Intramolecular crosslinking of poly(vinyl alcohol)

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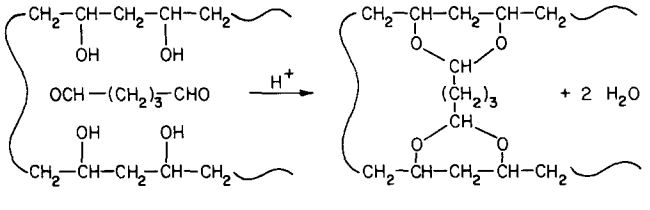
Poly(vinyl alcohol) is crosslinked in dilute solution ($c = 0.1$ wt%) with glutaraldehyde. The reaction product is characterized by viscometry and gel permeation chromatography (g.p.c.). The intrinsic viscosity decreases with increasing degree of crosslinking and does not depend on temperature. G.p.c. reveals that the reaction product is not homogeneous, but consists of a mixture of particles with different sizes, possibly both intra- and intermolecularly crosslinked molecules. The intramolecularly crosslinked molecules are smaller in size than the initial polymer molecules and their size depends on the degree of crosslinking. They possess a narrow particle size distribution even if the initial polymer sample had a broad molecular weight distribution.

(Keywords: poly(vinyl alcohol); intramolecular crosslinking; gel permeation chromatography; molecular weight distribution; intrinsic viscosity; fractionation)

INTRODUCTION

If a crosslinking agent is added to a polymer solution, two different modes of crosslinking can be expected[1,2]. The first one is the crosslinking between different polymer molecules, called intermolecular crosslinking, which will lead to an increase in viscosity and finally to a gelation of the system. The second mode is the internal crosslinking of a single polymer molecule, called intramolecular crosslinking, leading to a decrease in viscosity due to volume contraction of the polymer coils. In previous papers on this subject[1-5] viscosity measurements were performed to indicate the mode of crosslinking and to determine the volume contraction. Intramolecular crosslinking occurs preferentially in dilute polymer solutions.

In this paper we study the possibility of preparing monodisperse, globular nanoparticles with low deformability by the intramolecular crosslinking of linear, high molecular weight polymers. Following Aharoni[3] poly(vinyl alcohol) (PVA) was crosslinked with glutaraldehyde aiming at different degrees of crosslinking, i.e. the number of crosslinks per 100 structural units of the polymer chain.



The reaction product was characterized not only by viscosity measurements performed both at constant and at varying temperatures in order to study the effect of crosslinking, but also by gel permeation chromatography (g.p.c.) to study the particle size distribution. G.p.c. is a useful tool for the fractionation and separation of molecules according to their size. Molecules are eluted in order of decreasing molecular size. In this way g.p.c. could provide a means of detecting intermolecularly crosslinked molecules and a possibility of separating them from the intramolecularly crosslinked molecules. Furthermore g.p.c. is used as a fractionation method before crosslinking in order to reduce the molecular weight distribution of the initial polymer. Thus the influence of the molecular weight distribution of the initial polymer on the final particle size distribution of the intramolecularly crosslinked molecules was examined.

EXPERIMENTAL

Materials and methods

Two poly(vinyl alcohol) samples, supplied by Aldrich, were used with different molecular weights and different degrees of hydrolysis. Specifications of the samples are given in *Table 1*.

Molecular weights and molecular weight distributions were determined by h.p.l.c. in combination with low-angle laser light scattering, as described below. The degree of hydrolysis was determined making use of a saponification technique[6]. Glutaraldehyde, supplied by Merck, was used as received.

The crosslinking reaction

PVA was dissolved in water ($c = 1$ g/l) by refluxing and stirring for at least one day at 95°C. To 60 ml of this solution water (30 ml) containing an appropriate amount of glutaraldehyde was added and the reaction was started with 10 ml of 1 N hydrogen chloride solution. After stirring at room temperature for 20 h the reaction was stopped by neutralization with 10 ml of 1 N sodium hydroxide solution.

The anticipated degree of crosslinking could be varied by changing the ratio of PVA to glutaraldehyde. Previous studies[4] indicated that the NaCl formed had no influence on viscosity values so that the reaction mixture was employed for viscosity measurements without further purification. All crosslinking reactions were performed at

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Table 1 Specifications of the poly(vinyl alcohol) samples

Sample code	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Intrinsic viscosity (ml g^{-1})	Degree of hydrolysis (%)
PVA-96-88	82 500	2.06	79.5	89.0±0.5
PVA-126-98	101 000	1.60	105.1	97.7±0.5

polymer concentrations of 0.1 wt%.

The degree of crosslinking given in the text and in the Figure captions refers to the theoretical figure for complete reaction between PVA and glutaraldehyde.

Viscosity measurements

Viscosity measurements were carried out using an Ubbelohde viscometer. The temperature during the measurements was controlled within 0.001°C. The intrinsic viscosities of the initial polymer samples are given in *Table 1*.

Gel permeation chromatography

A glass column with an internal diameter of 5 cm and a fitted at the top and bottom. The column was packed as recommended with Sepharose 6 B gel (Pharmacia Ltd.).

The bed height was 88 cm. Twice distilled water with a trace of sodium hydrazide was used as the eluent, which trace of sodium hydrazide was used as the eluent which provided a continuous flow through the column under pressure of about 1.5 m water. An automatic fraction collector (LKB bromma, 2111 multirac) was employed, set to collect 140 fractions containing 300 drops each. Each fraction contained about 14 ml eluent depending on the amount of PVA present. Void volume (574 ml) and total volume (1834 ml) of the column were determined using a mixture of Blue Dextran and Vitamin B12. Blue Dextran was eluted at about fraction number 41, Vitamin B12 was eluted at about fraction number 130.

For each fractionation a 50 ml sample was applied at the column top and the fractionation lasted about 24 h. The fractions were tested for the presence and the amount of PVA using a total carbon analyser (Beckman, model 915).

The molecular weight and molecular weight distribution of the g.p.c. fractions and of the original PVA samples were determined using h.p.l.c. (high pressure liquid chromatography) in combination with LALLS (low-angle laser light scattering). TSK G 4000 PW and TSK G 3000 PW columns, connected in series, and a Chromatix KMX LALLS apparatus were used.

RESULTS AND DISCUSSIONS

Figure 1 shows the results of the viscosity measurements at different temperatures and different degrees of crosslinking of PVA-96-88. The intrinsic viscosity of uncrosslinked PVA decreases with increasing temperature. Apparently the conformation of the molecules changes with temperature. After crosslinking the molecules have clearly lost this ability to change their conformation since temperature does not seem to affect the intrinsic viscosity any more. This can be explained by loss of flexibility due to internal crosslinking. For the crosslinked polymers the intrinsic viscosity decreases with increasing degree of crosslinking (see also *Figure 1*). This is in agreement with earlier reports on intramolecular crosslinking[1-5]. According to Kuhn[1,2] and Aharoni[3] a decrease in intrinsic viscosity is an indication that the intramolecular crosslinking has been effective. It is explained as a progression in volume contraction of each polymer coil as a consequence of increasing degree of intramolecular crosslinking.

Surprisingly, however, the g.p.c.-elution curves of the crosslinked PVA samples, shown in *Figures 2* to *4* and in *Figure 6*, exhibit at least two peaks. One in the range between fraction numbers 40 to 80, representing particles of size and size distribution comparable with the initial polymer molecules, the other one after fraction number 100, representing much smaller particles with a narrow particle size distribution. Furthermore the latter peak can be divided into two peaks.

Further investigation of the fractions belonging to these peaks, i.e. of fraction numbers 40 to 80 and 100 to 140

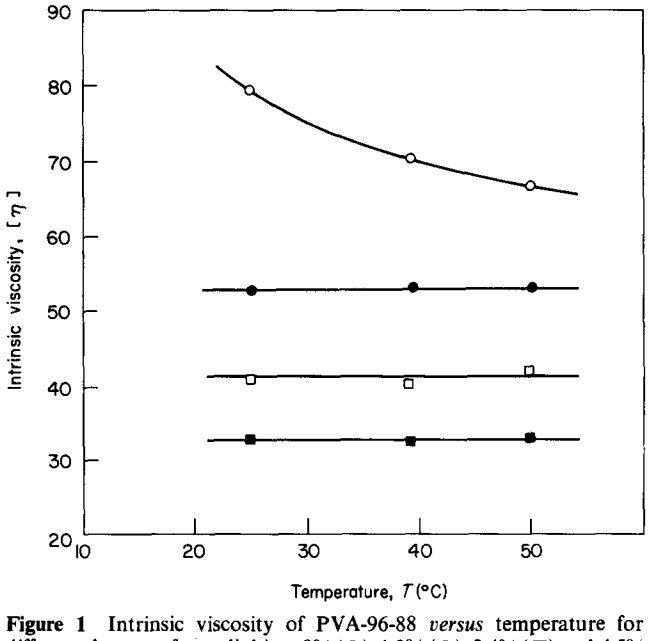

Figure 1 Intrinsic viscosity of PVA-96-88 *versus* temperature for different degrees of crosslinking, 0% (○), 1.2% (●), 2.4% (□) and 4.5% (■)

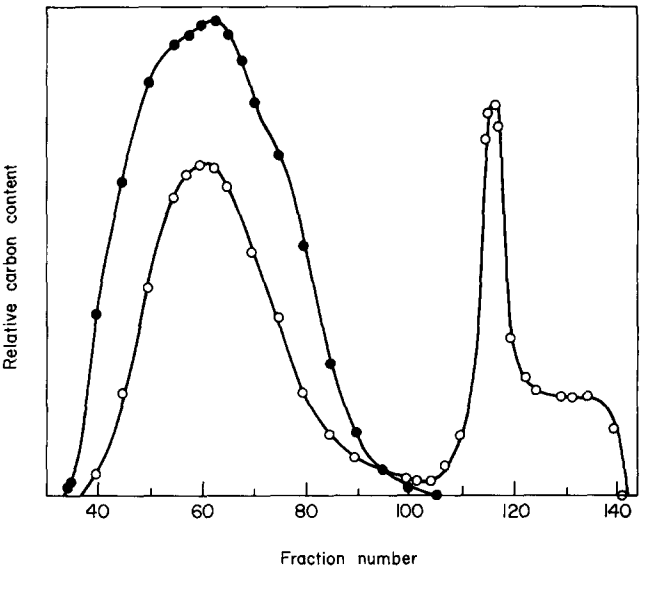

Figure 2 G.p.c. elution curves for PVA-126-98 (●) and for PVA-126-98 crosslinked to a degree of 1.5% (○)

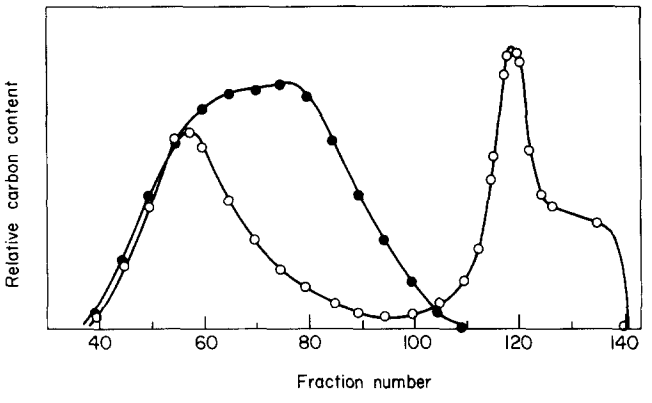

Figure 3 G.p.c. elution curves for PVA-96-88 (●) and for PVA-96-88 crosslinked to a degree of 2.5% (○)

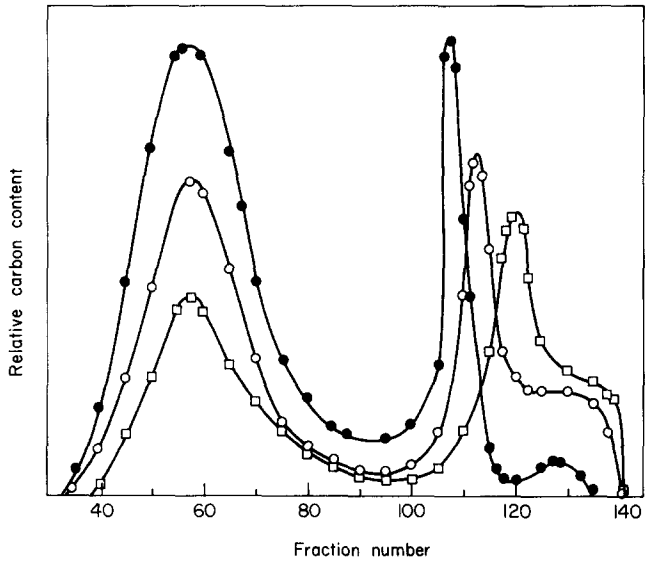

Figure 4 G.p.c. elution curves for PVA-96-88 crosslinked to three different degrees of crosslinking, 0.3% (●), 1.0% (○) and 2.5% (□)

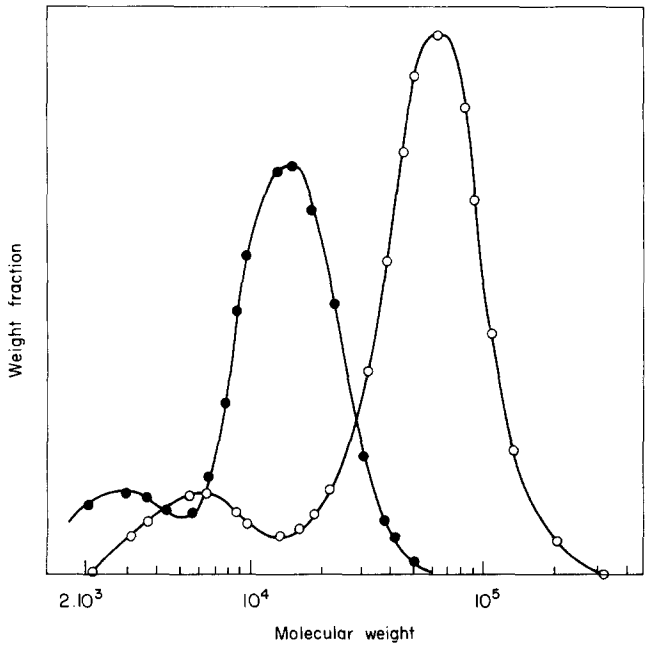

Figure 5 H.p.l.c. chromatogram for g.p.c. fractions of PVA-96-88, combined fractions 91–100 (●) and combined fractions 71–80 (○)

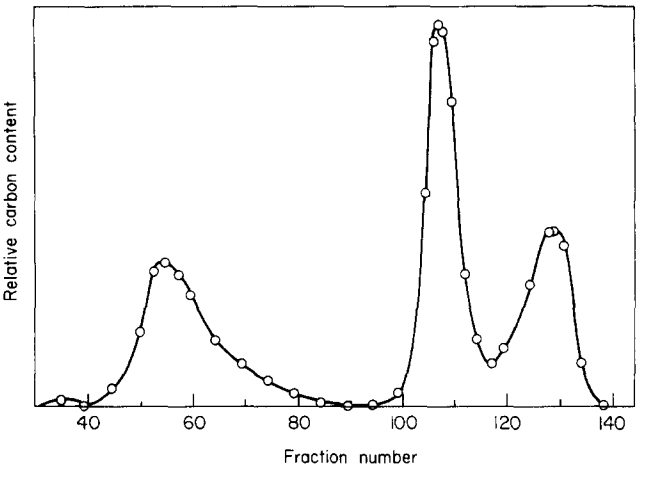

Figure 6 G.p.c. elution curve for fractionated PVA-96-88 (combined fractions 70–80) crosslinked to a degree of 1.0%

respectively, for the crosslinked sample PVA-126-98, shows that both have an intrinsic viscosity lower than that of the initial polymer, which does not decrease with increase in temperature (see *Table 2*). For the smallest particles, those eluted after fraction number 100, this low $[\eta]$ value can be explained by a decrease in particle size. In *Figure 4* the influence of degree of crosslinking on this size is shown for the crosslinked sample PVA-96-88. The sharp peak at about fraction number 110 moves to higher elution volumes for increasing degrees of crosslinking. Thus particle size decreases with increasing degree of crosslinking. This is in agreement with the theory of volume contraction due to intramolecular crosslinking. It is therefore reasonable to assume these particles to be the intramolecularly crosslinked molecules.

The lower $[\eta]$ value for the fractions between fraction numbers 40 and 80 as compared with the $[\eta]$ value of the initial polymer cannot be explained by assuming a smaller size, because particles eluted at the same elution volume have the same hydrodynamic volume[7]. This hydrodynamic volume is proportional to the product $\bar{M}_w[\eta]$. Hence these particles should have a higher molecular weight than that of the initial polymer. Therefore we assume these particles to be agglomerates of two or more PVA molecules, both inter- and intramolecularly crosslinked.

One intriguing problem remains: there seem to be two types of particles between fraction numbers 100 and 140. While the first peak (around fraction number 110) represents intramolecularly crosslinked PVA molecules the cause of the second peak remains unclear.

Firstly we could think of a degradation product as a consequence of the reaction circumstances. Vink[8], however, could not detect any degradation of PVA in aqueous

Table 2 Intrinsic viscosities of PVA-126-98 compared with crosslinked PVA-126-98 divided into two different g.p.c. fractions, measured at two different temperatures

Degree of crosslinking (%)	Fraction number	Intrinsic viscosity (ml g^{-1})	
		$T = 25°C$	$T = 40°C$
0.0	–	105.1	96.3
1.5	40–80	48.5	49.7
1.5	100–140	18.6	19.9

Table 3 Molecular weights and molecular weight distributions of the PVA samples and some g.p.c. fractions

Sample	Fraction number	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PVA-96-88	–	82 500	40 000	2.06
	54	173 500	144 500	1.20
	76	73 000	57 500	1.27
	94	17 000	14 500	1.19
	71–80	70 000	54 000	1.29
	91–100	17 500	13 500	1.28
PVA-126-98	–	101 000	63 000	1.60
	45	199 000	170 000	1.17
	60	107 000	87 000	1.23
	81	23 500	19 500	1.20
	61–70	111 500	91 000	1.23

1N hydrochloric acid at 25°C in an oxygen atmosphere. Hence, the particles belonging to the second peak around fraction number 130 are not expected to be degradation products formed under reaction conditions. A second explanation for the appearance of a different type of particles can be derived from an observation made during h.p.l.c. characterization of g.p.c. fractions of the original PVA samples. These g.p.c. fractions seemed to consist of two types of particles.

Results of g.p.c. fractionation of the original PVA samples are given in *Table 3*. By applying g.p.c. fractionation it is clearly possible to obtain PVA fractions with $\bar{M}_w/\bar{M}_n$ values of about 1.2. An example of an h.p.l.c. chromatogram for two g.p.c. fractions of PVA-96-88 is given in *Figure 5*. In this chromatogram, besides the appearance of a main peak, a second smaller peak is observed for each g.p.c. fraction. The $\bar{M}_w$ and $\bar{M}_n$ values were calculated only for the main peaks. The second peak was observed in all g.p.c. fractions. If PVA was absent from a fraction then no second peak appeared in the chromatogram. Clearly each g.p.c. fraction does contain two different species which are separated by h.p.l.c. The molecular weight of the second species, as occurring in *Figure 5*, does not have to be correct because it is calculated as if it were PVA-96-88. This phenomenon of two different species in one g.p.c. fraction cannot yet be explained. The most reasonable explanation seems to be that it results from a distinct difference in degree of hydrolysis within the PVA sample.

If unreacted PVA is fractionated and ten consecutive fractions are combined in order to increase the amount of fractionated PVA and then crosslinked in the usual way, the reaction product shows a g.p.c. elution curve (see *Figure 6*) which is almost the same as that for crosslinked, non-fractionated PVA.

Again there is a sharp peak around fraction number 110 and a second one around fraction number 130, so the occurrence of a more or less separated second peak is not prevented by the preceding fractionation of the PVA sample. This second peak could possibly represent the crosslinked second species present in the g.p.c. fractions of the original PVA. A distinct difference in degree of hydrolysis could perhaps result in a different degree of crosslinking.

Furthermore it seems that the particle size distribution of the intramolecularly crosslinked molecules, i.e. the particles eluted around fraction number 110, is independent of the molecular weight distribution of the initial polymer.

Apparently the process of intramolecular crosslinking itself leads to uniformity in size of the intramolecularly crosslinked molecules.

CONCLUSIONS

A decrease in intrinsic viscosity after crosslinking of PVA molecules does not necessarily mean that the crosslinking is only intramolecular. The crosslinked polymer consists of two (or three) types of particles of different size, possibly intra- and intermolecularly crosslinked. The intramolecularly crosslinked single PVA molecules are smaller than the initial polymer molecules and their size decreases with increasing degree of crosslinking. The size distribution of the intramolecularly crosslinked PVA molecules is narrow even if the original polymer sample has a broad molecular weight distribution. Fractionation of the original sample does not affect the particle size distribution of the intramolecularly crosslinked molecules. Intramolecular crosslinking is effective in making the PVA molecules less deformable. After crosslinking, temperature no longer has any effect on the intrinsic viscosity of the crosslinked polymer sample.

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