

# Study of Cryostructuration of Polymer Systems. XIV. Poly(vinyl alcohol) Cryogels: Apparent Yield of the Freeze–Thaw-Induced Gelation of Concentrated Aqueous Solutions of the Polymer

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**ABSTRACT:** Poly(vinyl alcohol) (PVA) cryogels, which are formed as a result of freeze–thaw treatment of concentrated solutions of the polymer, were studied in respect to the amount of gel and sol fractions in these heterogeneous macroporous gel materials depending on the conditions of the thawing step of similar cryotropic gelation. It was shown that the yield of gel fraction (the efficiency of the gelation process) was not quantitative; this was controlled by the initial PVA concentration in the solution to be frozen, and to a higher extent, by the thawing rate, when the yield increased with slowing of the defrostation process. The sol fraction could be extracted from the PVA cryogels by their rinsing with water at room temperature; the extraction of the sol was accompanied with the variations of the swelling parameters of the gels (initial slight upswelling and subsequent gradual deswelling), as well as with analogous, in their character, variations of the gel strength. It was also demonstrated that at the evaluation of the fusion enthalpies of PVA cryogels with the aid of the Eldridge–Ferry equation a consideration of the values of gel-fraction yield gave rise to the significantly higher  $\Delta H$  values than in traditional cases commonly used for the thermoreversible gels, where such an yield was not taken into account. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1822–1831, 2000

**Key words:** poly(vinyl alcohol) cryogels; efficiency of cryotropic gelation; gel-fraction yield; aging of PVA cryogels

## INTRODUCTION

Poly(vinyl alcohol) cryogels (cryoPVAGs) are heterophase macroporous thermoreversible noncovalent (physical) gels that are formed as a result of the freeze–thaw treatment of concentrated solutions of the polymer.<sup>1</sup> These gel materials were originally described in patents of Inoue at the beginning of

1970s,<sup>2–6</sup> and then the facts of the formation of similar gel-like species upon the freezing–thawing influence on PVA water solutions were reported (but without the studies of such a gelation) in the research papers of Kukharchik and Baramboim,<sup>7</sup> as well as of Peppas.<sup>8</sup> Several years later these gels were as if rediscovered *de novo*, when Nambu found out the approaches to the enhancement of mechanical strength of the final gel products by means of partial ice sublimation from the frozen specimens<sup>9–11</sup> or by using the iterative freezing–thawing cycles.<sup>12–15</sup>

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Nowadays, a lot of publications about PVA cryotropic gelation, influence of polymer properties, and conditions of the freeze-thaw procedure on the characteristics of resultant gels, as well as papers and numerous patents on the application of these materials thus formed, are known, including several reviews.<sup>1,16–19</sup> We have called similar gel-like polymer systems by the term *cryogels*,<sup>20</sup> i.e., the gels produced through the cryogenic technique. It was shown that cryoPVAGs can be prepared from both aqueous<sup>21–23</sup> and organic (DMSO) solutions<sup>24,25</sup> of the polymer, the intermolecular links in the spatial network being the multiple hydrogen bonds between OH groups of the neighboring PVA chains in the microcrystallinity zones. The latter ones, in their turn, represent themselves the junctions in such thermoreversible cryogels.<sup>23,26–28</sup> It was also established that cryotropic gel formation of PVA mainly occurs during the thawing step,<sup>29</sup> but in the still frozen system at the temperatures several degrees below the melting point, some additional amount of a liquid solvent arises, thus providing necessary conditions for the mobility of the segments of polymeric chains and for their efficient interactions, which results in the gel formation in the high-concentrated medium of similar partially thawed regions.<sup>30,31</sup> Electron microscopy studies revealed<sup>20,24,32–35</sup> high micro- and macroporosities of cryoPVAGs; this property, along with a good gel strength, makes them very promising materials of biotechnological and medical interest.<sup>1,16–19,36</sup>

Among the problems, which, however, remained unclear in the mechanisms of PVA cryo-induced gelation, there was the task of determination of the gel-formation efficacy (gelation yield), because the properties of cryogels strongly depended on the conditions of a cryogenic treatment, especially on the thawing regimes, when the differences in the gel's strength of the fast- and slow-defrosted samples of equal initial polymer concentration could reach several dozens times,<sup>29</sup> thus demonstrating very dissimilar gelation efficiency in these two cases. Therefore the goal of given work was to evaluate the gel-fraction yield quantitatively and to search the influence of the variation of some cryostructuration conditions on it.

## EXPERIMENTAL

### Materials

Poly(vinyl alcohol) of the trademark 20/1 (NPO "Polivinilatsetat," Yerevan, Armenia) was used in

the work. The technical grade polymer was purified by the reprecipitation from aqueous solution into the excess of methanol. The resultant PVA had the viscosity-average molecular weight of 81,700 and its degree of deacetylation was of 98.5 mol %.

### Methods

Initial solutions of the polymer for the formation of PVA cryogels were prepared by the suspending of the weighed amount of dry polymer powder in the required volume of bidistilled water, storing these mixtures for a night at room temperature to swell the polymer followed by its dissolution by heating the samples on a boiling water bath for 30 min with periodical shaking. The viscous hot solution thus obtained was then filtered through the sintered glass filter for the removal of possible insoluble admixtures, and the filtrate was, after cooling to a room temperature, used for the formation of cryoPVAG spherical beads. The latter ones (diameter of  $2.5 \pm 0.1$  mm) were produced with the cryogranulating setup "CryoMat"<sup>37</sup> (Bio-ChemMac Ltd., Moscow, Russia). Freezing temperature was  $-18^{\circ}\text{C}$ , frozen storage duration was 18 h; the thawing rates used are indicated in the text.

The 20-g portions of the wet beads obtained were poured into two chromatographic columns of  $\sim 40$  mL capacity, and a pure water was pumped through the columns with the constant rate of 3 mL/h. The absorbance at 220 nm was monitored (Model 557 UV-VIS spectrophotometer, Hitachi, Japan) in the effluent from the first column in order to register the extraction of the soluble PVA fractions from the beads in time (the extinction coefficient for the 1 g/dL aqueous PVA solution was found to be equal to 0.263), and from the second column 3–5 cryogel beads were taken periodically for the weighing (the procedure was described earlier<sup>38</sup>). The solid matter content in the same beads was determined by their drying until a constant weight.

The measurements of the apparent instantaneous elastic moduli ( $E_0$ ) of cryoPVAG beads were conducted in accordance with the procedure published in detail elsewhere<sup>39</sup>; also, the determination of the gel fusion temperatures ( $T_g$ ) was carried out as described in the same article.

## RESULTS AND DISCUSSION

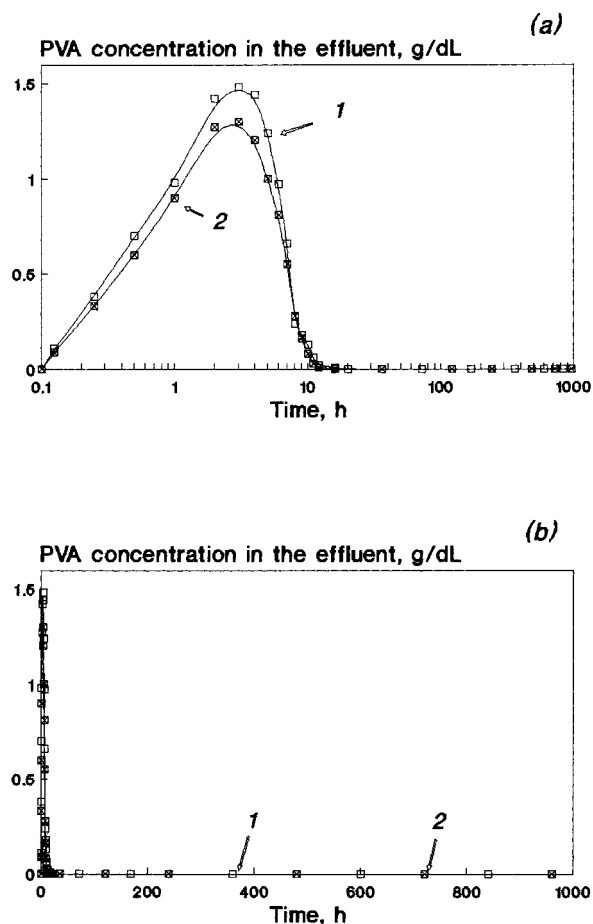
## Gel-Fraction Content in PVA Cryogels

When studying the formation of chemical (i.e., covalently crosslinked) gels, the measurement of the gel-fraction yield is a routine procedure commonly performing through the exhaustive extraction (with a hot solvent, if it is required) of soluble fractions from the crosslinked polymer network with the subsequent quantification of the dry weight of an insoluble residue. The values thus found allow one to evaluate the efficacy of the gelation process under the conditions employed. In the case of formation of thermoreversible non-covalent gels, the situation with respect to the determination of gel-fraction yield is fundamentally different. Indeed, it is impossible to rinse exhaustively such fusible gels with a hot solvent without danger of destroying their noncovalent spatial networks. Hence, for similar gels, it is possible to talk only about the values of the gel-fraction yield measured at some particular temperatures, i.e., these yield values should be considered as the apparent ones.

In the present research the experiments on the determination of such an apparent yield for the cryoPVAGs were conducted at  $22 \pm 1^\circ\text{C}$ ; for this purpose the gels were prepared in the shape of spherical beads of narrow distribution in size, then they were rinsed with pure water for the sol-fraction exhaustive extraction just at this temperature (see Experimental). The temperature of such experiments was chosen to be much lower than the fusion temperatures of both PVA cryogels ( $T_f > 60^\circ\text{C}$ )<sup>23,29,40</sup> and ordinary PVA hydrogels ( $T_f > 30^\circ\text{C}$ )<sup>41</sup> formed upon the prolonged aging of concentrated water solutions of the polymer at positive temperatures.

The variation of the concentration of soluble components in an effluent stream is depicted in Figure 1. In order to show the variation of the above values at both early and subsequent later stages, the time axis in this figure and thereafter upon the description of analogous prolonged experiments is given in both the logarithmic (a) and linear (b) scales.

The following trends of the sol-fraction leakage from the cryogel beads were observed: during the early stages the polymer concentration in the effluent liquid gradually increased, reached the maximum values and then, after a 1-day water passing-through, decreased virtually to zero (at



**Figure 1** The dynamics of the extraction with a water of soluble PVA fractions from the cryoPVAG beads formed from the 10 g/dL initial polymer solution (1: the beads thawed with a rate of  $0.2^\circ\text{C}/\text{min}$ ; 2: the beads thawed with a rate of  $0.02^\circ\text{C}/\text{min}$ ). (a) Logarithmic time scale; (b) linear time scale.

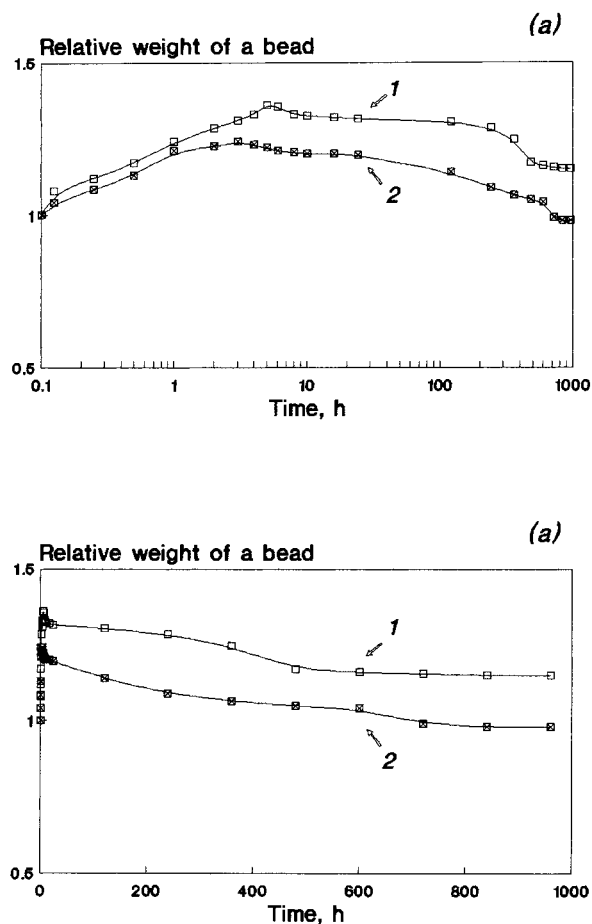
least, the sensitivity level of the analytical procedure employed was insufficient for the detection of soluble PVA traces in the waste water during the subsequent rinsing). In addition, it was evident that a larger amount of soluble products was extracted from cryoPVAG thawed with the rate of  $0.2^\circ\text{C}/\text{min}$  (curve 1) rather than from the beads defrosted 10 times slower ( $0.02^\circ\text{C}/\text{min}$ , curve 2). This latter trend testified on the higher gelation efficiency with the slowing of the defrostation rate (this latter point was also pointed out in the Introduction).

Earlier it was found out<sup>29</sup> that the range of negative temperatures, where the cryotropic gelation in the frozen water PVA solutions proceeded at the highest extent (the cryogels of the

highest strength were formed), lay in the vicinity from  $-6$  to  $0^{\circ}\text{C}$ . Hence, when thawing the samples with the slowest (among the other used) rate of  $0.02^{\circ}\text{C}/\text{min}$ , the yet-frozen specimens "resided" under these favorable conditions for  $\sim 5$  h, whereas when the thawing rate was  $0.2^{\circ}\text{C}/\text{min}$  ("moderate" thawing) the time was shortened down to 30 min, and when the even faster defrosting was used, e.g.,  $20^{\circ}\text{C}/\text{min}$ , this time was only 18 s. Therefore, under the conditions of a slow thawing the time was long enough for the efficient gelation events, and in the case of rapid thawing there was practically no time for such processes (that is why no cryogels could be obtained, when the thawing rate was higher than about  $10^{\circ}\text{C}/\text{min}$ ).<sup>29</sup> The data of Figure 1 showing the influence of the variation in defrosting regimes on the amount of sol-fraction extracted also confirmed these earlier observations on the promotion of a slow thawing to the cryotropic gelation of PVA aqueous solution, namely, markedly smaller amount of PVA was extracted from the cryoPVAG beads prepared by means of a slow thawing [lesser was the area under curve 2 than under curve 1 in Fig. 1(a)], i.e., a higher portion of the gelling agent was incorporated into the polymer networks formed in this case.

In parallel with the soluble polymer leakage from these heterogeneous gels, the variation of the swelling characteristics of the beads was also registered. Figure 2 shows a similar variation in their weight throughout the same duration of rinsing of the gels with pure water under the condition equal to the case of previous figure, and Figure 3 demonstrates the changes in the volume of the beads' column for that time.

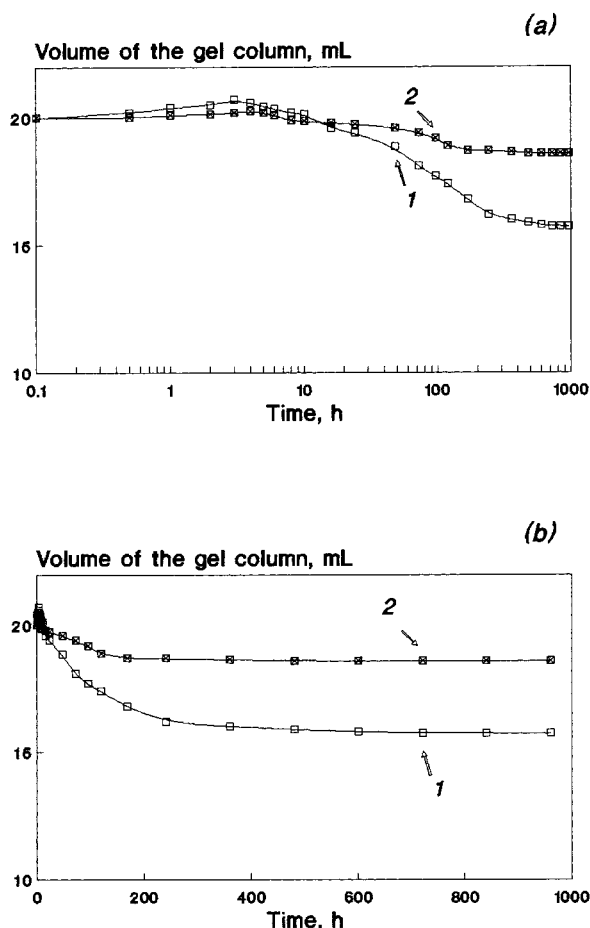
The increase in the weight of a bead (or, in the terms of ordinates axis in Figure 2, of the values of the relative weight of a bead) reached the maximum values of  $1.36 \pm 0.05$  and  $1.24 \pm 0.04$  times as related to the bead's initial weight for the both moderately and slowly thawed cryoPVAGs, while the washing-out of the sol fraction was virtually completed [the regions in the vicinity of 10–12 h, Fig. 1(a)]. Hence, the respective PVA solution (the water-containing PVA sol) in the inner regions of the cryogel's matrix was substituted by a pure water. Furthermore, due to the aging phenomena in the nonequilibrium PVA cryogels, a certain shrinking of the beads in time took place. Such a decrease in the bead weight occurred slowly for about two weeks at room temperature, and further, during the subsequent weeks of the experi-



**Figure 2** The variation, in the course of sol-fraction extraction, of the relative weight (the current weight of a bead divided for the weight of a bead just after its preparation) of cryoPVAG beads formed from the 10 g/dL initial polymer solution (1: the beads thawed with a rate of  $0.2^{\circ}\text{C}/\text{min}$ ; 2: the beads thawed with a rate of  $0.02^{\circ}\text{C}/\text{min}$ ). (a) Logarithmic time scale; (b) linear time scale.

ment, these values were varied no more (in the limits of sensitivity of the measurement procedure employed). Virtually the same trends were observed in the osmotic behavior of the cryoPVAG in time, i.e., the volume of the beads' column initially slightly grew and then gradually, during several days, diminished, reaching the constant level approximately after the two weeks of the experiment (Fig. 3). It is also clearly seen that larger variation of this volume was inherent in the cryogel thawed with the faster rate.

The "final" swelling extent, in fact, could be considered as the equilibrium one, and the values of relative weights of the cryoPVAG beads thus

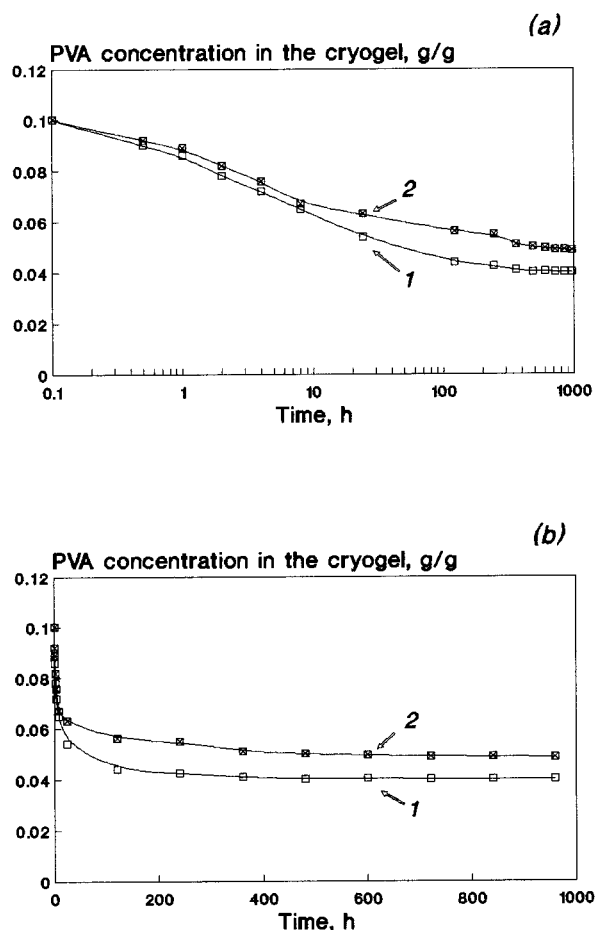


**Figure 3** The variation of volume of the gel column filled with cryoPVAG beads (formed from the 10 g/dL initial polymer solution) in the course of sol-fraction extraction (1: the beads thawed with a rate of 0.2°C/min; 2: the beads thawed with a rate of 0.02°C/min). (a) Logarithmic time scale; (b) linear time scale.

reached were  $1.15 \pm 0.03$  and  $0.98 \pm 0.03$  (curves 1 and 2 in Fig. 2, correspondingly)—that is, for the slowly thawed gel species this value was very close (practically equal) to the weight of the initial nonwashed bead. But if the freshly prepared cryoPVAG contained the gel and sol fractions together in an amount of 10 g of PVA per 1 dL of the cryogel formed or 9.1% in account for a weight % scale, the rinsed beads included insoluble gel material only. Consequently, this polymer content in the PVA cryogels could be used for the calculation of the apparent yield of the gel fraction. The values of the PVA concentration in the beads were found gravimetrically after drying to a constant weight of the swollen gel material taken from the water medium at different time of the rinsing (see

Experimental). The curves in Figure 4 demonstrate the dynamics of the variation of PVA content in the cryogel beads (g of PVA per 1 g of the gel) for such a case.

The most marked decrease in the PVA concentration within the beads was found for the first 10–12 h of the washing-out of the most of the soluble polymer fractions (Fig. 1), and these values stopped to vary significantly virtually in parallel with the corresponding curves of the swelling degree (Fig. 3). The amount of the “cryogel-inserted” PVA macromolecules—that is, the gel-fraction yield—was higher for the slower thawed samples, and the final values of similar apparent yield for these cryogels were around 50% (curve 2), contrary to 44% for the samples



**Figure 4** The variation of the concentration of PVA in the cryogel beads (formed from the 10 g/dL initial polymer solution) in the course of sol-fraction extraction (1: the beads thawed with a rate of 0.2°C/min; 2: the beads thawed with a rate of 0.02°C/min). (a) Logarithmic time scale; (b) linear time scale.



thawed faster (curve 1). If one compares the course of the respective curves in Figures 1(a) and 4(a) in time, one can see that after the completion of the soluble fraction release from the cryoPVAG beads and reaching the zero level of the polymer concentration in an effluent, the concentration of PVA in the gel phase continued to decrease for a long time, and only then stabilized (see curves in Figures 2 and 3). In this respect, it should be pointed out that the rates of the manifestation of various processes depicted in Figures 1–4 were somewhat different. First of all, the leakage of the sol fraction was controlled, naturally, by the rate of diffusion of PVA macromolecules and their soluble aggregates from the cryogel beads. Since the initial size of the beads was equal for the both moderately and slowly thawed preparations, any possible differences in such diffusion rates could only be the consequences in the porosities of these gel materials. However, inasmuch as the diameter of macropores in cryoPVAG is gross enough ( $\geq 0.1\text{--}1.0\text{ }\mu\text{m}$ )<sup>1,18,20,33–35</sup> for the unhindered diffusion of the solutes of any molecular weight, including certain colloid-size particles—likewise protein micelles or even viruses<sup>42</sup>—it is reasonable to suppose that the porosity of the macroporous PVA cryogel thawed with the rates studied did not influence markedly the rate of the sol-fraction leakage from the beads. On the other hand, the graphs showing a certain upswelling for the first several hours of the experiment [Figs. 2(a) and 3(a)] and subsequent slow deswelling of the beads [Figs. 2(b) and 3(b)] testified that thawing regimes affected the gel aging dynamics. Since the gelation efficiency (gel-fraction yield) depended strongly on the defrostation conditions and increased with slowing of the defrostation rate, both weaker upswelling of the more concentrated gel phase of the slowly thawed samples and lower rate of their subsequent deswelling are understandable. At the same time, a gradual decrease in PVA concentration in the beads not only during the upswelling stage [Fig. 4(a)], when a higher amount of water was held by the polymer network and average polymer concentration in a bead diminished, but also when the swelling extent tended to decrease [Fig. 4(b) and the descending branches of the curves 1 and 2 in Figs. 2 and 3] required special discussion.

Figure 1(a) demonstrates that after approximately 10–12-h rinsing of cryoPVAG beads with a pure water, virtually all soluble fractions were washed from the gel material; however, as the

analyzing method employed was capable of determining the PVA concentration in the rinsing effluent, no less than 0.01–0.02 g/dL, we were unable to detect smaller amounts of PVA sol. While the flow rate of the rinsing water through the column filled with cryoPVAG beads was 3 mL/h, the volume of the effluent for 1 day was 72 mL—hence, about 0.007–0.014 g of PVA could potentially leak from the  $\sim 20\text{-mL}$  of the packed bed every day without the quantification of the polymer concentration in the waste water after the first 10–12 h of rinsing. This meant that, assuming the packing coefficient for spherical particles to be equal to  $\sim 75\%$ ,<sup>43</sup> at the net bead volume of  $20\text{ mL} \times 0.75 = 15\text{ mL}$  or about 15 g of the initial weight of the beads or  $15\text{ g} \times 0.091 = 1.365\text{ g}$  of PVA (0.091 due to the 9.1% content of PVA in the initial polymer solution), this gel column could lose around 1–0.5% of the polymer matter daily or, respectively, 10–5% from the initial polymer content every 10 days with a gradual lowering of the process intensity. Therefore, in spite of the decrease in the swelling degree of the cryogel beads in time, which should result, in principle, in the apparent increase in polymer content compared with the PVA concentration in the beads in the maximum-swollen state [the points in the region of 10–12 h in Figs. 2(a) and 3(a)], a slow release of soluble polymer matter from the beads upon their prolonged rinsing could be one reason for the descending character of the curves in Figure 4(a) in the time range of 10–100 h. One may see that the values of polymer concentration stopped to vary markedly only after this period of rinsing of PVA cryogels at room temperature, thus apparently indicating the completion of the leakage of sol fractions from cryoPVAG to the elapse of this time.

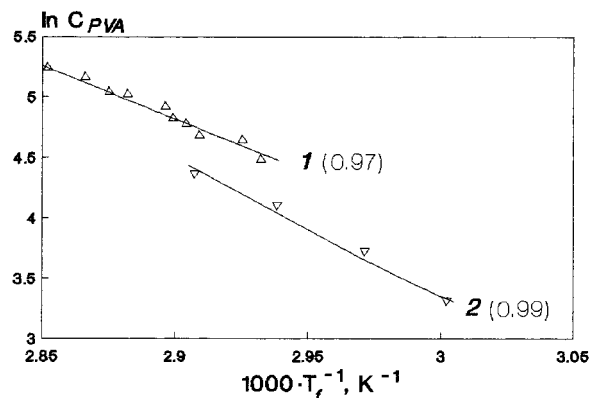
#### On the Thermophysical Parameters of the Polymer Network in PVA Cryogels

It was also of interest to evaluate the thermodynamic characteristics of the interchain junctions in cryoPVAG, taking into account the presence of the gel and sol portions together in the samples after their defrostation. Thus, earlier it was shown<sup>29,44,45</sup> that for the determination of fusion enthalpies of PVA cryogels formed under various freezing–thawing conditions, a well-known approach based on the Eldridge–Ferry equation (EFE) [ $\ln C = (\Delta H/RT_f) + \text{const.}$ ]<sup>46</sup> could be used, implying the measurements of gel-fusion temper-

atures depending on the polymer concentration in the samples. However, virtually always, when applying such an equation for the analysis of any thermoreversible noncovalent gels, the values of polymer concentration ( $C$ , g/L) are considered to be equal to its content in the initial gelling system, thus, in fact, assuming that all the polymer macromolecules are being constituted within spatial network of the physical gel of particular interest. In the previous research, where the EFE was used in respect to cryoPVAGs, the same "inadvertent" assumption (certainly, without the knowledge on the sol/gel-fraction ratio) was also made.<sup>29,45</sup> But the data of the present work evidently demonstrated that only a definite portion of the initial amount of PVA macromolecules was involved in the structure of gel framework of macroporous cryogels, and consequently, only these "gel-inserted" chains should be responsible for the values of fusion enthalpies found in the experiments.

In order to take into account these speculations, the following tests were carried out:

First of all, we have measured the fusion temperatures inherent in the cryoPVAGs prepared from the water solutions of the polymer of various initial PVA concentrations ( $C_{\text{PVA}}$  values were from 80 to 200 g/L). The data obtained are presented in coordinates of the EFE in Figure 5 as the line 1. The value of  $\Delta H$  found turned out to be equal to  $71.7 \pm 1.5$  kJ/mol. Then the cryogel beads were formed from the four PVA solutions with the initial polymer concentrations of 52, 67, 89, and 115 g/L, respectively. These beads were rinsed for 1 month with a pure water from the soluble fractions, and the final PVA content was measured by means of the dry weight determination. The values of the gel-fraction yield thus found have tended to increase with the increase in the initial polymer concentration, and they were as follows: 52, 63, 66, and 68%, correspondingly (error was no more than 3%). In other words, these rinsed cryogels contained (in terms of the ordinate axis of Fig. 4) 0.027, 0.042, 0.059, and 0.078 g of PVA per 1 g of a gel, or, in the magnitudes of the EFE, the polymer concentrations in them were 27, 42, 59 and 78 g/L, correspondingly. In this latter case, we assumed that the specific gravity of cryoPVAGs was virtually the same (with insignificant error) as for water, i.e., 1 g/mL. Knowing the fusion temperatures for the respective "nonrinsed" cryogels and using the  $C_{\text{PVA}}$  values in their insoluble (at 22°C) gel fraction, we obtained



**Figure 5** The plot in the coordinates of Eldridge–Ferry equation for the reciprocal fusion temperatures ( $T_f$ , K) of PVA cryogels of various polymer concentration ( $C_{\text{PVA}}$ , g/L). (1: the data in a traditional version, when the polymer concentration in the gel is assumed to be equal to the PVA concentration in the initial solution to be frozen; 2: the data taking into account the gel-fraction yield, see the text). All gel samples were thawed with a rate of 0.02°C/min; the digits in the parentheses are the coefficients of determination calculated for these straight lines by the least squares method.

line 2 (Fig. 5), whose tangent of a slope angle gave the value of  $\Delta H$  equal to  $94.3 \pm 0.8$  kJ/mol. This magnitude are clearly seen to be for ~30% higher than that calculated in account that all the gelling polymer was included into the spatial network of cryoPVAGs and was responsible for the manifestation of such their property as the thermoresistance.

It could be also pointed out that we, unfortunately, were unable to find in the literature any data on the taking into account of the gel/sol-fractions ratio upon the similar studies of thermal properties of various physical gels with the aid of EFE, although, no doubt, the yield of similar gelation processes, especially when the polymer concentration in the system exceeds the critical concentration of gel formation not very strongly, cannot be absolutely equal to 100%.

#### Variation of Mechanical Strength of PVA Cryogels During Their Aging

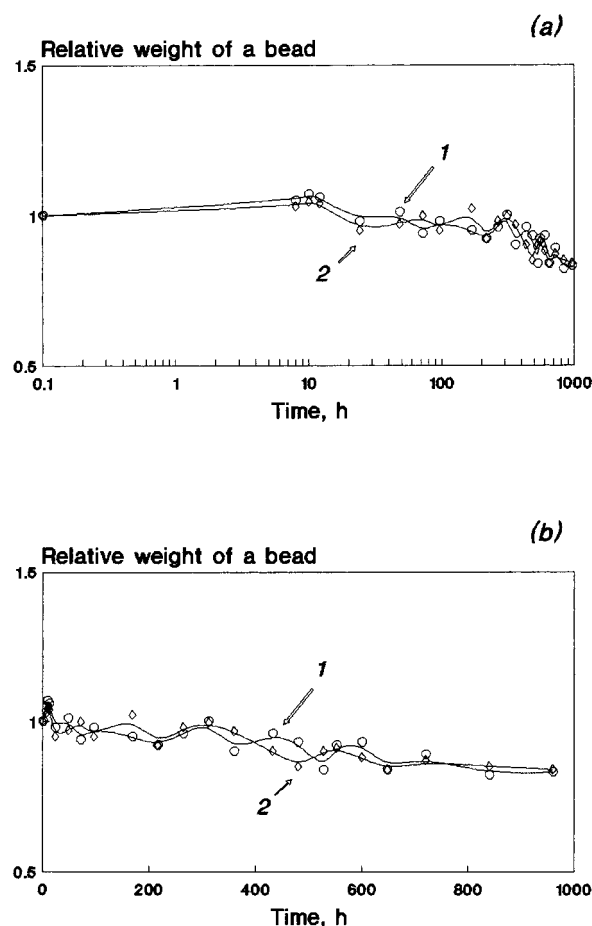
In parallel with the variation of swelling characteristics of cryoPVAG beads in the course of their rinsing from the solutes, mechanical properties of the beads varied (the gel's strength was gradually increased, see below) as well. This obviously tes-

tified to certain changes in the structure of a gel phase of heterogeneous PVA cryogels upon their prolonged residence in water medium.

For obtaining of quantitative information on similar time-dependent variations of the rheological properties of cryoPVAG, the following experiments were accomplished:

The gel beads were formed from the 12.5-g/dL initial PVA solution in order to obtain the "optimum" samples suitable for the rheological measurements with the instrument in our disposal. Then two 20-g portions of the wet beads were placed into the glass cylinders of equal capacity, and pure water was added to each vessel so as the total volume of the system was 100 mL. The first cylinder was kept at room temperature for 40 days, every 1–2 days the liquid was replaced with a fresh batch, and several beads were taken periodically for the weighing and rheological tests (see Experimental). Below, this case will be referred as the static regime, whose conditions were somewhat distinct from those for the case of discontinuous rinsing of the beads in a flow-through column (Figs. 1–4); such a regime will be referred as the packed-bed one. The second cylinder was equipped with the electromechanical bubbler (the device used for the aeration of home aquariums), which stirred the gel beads by the air bubbles stream, thus modeling the reactor of a fluidized-bed type (dynamic regime). The goal of this experiment was to trace the influence of the continuous dynamic stresses, arising upon the collisions of the cryogels beads each together, on its swelling behavior and mechanical strength. The results of these examinations are presented in Figures 6 and 7 (curves 1: static regime; curves 2: dynamic regime).

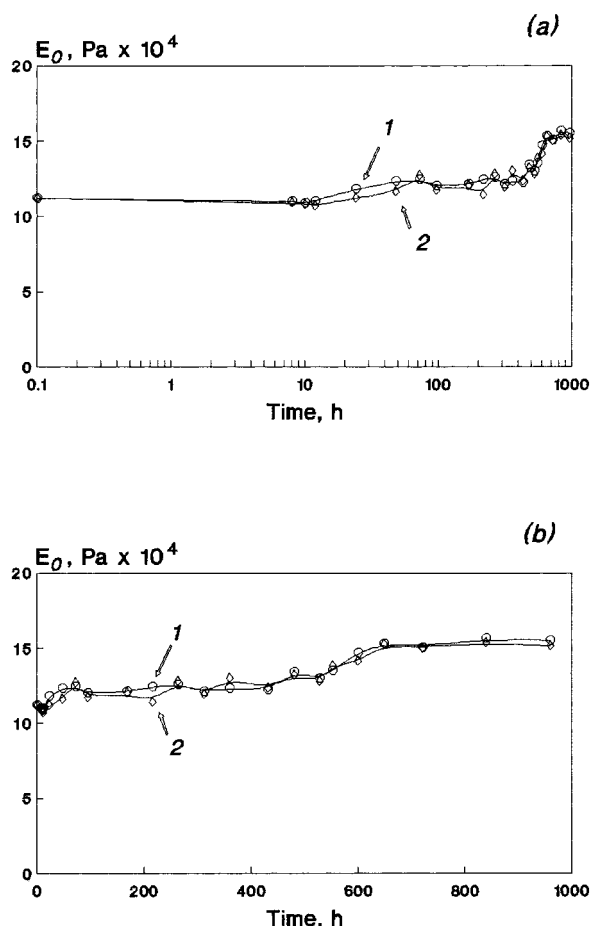
The comparison of the data on the variation of a relative bead weight in the packed bed (Fig. 2), in the static and dynamic (Fig. 6) regimes, showed close similarity of the tendencies observed, namely a slight upswelling of the beads during the first 10–12 h followed by the gradual decrease in the bead weight practically independently on the mode of their rinsing. However, in the latter case, i.e., for the more concentrated beads, the changes were smaller in their magnitudes [cf. Figs. 2(b) and 6(b)], thus confirming the above-discussed trend on the increase in gel-fraction yield with increase in initial polymer concentration in the PVA solution to be cryostructured. The only difference was the somewhat higher deviation of the experimental values in the data of



**Figure 6** The variation of the relative weight of cryoPVAG beads (formed from the 12.5 g/dL initial polymer solution) in the course of their rinsing with water in static (1) and dynamic (2) regimes. The cryogel samples were thawed with a rate of 0.02°C/min. (a) Logarithmic time scale; (b) linear time scale.

Figure 6 (in both static and dynamic regimes) as compared to the values of Figure 2. The reason of such an effect is not yet clear. Nonetheless, a rather important conclusion could be drawn regarding to a very high erosion stability of the cryoPVAG beads, since they did not practically loose their matter as a result of abrasion, otherwise their weight should be considerably less than that of the beads being incubated in the static regime. As concerns the mechanical properties of the same cryogel beads, it was found that their elastic moduli increased  $\sim 1.5$ -fold during the static and dynamic experiments (Fig. 7), thus demonstrating that removal of the sol fraction from cryoPVAG and simultaneous aging of the gel phase resulted in the strengthening of this poly-





**Figure 7** The variation of the strength of cryoPVAG beads (formed from the 12.5 g/dL initial polymer solution) in the course of their rinsing with water in static (1) and dynamic (2) regimes. The cryogel samples were thawed with a rate of 0.02°C/min. (a) Logarithmic time scale; (b) linear time scale.

mer system, obviously through the increase of the order of supramolecular packing of PVA chains in the spatial network in the gels under discussion.

## CONCLUSIONS

Poly(vinyl alcohol) cryogels attract great attention in biotechnology and medicine as promising gel materials of diverse use. For the deliberate implementation of these gel systems, various data on the influence of preparation conditions on the properties of cryoPVAG obtained are necessary, as well as the information about the behavior of these materials during their operation is naturally required. The results of the given study have

allowed us to recognize that the yield of the cryotropic gel formation of concentrated aqueous solutions of PVA was not quantitative and it has depended, providing all other process parameters were the same, on both the initial polymer concentration and the thawing rate. Therefore, for the reduction of amount of the sol fraction in respective PVA cryogels (these extraction products could "pollute" with PVA dissolved the media, where the gels operate) it is better to use high-concentrated initial solutions of the polymer and to thaw the frozen samples as slow as possible.

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