Polymer Bulletin 11, 421–427 (1984)

Polymer Bulletin

Gel Swelling

Some Peculiar Properties of Cross-Linked Polyvinyl Alcohol (CL-PVA) Related to the Reticulation Degree[+]

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SUMMARY

Unlike usual polyhydroxilic packing materials for liquid chromatography based on cross-linked agarose, CL-amylose and CL-dextrans (Sephadex), the cross-linked PVA gels exhibit an increase of swelling properties with the reticulation degree, up to a certain limit. Afterwards more advanced reticulation degrees induce a decrease in swelling capacities just as in case of other cross-linked polyhydroxilic polymers. This abnormal behaviour of CL-PVA was supposed as being due to the interchain hydrogen associations. IR spectra, X-ray data and 8 M urea treatments strongly supported our supposition pointing out a maximum association by hydrogen bonds in CL-PVA gels with a reduced degree of reticulation.

INTRODUCTION

In previous papers (1)(2) syntheses and some properties of certain macroporous beaded ionic exchangers based on cross-linked polyvinyl alcohol (CL-PVA), with different reticulation degrees were described.

It is wellknown that polyhydroxilic chromatographic stationary phases based on cross-linked dextrans (Sephadex)(3), agarose (3)(4) or amylose (5), with low reticulation degrees exhibit pronounced swelling properties, whereas higher reticulation degrees generate reduced capacities to swell, due to the high number of interchain glycerine bridges that do not permit the swelling of gels, even if the HO- groups are hydrated.

Unlike the above compounds, CL-PVA gels exhibit an increase of swelling properties in a linear dependence with the increase of reticulation degree, up to a certain limit and after

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[+] Part of the paper was presented at the 29th IUPAC Symposium Macro'83, Bucharest, ROMANIA, September 5-9, 1983.

that, much higher reticulation degrees induce a decrease in swelling properties, like other hydroxilic polymers. We supposed this peculiar behaviour of CL-PVA to be due to interchain hydrogen bonds between hydroxilic groups, more frequent in case of low reticulation degree - therefore these gels are stabilized and contracted.

In this paper, IR spectra and X-ray diffraction data supporting our supposition are presented.

EXPERIMENTAL

Macroporous PVA beads (0.2 - 0.4 mm diameter), obtained by Dimonie et al (6) patented procedure, were used.

Cross-linking of PVA beads was performed by epichlorohydrine treatment as previously described (1)(2). In function of PVA/epichlorohydrine ratio, different preparations with various reticulation degrees, called PVA-X-10, PVA-X-20, PVA-X-30 and PVA-X-40 were obtained (X letter indicates that the PVA is cross-linked and the number the amount in terms of grammes of epichlorohydrine used to cross-link 100 g of PVA).

Swelling properties : water regain (g H_2O/g dried product) bed volume (ml/g dried product) and humidity (g H_2O/100 g dried product) of different CL-PVA gels were determined.

Drying of CL-PVA gels was performed with acetone (7).

IR spectra of various dried CL-PVA preparations heated for 1 h at 90° C and kept with dehydrants to eliminate adsorbed water, were performed using 2.7 mg sample in 400 mg of KBr pellets.

X-ray diffraction data were obtained with a Dron 3 diffractometer using the $Cu^{k_{\alpha}}$ radiation ($\lambda = 1.54$ Å) and a pyrolytic graphite monocrystal as monochromator between the sample and detector. The angular positions (θ) of the diffraction peaks permitted the estimation of crystalline spacings $d = \lambda /2 \sin\theta$ The inter- and intrachain distances were correlated with the molecular sizes calculated from the known bond lenghts taking into account the probable valence angles. The samples (dried beads of PVA gels) volumes were of 0.25 cm^3 each; they were fixed in the sample holder with a diluted collodium solution. The width at half peak maxima ($\Delta\theta$) - as a measure of the organization degree of the network, intensities (I) of diffraction maxima and relative intensities (I/I_m) - the ratio between the intensities of different diffraction maxima and those of the peak with maximum intensity were also determined.

RESULTS AND DISCUSSIONS

The swelling properties of obtained CL-PVA gels are presented in table 1. We supposed the interchain hydrogen bonds between HO-groups responsibles for the peculiar behaviour of CL-PVA gels, considering the fact that a high number of glycerine transversal bonds (calculated size 8.34 Å) do not permit the hydrogen interchain associations (calculated size 5.5 Å). In case of a low reticulation degree (PVA-X-5) these glycerine bridges are sufficiently distanced to permit the hydrogen associations the network being contracted (scheme I).

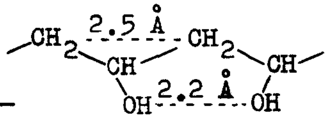
Table 1 - Swelling properties of CL-PVA gels with various reticulation degrees

Type of gels	Bed volume (ml gel/g)	Water regain ($g\ H_2O/g$)	Humidity ($g\ H_2O/100\ g$)	Observations
PVA-X-5	3.33	1.39	5.31 %	Abnormal behaviour (different from other hydroxilic gels)
PVA-X-10	3.90	1.86	5.48 %	
PVA-X-20	4.45	2.28	5.66 %	
PVA-X-30	3.90	1.98	3.98 %	Normal behaviour (like other hydroxilic gels).
PVA-X-40	3.35	1.88	3.90 %	

IR data of various CL-PVA gels supported our assumption. Thus, the range of characteristic frequencies for the associated HO- groups is much larger (2980 - 3660 cm^{-1}) in case of PVA-X-5 in comparison with the case of PVA-X-20 (3090 - 3600 cm^{-1}) and PVA-X-40 (3100 - 3600 cm^{-1}). The largest frequency field obtained for the PVA-X-5 denoted the highest number of HO- associated groups that generate a maximum contraction for this gel with a minimum reticulation degree. On the other hand higher absorbancy values at $\tilde{\nu} = 3420\ cm^{-1}$ were obtained for the PVA-X-20, PVA-X-30 and PVA-X-40, suggesting higher numbers of free HO- groups than in case of PVA-X-5.

X-ray obtained data are presented in table 2 and fig.1. The obtained diagrams show beside a characteristic amorphous structure, three peaks which may be assigned to ordered (crystalline) structures.

Table 2 - X-ray diffraction data for various CL-PVA gels

X-ray data	Sample				Assigned[+++] to
	PVA	PVA-X-5	PVA-X-20	PVA-X-40	
θ_1		5.648°	5.581°	5.466°	-interchain glycerine bridges (calculated size 8.34 Å).
d_1		7.818 Å	7.912 Å	8.078 Å	
I/I_m		0.111	0.117	0.088	
$\Delta\theta_1$		$1.65^{\circ ++}$	2.40°	2.85°	
θ_2	9.800°	9.837°	9.837°	9.707°	-interchaim hydrogen association (calculated size 5.5 Å).
d_2	4.521 Å	4.504 Å	4.504 Å	4.564 Å	
I/I_m^+	1	1	1	1	
$\Delta\theta_2$	1.725°	$1.35^{\circ ++}$	1.50°	1.72°	
θ_3	20.504°	20.463°	20.620°	20.454°	-hydrogen bonds between vicinal HO- groups.
d_3	2.197 Å	2.201 Å	2.185 Å	2.202 Å	
I/I_m	0.151	0.115	0.136	0.153	
$\Delta\theta_3$	2.55°	$1.57^{\circ ++}$	1.875°	2.10°	

[+] Maximum intensity of these peaks denote the large frequency of this distance (d_2) in the ansambly of th organized structure.

[++] The minim values for $\Delta\theta_2$ in all directions of PVA-X-5 denote the highest regular organized structure.

[+++] The deviations from standard distances have been accounted on the local distorsions induced by hydrogen bonds and/or the complex conformations of PVA compounds.

In order to obtain some additional arguments in favour of our supposition regarding the main role of hydrogen bonds in behaviour of CL-PVA, experiments concerning the swelling properties in 8 M urea solutions were performed. If identical amounts of PVA-X-5 and PVA-X-20 are allowed to swell in dis-

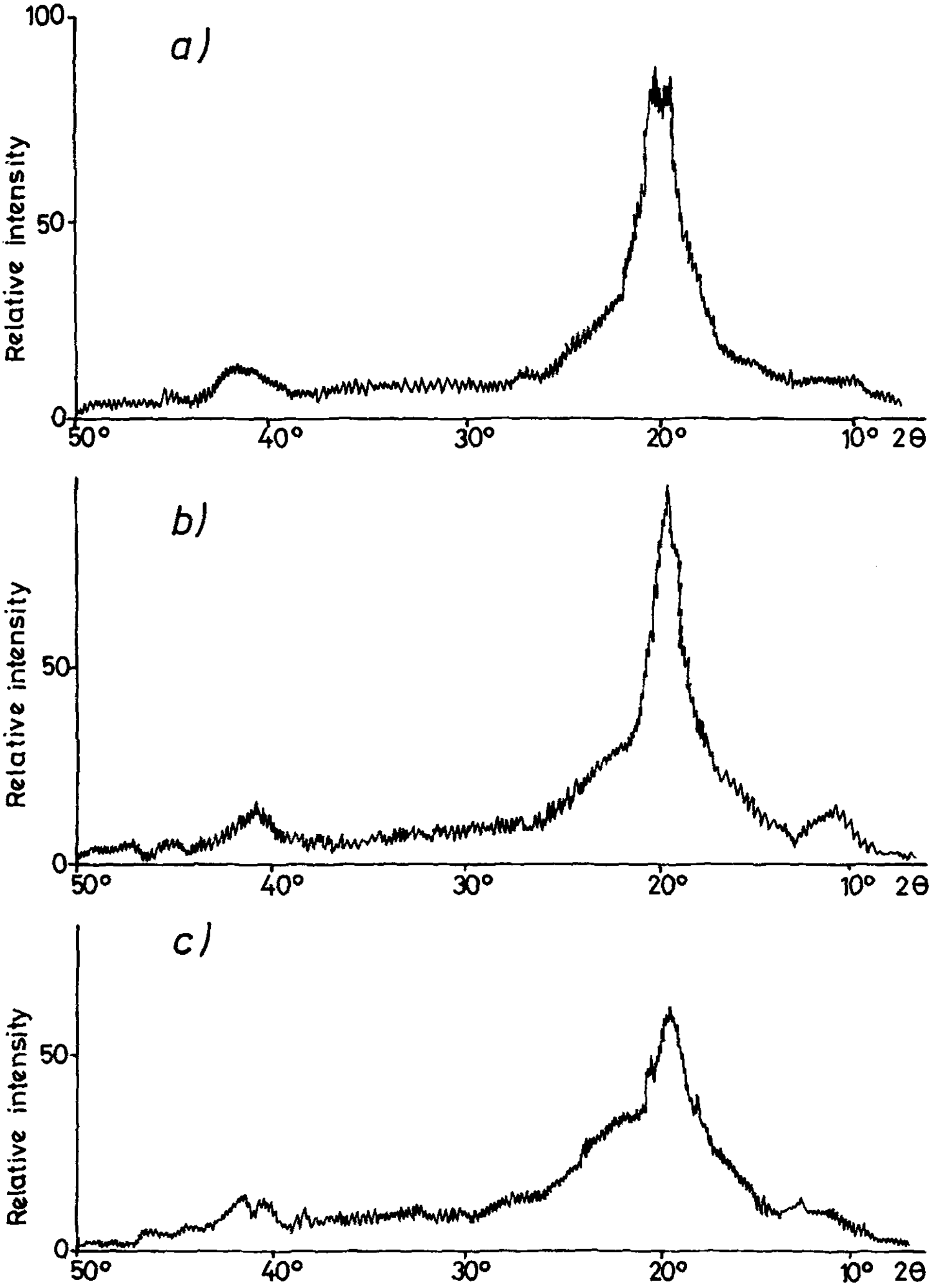
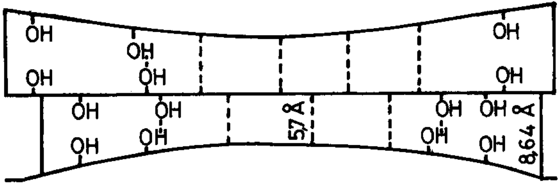
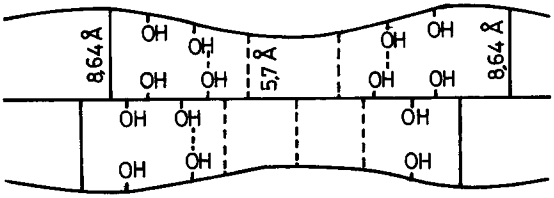
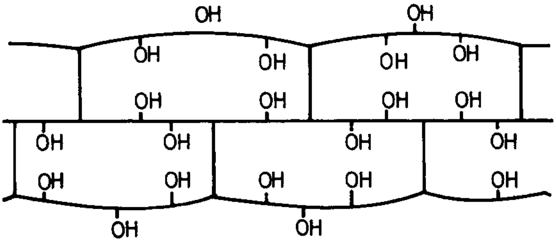
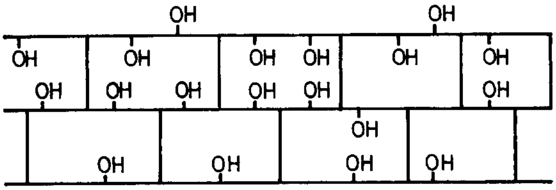


Fig. 1. X-ray spectra of PVA (a), of cross-linked PVA-X-5 (b) and of PVA-X-40 (c).

Scheme I - Hypothetical structure of CL-PVA with various cross-linking degrees

Type of gel	Schematical diagram of hypothetical structure of CL-PVA with various degree of cross - linking	Gel bed ml/g	Observations
PVA-X-5		3.33	Reduced reticulation degree; most contracted network - high hydrogen association.
PVA-X-10		3.90	Tight network; more interchain glycerine bridges; reduced number of hydrogen bonds than in case of CL-PVA-X-5.
PVA-X-20		4.45	High reticulation degree; much more interchain glyceric bridges; hydrogen association is avoided; the most expanded network.
PVA-X-30		3.90	Advanced reticulation degree; closed network due to the high number of interchain glycerine bridges.

——— = PVA chains; | = interchain glycerine bridges;

⋮ = interchain hydrogen bonds.

tilled water and in 8 M urea solutions, the bed volumes obtained in urea solutions are with 14 % higher than in H_2O in case of PVA-X-5, whereas in case of PVA-X-20 the difference was only of 9 %. Much more, if swollen PVA-X-5 and PVA-X-20 beads were transferred from water in 8 M urea solution, the increase of bed volume was of 15 % in case of PVA-X-5 and only 11% in case of PVA-X-20. The higher values of volume increases, in case of PVA-X-5 are explained by the higher number of hydrogen bonds broken by 8 M urea treatment, and consequently the gel is more expanded by this procedure.

From the above data, evidence is offered for our supposition concerning the main role of hydrogen bonds in the network organisation; they can be schematically presented in scheme I. These hydrogen interchain associations can be, to a certain extent, responsible for the excellent mechanic properties and for the high osmotic shock resistance (86 -91%) (8) of CL-PVA beads, with perspectives to be used as stationary phases in exchange and affinity chromatography and as supports for enzymes immobilizations.

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Accepted February 17, 1984