution to be analyzed is mixed with an equal volume of the I_2/KI reagent solution, and then a green–blue color is developed upon incubation of the reaction mixture for about 1–3 days.[9] Visible light absorption at the wavelength in the vicinity of 600 nm should be proportional to the PVA concentration for the low-concentrated ($\leq$0.5 g/dL) polymer solutions. It was recognized[10–12] that the major factors affecting such a photometric analysis were as follows: PVA molecular weight, the amount of residual *O*-acyl groups, the presence of 1,2-glycol units, and, as was recently again clearly proved by Matsuzawa and coworkers,[13,14] the stereoregularity of the polymer, that is, its tacticity. The latter authors observed the formation of blue iodine–PVA complexes for syndiotactic-rich brands of the polymer and the absence of similar complexes for common atactic commercial PVAs provided for the analysis conducted at 30°C. At the same time, Imai and Matsumoto, whose procedure was used throughout our studies, detected[9] these blue complexes for the atactic PVA when the analyses were carried out in the vicinity of room temperature. Indeed, during our experiments, when the temperature in the laboratory rooms rose higher than 18–20°C, we failed to obtain the blue color of the PVA/iodine reagent mixtures at all, and at 15–18°C, the results of the photometric measurements were very poorly reproducible. This testified to the necessity to research the influence of temperature on the spectral characteristics of the products of such an analytical reaction. The data obtained are depicted in Figure 1 as absorption spectra (visible wavelengths) of the identical (in respect to the composition) samples incubated at different temperatures for 24 h after the mixing of identical aliquots of 0.5 g/dL of the PVA solution and the I_2/KI reagent solution.

Very negligible absorbance around 600 nm of the solutions incubated for 1 day at 25 and 20°C is seen, whereas analogous solutions being kept for the same period at low positive temperatures (at 6–8°C in a refrigerator, at 0–2°C in a ice-water bath) showed pronounced absorption with maxima at 610–620 nm. The spectrum of the sample stored at 15°C showed the "intermediate" position. These results clearly pointed out, on the one hand, the possibility of using the iodine-staining procedure for quantitative determination of the concentration of atactic PVA in the respective solution and, on the other hand, the necessity of strictly controlling the temperature regimes during accomplishment of this analysis. Therefore, in the course of further studies, we manipulated the

Table I Yield of a Cryoprecipitate Depending on the Initial PVA Concentration

Initial PVA Concentration in the Solution to be Frozen (g/dL)	Conditions of the Cryogenic Treatment			Yield of a Cryoprecipitate (%)
	Freezing/Frozen Storage Temperature (°C)	Frozen Storage Duration (h)	Thawing Rate (°C/min)	
0.1	−20	24	0.3	51.8 ± 1.6
0.25				53.2 ± 1.0
0.5				58.1 ± 1.5
0.75				55.9 ± 1.3
1.0				53.9 ± 1.7

samples of the PVA/iodine reagent mixtures only under ice-water bath conditions. In this case, the experimental error of the quantification of the PVA concentration did not exceed 5–8%. For more reliable results, all the analyses were repeated no more than three times.

Influence of the Cryogenic Treatment Parameters on the PVA Cryoprecipitation Efficacy

Capillary viscometry allowed us to determine the value of the intrinsic viscosity of the PVA used in this work; $[\eta]$, thus, was found equal to 1.03 ± 0.01 dL/g for the water solvent at 25°C. Based on this value, the magnitude of the critical concentration ($C^* = 1/[\eta]$) of the transition from dilute to semidilute solutions of this particular polymer was easily computed as 0.97 ± 0.01 g/dL. Hence, in the PVA concentration range of 0.1–1.0 g/dL, we dealt virtually with the dilute solutions of the polymer. For this case, the influence of the initial PVA concentration on the yield of the microgel fraction (cryoprecipitation efficacy) is illustrated by the data of Table I.

At the beginning, it should be noted that no precipitation or even dimness of these dilute PVA solutions was observed after their nonfrozen incubation for 24 h at 20–25 and 2–4°C, and only the cryogenic treatment gave rise to the formation of an insoluble matter—in this particular case, cryoprecipitates (PVA concentration ≤ 0.5 g/dL) or a very weak cryogels (PVA concentrations of 0.75 and 1.0 g/dL). Nonetheless, the latter were very strongly compacted by the centrifugation, thus producing a large amount of a transparent, supernatant polymer concentration in which could be easily determined by the iodine reaction.

These results demonstrate one of the fundamental effects inherent in the processes of cryotropic gel formation, in general, namely, the apparent decrease in the critical concentration of gelation as compared to the gelling behavior of solutions of the same gelling agents at positive temperatures. The major reason for such an effect has been recognized[1,15] to be cryoconcentrating phenomena, that is, increase in the solute concentration in unfrozen regions of the system's bulk. These unfrozen inclusions are termed the "unfrozen liquid microphase,"[16,17] where the prefix "micro-" reflects the fact that such a phase constituted only a minor portion of the volume of a solid macrofrozen sample (for nondeeply frozen concentrated water–PVA solutions, the volume of the unfrozen liquid microphase was found to be several percent).[18,19] Due to similar cryoconcentrating effects, the entanglement and associative interactions of the PVA chains are promoted, thus favoring the intermolecular H bonding and the formation of the microcrystallinity zone.[1]

The influence of the initial PVA concentrations in the range studied in this work was of extreme character: From 0.1 to 0.5 g/dL, the yield of the cryostructuration process increased and then began to somewhat decrease (Table I). It is thought that a similar observation may be explained as follows: When the final cryostructurate represented separated particles of the cryoprecipitate matter, the hindrance for molecular aggregation existed only within the boundaries of each particle, but when the cryogelation threshold (>0.5 g/dL) was overcome, the additional hindrance arose for the diffusional movements of the macromolecules and their kinetic segments because of the interfering influence of the spatial network formed. Therefore, above the gel-point concentration, certain inhibition of the association phenomena took place. Based on these data, we used, throughout the subsequent studies, the solutions of PVA containing the polymer in the amount of 0.5 g/dL.

Table II Influence of the Freezing/Frozen Storage Temperature on the Yield of PVA Cryoprecipitation

Initial PVA Concentration in the Solution to be Frozen (g/dL)	Conditions of the Cryogenic Treatment			Yield of a Cryoprecipitate (%)
	Freezing/Frozen Storage Temperature (°C)	Frozen Storage Duration (h)	Thawing Rate (°C/min)	
0.5	−10	24	0.3	39.1 ± 0.5
	−20			58.1 ± 1.5
	−30			44.6 ± 3.4

As for the influence of the freezing/frozen storage temperature on the yield of the cryoprecipitation process, it was found that the temperature dependence of the efficiency of the formation of the microgel fraction for the range from −10 to −30° C was of extreme character (Table II), thus indicating a certain effect of this cryogenic treatment parameter on the association of the PVA macromolecules in the unfrozen liquid inclusions of the macrofrozen solid samples.

Interestingly, earlier, it was shown[20–22] that upon the freeze–thaw-induced formation of PVA cryogels on the basis of concentrated (>5 g/dL) aqueous solutions of the polymer the gel's strength and thermostability also depended on the freezing temperature in an extreme fashion when the frozen storage duration was 18–24 h, that is, practically the same conditions as we used in the present study. Such similarity in the trends observed evidently pointed to the analogous mechanisms of the processes resulting in the formation of both PVA cryogels (originating from the concentrated initial solutions of the polymer) and the PVA microgel phase (when the low-concentrated polymer solutions were subjected to a cryogenic treatment). In other words, more exactly, the temperature of the frozen storage and, hence, the amount of the unfrozen liquid microphase and solute content therein first influence the efficiency of the primary aggregation of the PVA macromolecules into the "germ" clusters, and the extent of this aggregation, in turn, further is reflected on the yield of microgel particles precipitated from the frozen–thawed dilute PVA solutions, or, in the case of cryogenic treatment of concentrated solutions of the polymer, on the physical characteristics of the PVA cryogels formed. In addition to these data, the similarity of the mechanisms under discussion is also confirmed by the results of the experiments, where the influence of the thawing rates on the yield of the microgel fraction was investigated (Table III).

The necessity to perform such tests was caused by the known importance of the defrostation dynamics for the efficiency of the cryotropic gelation of concentrated PVA solutions, virtually determining all physicochemical characteristics of the gel materials produced[23–25] and the yield of the gel fraction upon their formation.[26] In general, the faster the thawing-out of the frozen samples, the less strong and lower-fusible PVA cryogels obtained and the smaller the gel-fraction yield, and if the thawing rate exceeded about 10°C/min, no gel formation took place at all.[23] It might be well to note that such an effect of the thawing rate on the formation of physical thermoreversible

Table III Influence of the Thawing Rate on the Yield of PVA Cryoprecipitation

Initial PVA Concentration in the Solution to be Frozen (g/dL)	Conditions of the Cryogenic Treatment			Yield of a Cryoprecipitate (%)
	Freezing/Frozen Storage Temperature (°C)	Frozen Storage Duration (h)	Thawing Rate (°C/min)	
0.5	−20	24	~3	11.8 ± 0.6
			0.30	58.1 ± 1.5
			0.03	77.8 ± 0.8

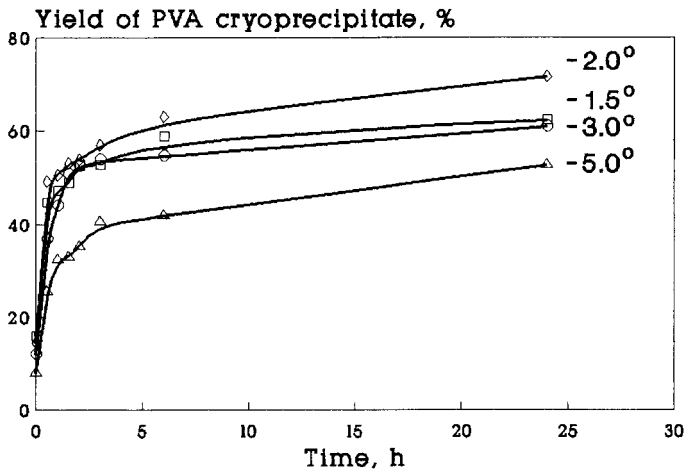

Figure 2 Dynamics of the formation of PVA cryoprecipitates during the incubation at subzero temperatures of 0.5 g/dL PVA water solutions initially frozen for 24 h at −20°C.

cryogels (not only on the basis of PVA, but also other polymers capable of similar gelation, e.g., gelatin or agar)[27] is typical for the processes of noncovalent cryostructuration in general.[1,15] From the data of Table III, one may see that, in fact, the same influence of this cryogenic treatment parameter (i.e., the rate of thawing) was exerted on the efficacy of the formation of the microgel phase upon the freezing–thawing of low-concentrated PVA solutions: The faster the defrostation rate, the lower the yield of the polymer cryoprecipitate.

Dynamics of the Formation of PVA Cryoprecipitate Fraction

To determine the optimum freezing–thawing regimes capable of providing the most favorable conditions for the "cryoassociation" of PVA macromolecules during the cryogenic influence on the low-concentrated aqueous solutions of the polymer, the following experiments were conducted:

Five-milliliter portions of the 0.5-g/dL PVA solution were frozen at −20°C for 24 h, and then the temperature in the cryostat chamber was increased until it reached one of the preassigned subzero temperatures in the range of −5 to −1.5°C (at −1°C, some of the samples often thawed-out, and, therefore, the reproductivity of the results was very low). The increasing rate of the temperature was ≈1.5°C/min; this value was the highest possible rate supplied with the instrument's own heater. Further, the temperature was maintained at the specified level during the subsequent 24 h, and three frozen samples were taken periodically from the cryostat chamber, placed into the water thermostat at 40°C for "fast" defrostation, and, afterward, the yield of the microgel fraction in them was determined in accordance with the procedure described in the Methods section. Such an experimental protocol allowed us to obtain the profiles (Fig. 2) of the "evolution" of the cryoprecipitation processes at every temperature in the above-indicated subzero range, where major gelation phenomena were earlier recognized[23] to occur during the formation of PVA cryogels from concentrated solutions of the polymer.

First, it turned out that, in reality, the formation of the microgel fraction occurred very slightly below −5°C, since the 24-h incubation at −20°C and subsequent short-term heating of the frozen system up to −5°C gave rise to a cryoprecipitate yield only of 7.9 ± 0.4%, that is, approximately 8% (the point "0 h" onto the curve "−5°C"). Hence, one may conclude that the final yield values of ≈58 and ≈78% reached, when the thawing rates of 0.3 and 0.03°C/min were employed for the defrostation of the frozen samples stored at −2°C for the same 24 h (Table III), were mainly the result of the residence of these specimens between −5 and ≈0°C in the course of "moderate" and "slow" thawing, that is, the processes of the association of the PVA macromolecules were mainly manifested just in this range of "high" negative temperatures.

In this respect, it was of interest to trace the behavior of PVA macromolecules of various lengths (degree of polymerization) in the course of such an association, resulting in the formation of

Table IV Variation of the Molecular Weight Characteristics of PVA Dissolved as a Results of Cryoprecipitation of the Polymer

Initial PVA Concentration in the Solution to be Frozen (g/dL)	Conditions of the Cryogenic Treatment					Yield of a Cryoprecipitate[a] (%)	$[\eta]$[b] (dL/g)	M_η (Calculated)[c] (kDa)
	First Stage		Second Stage		Thawing Rate (°C/min)			
	Temperature (°C)	Time (h)	Temperature (°C)	Time (h)				
0.5	—	—	—	—	—	—	1.03 ± 0.01 (0.995)	138.0 ± 2.1
	−20	24	—	—	~ 3	11.8 ± 0.6	1.02 ± 0.02 (0.994)	136.0 ± 4.3
			−1.5	0.5		44.7 ± 1.1	0.96 ± 0.02 (0.990)	129.7 ± 2.1
				24		62.2 ± 0.8	NA	NA

NA: Data not available since PVA concentration in the supernatant liquid was low enough for the reliable determination of $[\eta]$ values.

[a] See also curve "−1.5°C" in Figure 2.

[b] The supernatant liquids before viscosity measurements were heated in sealed ampules for 20 min in a boiling water bath to thermally dissociate soluble PVA aggregates; the polymer concentrations in these liquids were determined by the iodine-staining method.

[c] $[\eta] = 5.95 \times 10^{-4} M_\eta^{0.63}$ (25°C, water)[8]; nos. in parentheses are the coefficients of determination found upon mathematical treatment of experimental data with the least-squares method.

the cryoprecipitate fraction. For this purpose, the intrinsic viscosities of PVA in the initial solution and, for the sake of comparison, in the supernatant liquids after their separation from the insoluble matter of the cryogenically treated samples were measured with a capillary viscometer. The data presented in Table IV clearly show that the incubation of a 0.5-g/dL PVA–water solution in the frozen state at −20°C for 24 h followed by fast thawing, which gave rise to a low cryoprecipitation yield (≈12%, Table III), also did not virtually result in the variation of molecular weight characteristics of the gelling polymer. At the same time, even 0.5-h subsequent storing of the identical samples at −1.5°C resulted not only in a significant increase in the cryoprecipitation yield (≈45%, curve "−1.5°C" in Fig. 2), but in a certain decrease in the viscosity-average molecular weight of the PVA remaining in the dissolved state. This evidently testified that upon the formation of cryoprecipitates they were somewhat enriched with the higher molecular fractions presented in the initial polymer and the lower molecular fractions inserted into the insoluble matter to a lesser extent.

The curves in Figure 2 also show that with the highest rate the increase in the yield of the microgel fraction occurred at −2°C; even 0.5°C above and 1°C below this temperature the efficiency of the process under consideration was lower, and at −5°C, the final (after the 24-h-incubation) yield of the precipitated matter was 52.7 ± 0.9% as against the value of 71.6 ± 2.4% at −2°C. This obviously testified to the extreme character of the temperature dependence, which was inherent in the dynamics of microgel fraction formation in the unfrozen liquid microphase of such a system. In this respect, the data of Figure 3 serve as a pictorial illustration of a similar extreme dependence (here, the values from Fig. 2 on the microgel phase yielded at various stages of the cryostructuring were redrawn as a function of the incubation temperature). The digits near the right side of the corresponding curves show the time after the commencement of such an incubation. The bottom curve "0 h" refers to the points when the temperature in the cryostat chamber reached the incubation temperature, and the small digits near these points show how many minutes have elapsed from the beginning of heating of the respective frozen samples from −20°C (freezing temperature) to the particular incubation thermal conditions.

These data demonstrate the intensities of the formation of the PVA microgel fraction in the subzero temperature range: When the temperature was increased from −5 to −2°C at the rate of 1.5°C/min, the yield values grew around twofold

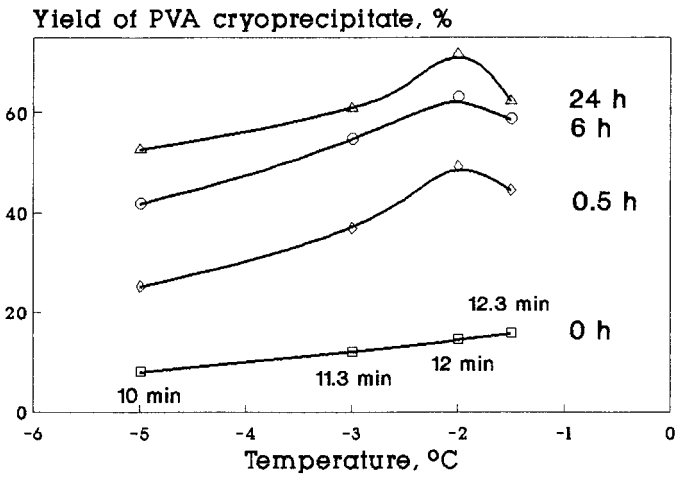

Figure 3 Temperature dependencies of the yield of the cryoprecipitation process at different stages of incubation of the frozen samples at subzero temperatures.

only for 2 min from 7.9 ± 0.4 to 14.4 ± 0.6% (curve "0 h"), and already during the 0.5-h incubation of the samples at the most favorable temperature (−2°C, the vicinity of the extreme points for all the curves in Fig. 3), the yield values reached 49.3 ± 0.5%. In other words, this meant that upon the defrostation stage, when the temperature of the still frozen sample reached this subzero region, the association of PVA chains in the unfrozen microphase was accelerated considerably.

Earlier, with NMR and ESR studies, it was recognized[18,19] that just in the vicinity of −7 to −5°C below the melting point of similar frozen-water–PVA systems, the major amount of a fluid solvent disappeared (solidified) and an apparent boundary of the retardation of intense segmental mobility of the PVA macromolecules dissolved in the nonfrozen liquid portion of the water which also was at these temperatures. Therefore, one obviously may conclude that the above-mentioned acceleration of the microgel formation was the consequence of a certain increase in the amount of the liquid solvent and of the intensification of thermal movements of the segments of the polymeric chains, resulting in pronounced interchain interactions when a defrosting sample turned out at temperatures exceeding −7 to −5°C. It, therefore, meant that for effective (from the viewpoint of PVA aggregation) intermolecular interactions, the necessary condition was not only the freeze-induced concentrating of the polymer in the unfrozen microphase, but also the existence here of a large enough amount of a liquid solvent being the medium, where the thermal movements of the chains' segments in a very viscous environment were able to proceed. On the other hand, above −2°C, but still before melting of the sample as a whole physical body, the already-thawed-out solvent appeared to be the diluent of the unfrozen microphase in respect to the polymer, thus diminishing the probability of the entanglement of chains and intermolecular association. Such competition between these factors was responsible for the extreme temperature dependencies (Fig. 3) observed in this experiment.

CONCLUSIONS

The preparation of high-modulus PVA cryogels as a result of the freeze–thaw treatment of concentrated solutions of the polymer attracts significant attention from both scientific and practical viewpoints, because these gel materials are of increasing interest for biotechnological and biomedical applications.[1,6,7,28,29] At the early stages of the formation of similar cryogels, the association of PVA macromolecules into the primary clusters, their aggregation into microgel grains, and subsequent building of more large particles should influence the properties of a resultant macrogel, since the former structured ones perform as the "primary bricks" upon the formation of a gel in the total bulk of the system. The studies of the effects of cryogenic treatment on the low-concentrated PVA solutions allowed us to model these early stages of cryogel formation. The data obtained have soundly demonstrated that with the highest efficiency such polymer–polymer associative processes in these frozen water–PVA

systems took place in the subzero temperature range, especially in the vicinity of −2°C. Now, we are studying the kinetics of cryotropic gelation of the more concentrated solutions of this polymer in order to elucidate the commonness of the regularities observed in a wide range of the initial PVA concentrations. The results will be reported in subsequent publications of this series.

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