

## **On the Possibility of Mechanoestruction of Poly(Vinyl Alcohol) Molecules Under Moderate Freezing of its Concentrated Water Solutions**

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### SUMMARY

The freezing of the concentrated PVA water solutions results in obtaining (after thawing) hydrogels of non-covalent nature. In the course of a single freezing-thawing cycle there is no any noticeable destruction or covalent cross-linking of PVA macromolecules.

### INTRODUCTION

It is known (1-11) that moderate freezing ( $-5 \div -40^{\circ}\text{C}$ ) of concentrated poly(vinyl alcohol) (PVA) water solutions, keeping them in the frozen state for a certain period of time and the subsequent thawing of the system results in obtaining highly elastic gels which are stable at room temperatures. The properties of such "cryogels" depend on PVA concentration in the initial solution, the molecular weight of polymer, the number of residual O-acetyl groups, the temperature and time of cryoexposure (3,8-11).

Different opinions have been expounded in literature with respect to the nature of processes inducing gel-formation as a result of the freezing of water-PVA system. A number of authors believe that PVA cryogels (cryoPVAGs) are non-covalent thermoreversible gels whose structure is maintained by the system of hydrogen bonds and/or microcrystallinity zones (8,9,12-14). There exists, however, another opinion. For instance, in (4-7) it was assumed that the factor stabilizing the cryoPVAG's structure is the covalent cross-linkage of the polymer macromolecules. As the authors of this concept believe, it is taking place as a result of the chemical interaction between reactive macroradicals and the neighbouring polymer chains, which leads to intermolecular covalent cross-links and then to the covalently cross-linked network. The reason for the formation of the above-mentioned radicals is cryolysis (cryocracking) of PVA macromolecules, presumably (4-7) subjected to the action of mechanical stresses' developing with the ice crystallization. According to the published results (4,6,7), films based on cryoPVAGs proved, as a result of such cross-linking, to be insoluble even when kept in boiling water for a long time.

In the course of our investigations of the cryostructurization of the water-PVA system it was, on the contrary, shown (10, 11) that PVA cryogels melted after a short time heating up to the temperature of the order of  $70-80^{\circ}\text{C}$ , or dissolved very rapidly in an excess of boiling water. In other words, cryo-

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PVAGs behaved as a typical non-covalent thermolabile gel (of the agar-agar or gelatin hydrogels type) and not as chemically cross-linked polymer networks.

At the same time, the possibility of mechanodestructive processes occurring in the freezing of solutions of different polymers has been once and again demonstrated in the case of multiple freezing-thawing cycles (15-23). It is true, however, that usually observed in this case was not the cross-linking of polymeric chains but a decrease in their degree of polymerization, i.e. the mechanodestruction of the corresponding macromolecules was taking place.

To verify the chemical nature of the interactions responsible for the formation of gels in the cryostructurization of water-PVA system we attempted to detect experimentally the cryolytic mechanodestruction of PVA macromolecules or the consequences of its manifestation. Used in the work were the same PVA brands, the same range of negative temperatures and the same duration of cryogenic treatment of polymer solutions as in the investigations where formation of covalently cross-linked cryoPVAGs was observed (4-7).

#### EXPERIMENTAL

##### Materials

Used in the work was poly(vinyl alcohol), trade marks: 16/1, 20/1 and 40/2 produced by the "Polyvinylacetate" plant (Yerevan, USSR). The technical grade polymers were additionally purified by extraction with hot methanol in a Soxhlet apparatus. Viscosity-average molecular weights and the degrees of deacetylation of the used PVA samples were as follows: 16/1 - 69 kDa and 99.0%, 20/1 - 90 kDa and 98.0%, 40/2 - 110 kDa and 97.5%. Details of the purification procedures and the characterization of the above polymers are given in (11).

Without additional purification were used acrylamide (Serva, FRG) and diethylenetriamine (Reakhim, USSR).

##### Methods

Cryostructurization: A weighted quantity of polymer was suspended in distilled water, and it was left to swell at room temperature for 1 h. After that the suspension was heated on a boiling water bath up to complete PVA dissolution (15-20 min). The obtained solution was filtered in vacuo through a porous glass filter to remove the possible mechanical impurities, and then centrifuged for 20 min at 8000 rpm (TsL-2 centrifuge, USSR) to remove air bubbles from the polymer solution. PVA solutions prepared in this way were frozen either in polyethylene, or teflon, or duralumin containers in the chamber of ultracryostat MK 70 (MLW, GDR). After the necessary time interval the samples were removed from the cryostat and thawed-off at room temperature. Preliminary tests have shown that the results of viscometric measurements were not affected by which of the above materials the vessel for the freezing of PVA solutions was made from.

In the case of multiple freezing-thawing cycles the samples were frozen at  $-20^{\circ}\text{C}$  during 1 h. After that the thawing was performed in two regimes for parallel samples: 1) keeping the sample in a thermostat at  $+30^{\circ}\text{C}$  for 40 min (resulting in a cryogel) or 2) keeping the sample in a thermostat at  $+80^{\circ}\text{C}$  for 40 min (resulting in a polymer solution). The freezing was then repeated again.

In the case of experiments on the freezing of PVA solutions in the presence of acrylamide the monomer was dissolved at room temperature in already prepared polymer solution.

Viscometric measurements: Dynamic viscosity of the concentrated PVA water solutions was determined at 25°C with the help of Hoeppler viscometer (VEB Prüfgeräte-Werk Medingen, GDR). To obtain polymer solutions from the corresponding cryogel the latter was melted at 90°C during 40 min. This solution was then placed in a measuring cell which was thermostated in the rheo-viscometer chamber during 30 min, after which the dynamic viscosity was measured. Each measurement was performed no less than three times, the obtained results were averaged.

The intrinsic viscosity values of diluted PVA water solutions were determined at 25°C with the help of Ubbelohde capillary viscometer. For this purpose the polymer samples were prepared in the following way: the same volumes of the corresponding PVA solution - the initial solution and that obtained by melting of the cryogel - were poured at stirring into the same volumes of methanol (the volume ratio of methanol and PVA solution was 10:1). The precipitates formed were separated by filtration, washed with methanol and dried in a vacuum desiccator over NaOH up to a constant weight. Polymer yield (within the limits of experimental error) was in all cases the same for both samples, which indicated the absence of dissimilar fractionation of the polymer in the course of reprecipitation. The preparations obtained in this way were used in  $\eta$  measurements.

Exclusion chromatography: Gel-chromatographic analysis was performed on the column (7.5x300mm) TSK-Gel Type G 4000 PW (Varian, USA) by liquid chromatograph Model 601 (Perkin-Elmer, USA); detection with a refractometric attachment Refracto-Monitor (LDC USA). Eluent - water, temperature 22-1°C.

Thermomechanical measurements: Thermomechanical curves for the cryoPVAGs were made under conditions of uniaxial compression on modified Kargin-Sogolova balances (24) equipped with a heating cell for a linear rise of temperature, measured by a chromel-copel thermocouple attached to the proportional recorder TZ-21S (Laboratorni přístroje, CzSSR).

IR-spectroscopy: IR spectra of polymers (dry films) were recorded on an IR-spectrophotometer 260-10 (Hitachi, Japan).

## RESULTS AND DISCUSSION

Viscometry. Viscosity properties of polymer solutions are known (25) to be very sensitive to such processes as cross-linking or degradation of macromolecules. That is why, first of all, it was of interest to compare the results of viscometric measurements for PVA solutions before and after the cryogenic treatment. The experimental data obtained are given in Table 1. It is seen that the values of dynamic viscosity in initial PVA solutions and in those obtained by melting the corresponding cryogels practically did not differ. The values of PVA intrinsic viscosity before and after the freezing-thawing operation were also the same. A similar result has been obtained when the duration of keeping the system frozen increased from 1 to 10 days. Viscometry data thus indicated the absence of both any noticeable destructive processes and intermolecular cross-linking in a single moderate freezing of concentrated PVA solutions.

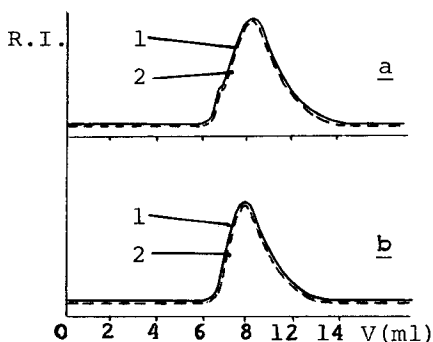
**Table 1.** The influence of the freezing of concentrated PVA water solutions on the viscosity values.

PVA mark	PVA conc. in init. solution	Conditions of cryogel preparation		Dynamic viscosity of PVA solution (Pa·s)		Intrinsic viscosity (m <sup>3</sup> /kg)	
		Temperature	Time	before freezing	after cryogel melting	before freezing	after cryogel melting
16/1	10%	-15°C	12 h	0.370 <sup>±</sup> 0.002	0.370 <sup>±</sup> 0.002	0.078 <sup>±</sup> 0.002	0.078 <sup>±</sup> 0.002
20/1	8%	-10°C	24 h	0.230 <sup>±</sup> 0.002	0.230 <sup>±</sup> 0.002	0.083 <sup>±</sup> 0.002	0.086 <sup>±</sup> 0.002
40/2	6%	-20°C	18 h	0.092 <sup>±</sup> 0.001	0.092 <sup>±</sup> 0.001	0.101 <sup>±</sup> 0.003	0.103 <sup>±</sup> 0.003
			240 h	0.093 <sup>±</sup> 0.002	0.093 <sup>±</sup> 0.002	0.100 <sup>±</sup> 0.003	0.098 <sup>±</sup> 0.003

**Exclusion chromatography.** The elution curves of PVA solutions before and after cryogenic treatment are shown in Fig.1. It is seen that in both cases the chromatograms are practically identical, this fact being observed for different PVA brands (Figs.1a and 1b). Such result seems to indicate the absence of changes in the molecular-weight distribution of the PVA samples - the initial one and after a single freezing-thawing cycle followed by the melting of cryogel.

**Solubility and melting of cryoPVAGs.** It is well known (26, 27) that hot water is a solvent for PVA. The covalently cross-linked gels of a given polymer must, therefore, swell to limited level in it (provided the covalent cross-links are not decomposed by the solvent, e.g., hydrolytically).

Since cryoPVAGs are dissolved in hot water (80-90°C) within several minutes, but the chemical structure of PVA is known, and  $\sigma$ -bond between two carbon atoms of the carbo-chain polymer should rupture upon cryomechanodestruction (4-7), one is completely unable to say what type of intermolecular covalent bonds should be broken so readily. It is also known (26) that at room temperature PVA is soluble in some amines, e.g., diethylenetri-



**Fig.1**

Gel-chromatograms of PVA solutions before (1), after (2) cryogenic exposure (-20°C, 24 h)

a - PVA mark - 16/1  
b - PVA mark - 20/1

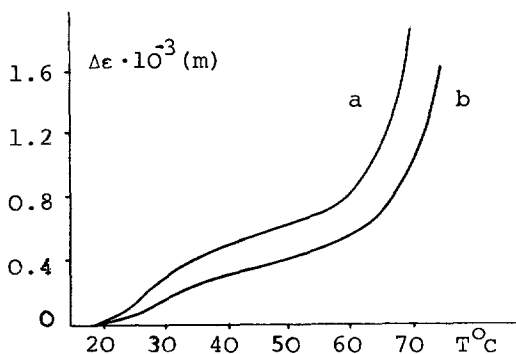


Fig.2

Thermomechanical curves of PVA cryogels obtained by freezing of 14% water solution of PVA (mark 16/1) during 24 h

a - gelling at  $-10^{\circ}\text{C}$   
b - gelling at  $-20^{\circ}\text{C}$

amine. The experiments performed have shown cryoPVAGs, formed at  $-10 \div -20^{\circ}\text{C}$  within 1-15 days, to dissolve in the above medium. This dissolution, however, proceeded somewhat slower than in the case of dry PVA, which seems to be associated with the presence of water in cryogels. It should also be noted that similar results on dissolution of cryoPVAGs in hot water or diethylenetriamine were obtained when the PVA solutions were frozen not in closed containers but in a thin layers at a constant spontaneous sublimation of moisture during 1-10 days, as described in (4,6,7).

Thus, the data of cryoPVAGs solubility also indicate the absence of covalently cross-linked polymer network in these materials.

As already noted above, cryoPVAGs melted at heating up to the temperature of the order of  $70-80^{\circ}\text{C}$ , yielding PVA solutions whose dynamic viscosity values were the same as those of the initial ones. Moreover, the absence of covalent cross-links in the studied cryogels is additionally confirmed by the thermomechanical curves (Fig.2) whose shape is typical for the melting of not cross-linked hydrogels (28).

Attempt of preparing block-copolymer. When a water solution of PVA containing a vinyl monomer (acrylamide) was subjected to freezing, then, as a result of homolytic destruction of the macromolecules of this polymer (as assumed in (5)), we should have expected a block-copolymer to be formed owing to the graft polymerization of acrylamide on the macroradicals appearing in the system. Such an effect was observed when similar experiments were conducted on other polymer-monomer systems (16,19,23). For instance, in (19) the authors succeeded in obtaining the corresponding block-copolymer after of 20-30 times of freezing and thawing of benzylcellulose solution in dioxane in the presence of acrylonitrile.

However, in our case, element analysis of the polymer isolated after a single freezing ( $-20^{\circ}\text{C}$ , 24 h) of a 10% PVA solution in a 5% solution of acrylamide did not show even traces of nitrogen in the product, and IR-spectroscopy (Fig.3) revealed no absorption bands typical for the amide group oscillation, i.e. the fact of a block-copolymer formation was not established. In other words, an attempt at finding the consequences of a poss-

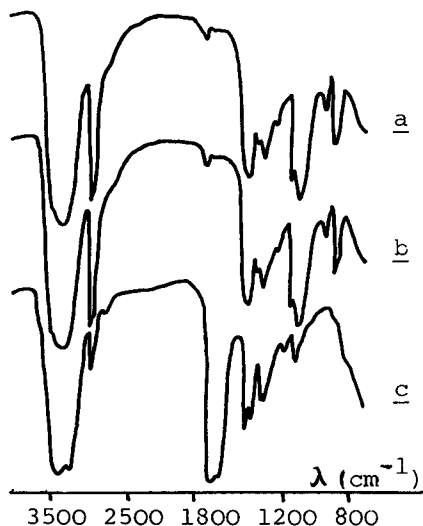


Fig.3

IR spectra of polymer films:

- a - initial PVA (mark 20/l)
- b - PVA after a single freezing-thawing cycle ( $-20^{\circ}\text{C}$ , 24 h) in the presence of acrylamide
- c - polyacrylamide (for comparison)

ible cryolytic mechanodestruction of PVA macromolecules by chemical methods also proved unsuccessful, which is, most probably, indicative of its absence under the conditions of a single moderate freezing of the aqueous solution of this polymer.

Multiple freezing of the water-PVA system. Since as a result of the freezing of concentrated PVA water solutions gels are formed after the thawing of the system, the experiments on multiple freezing-thawing were conducted in two modifications: 1) the cryogel was repeatedly frozen and 2) the cryogel was melted, and the solution was repeatedly frozen (see details in experimental part). After 4 cycles both samples were melted, and then the dynamic viscosities were measured. The results obtained are shown in Table 2.

Table 2. The influence of multiple freezing-thawing on the dynamic viscosity of PVA solutions.

Dynamic viscosity (Pa·s) of initial 8% PVA (mark 20/l) solution	Number of freezing-thawing cycles	Dynamic viscosity of PVA solution after cryogenic treatment (Pa·s)	
		Variant 1	Variant 2
0.230 <sup>±</sup> 0.002	4	0.197 <sup>±</sup> 0.004	0.214 <sup>±</sup> 0.014

It is seen that repeating the freezing-thawing cycles results in a noticeable decrease in the PVA solution viscosity. This seems to be indicative of a certain destruction of the polymer. Note that a decrease in viscosity is more clearly expressed for PVA subjected to multiple cryogenic treatment in variant 1, i.e. when not the polymer solution but the gel was repeatedly frozen. In other words, in the freezing of the gel itself, i.e. spatially structured system, cryolysis seems to be taking place. Such a possibility was earlier noted in (29, 30). In the case of variant 2 the results are less unambiguous.

This may be associated with the incomplete melting of the cryogel (which is, unfortunately, difficult to control in the conditions of experiment) before one of the cycles of repeating freezing. This assumption is supported by the fact that out of 8 series of experiments in 3 of them the values of dynamic viscosity for PVA solutions after 4 freezing-thawing cycles were the same as those for the initial polymer solution. More comprehensive studies are, undoubtedly, still needed here.

#### CONCLUSION

The performed experiments make it possible to conclude that a single freezing ( $-10 \div -20^{\circ}\text{C}$ ) of concentrated PVA water solutions does not result in any noticeable mechanodestruction of the macromolecules of this polymer. Its manifestation are only revealed after several times repeated freezing-thawing operations. It can be assumed that the latter fact is most probably associated with the destructive action of stresses (between the faces of the growing crystals of the solvent when it is being frozen) upon the structurized regions of the polymeric system: gel in the whole sample volume or microgel particles whose size is commensurable with the solvent polycrystals (see also (20)).

However, in the light of the above facts it is not clear why cryoPVAGs obtained by a single freezing ( $-16 \div -18^{\circ}\text{C}$ ) of a 10% PVA solution over a period of 1-10 days proved, according to the data in (4-7), to be covalently cross-linked. One can only assume that this was caused by an insufficient degree of purification of the used polymer. Since in the freezing of solutions the first to crystallize is the pure solvent, while the dissolved substances are concentrated in the so-called liquid microphase (31), the coccentration of impurities (if these are present) also increases. In the samples of a technical-grade polymer it was quite possible that rather reactive substances could be present among these impurities. Consequently, not only chemical modification but even cross-linking are possible in this case. It should be noted here that previously, for other polymer systems, it was already shown (32-34) that concentrating processes play an important part under the freezing of polymer solution in the presence of the corresponding cross-agents. In this case the cross-linking occurs at much smaller concentrations of the agents than those necessary for the formation of a covalently cross-linked gel in a liquid solvent at temperatures above the freezing point of the system.

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