

The Structure and Extent of Supramolecular Formation in Aged Aqueous Poly(vinyl alcohol) Solution

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Summary: Two commercial samples of PVA were subjected to determine the supramolecular structure formation in aqueous media, by light scattering and viscometric method. Solutions of various concentrations were aged upto 80 days and then, the intrinsic viscosity $[\eta]$, weight average molecular weight (Mw), radius of gyration $(R_g^2)^{1/2}$ were determined. From this, the extent of supramolecular formation of fresh solutions as well as the aged solutions was determined. It was found that supramolecular formation occurs to a lower degree during aging, and it increases with the concentration of the aging solution.

Introduction

Aqueous solutions of poly (vinyl alcohol), (PVA), are not stable and undergo the process of aging, reflected predominantly, in rise in their viscosity with time which in concentrated solutions is followed by gel formation [1]. This effect has been known for a long time and is the cause underlying the formation of aggregated supramolecular structure [2]. The formation of such structures is effected by the tacticity of the polymer and by the content of residual acetate groups. The structures are supposedly formed also in dilute solution and contain amorphous and paracrystalline parts [3-4].

Previously, the aging of aqueous PVA solutions was characterized by its non-zero normal stress values and some time gel consistency [5-6]. No accurate method is available for determining this property. In the present study an attempts has been made to study the aging effect by viscosity and light scattering method, because these methods are sensitive to even the presence of a small amount of supramolecular particles in a system [7-9]. By using light scattering techniques we investigate the process of aging by studying the time dependence of the increase in weight average molecular weight (Mw) and average radius gyration $(R_g^2)^{1/2}$. These results were supplemented by information from intrinsic viscosity measurements.

Results and Discussion

For both PVA samples, the concentration of aging solution were within a range in which the

polymer at room temperature remains in solution and does not turn into gel. All measurements were performed after the aged solution had been diluted to a suitable concentration less than critical concentration. The purification process of dilute solution for light scattering measurement took some time. This time could be short for entanglements to become completely disentangled, especially in strongly aged solution (i.e. after 80 days).

We first determined the intrinsic viscosity of the freshly prepared solutions and then of the aged solutions, that is after 10 days, 20 days, 30 days, 40 days, 50 days and finally after 80 days. These values of $[\eta]$ are given in the second column of Tables (1 and 2). These values when plotted against the days (Fig. 1) indicate that the intrinsic viscosity of aged solutions increases with time to some extent and then becomes more or less constant. This is probably due to the formation of supramolecular network very soon after cooling the solution prepared at 80 °C. The increase in $[\eta]$ is pronounced in the beginning and then after sixty days a lesser increase is observed. This may be due to the fact that stable intermolecular contacts form rapidly in the beginning and then their number increases slowly with time [6].

Average values of weight average molecular weight (Mw) for fresh solutions and aged solutions of PVA determined by light scattering technique at two different wave lengths i.e. 436 nm and 546 nm, are given in the third column of the Tables (1 & 2). Figure (2 & 3) represent the plot of Mw vs days

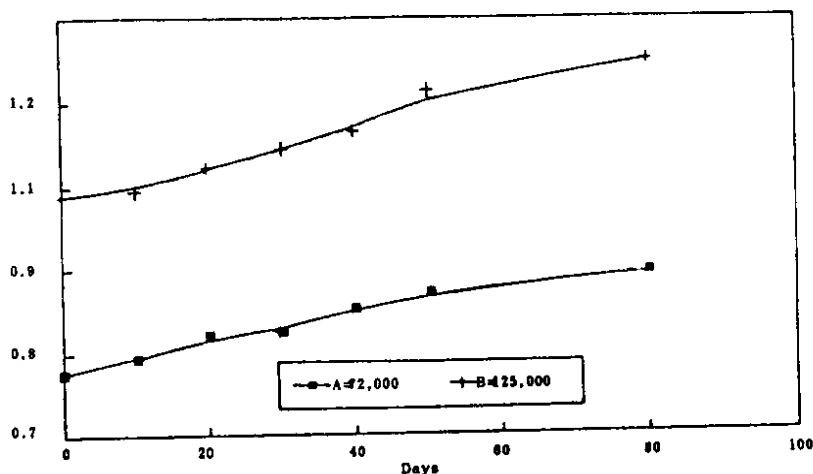


Fig. 1: Plot of intrinsic viscosity against number of days for sample A and B.

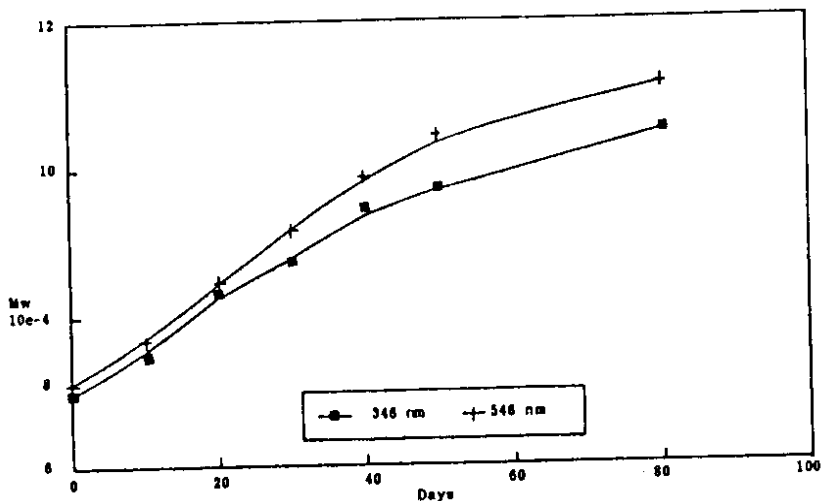


Fig. 2: Variation in molecular weights of sample A with time (days).

Table 1: Values of intrinsic viscosity $[\eta]$, weight average molecule weight (M_w), radius of gyration $(R_g^2)^{1/2}$ and supermolecular dimension for PVA-water system (sample A) after various days.

Days	$[\eta]$	$M_w \cdot 10^{-4}$	$(R_g^2)^{1/2} \cdot 10^3$ (E.A)	
F.S	0.775	7.019	108.154	-
10	0.792	7.577	111.753	5.123
20	0.819	8.381	116.876	5.000
30	0.828	8.961	119.947	3.071
40	0.852	9.650	124.124	4.177
50	0.868	10.070	126.685	2.561
80	0.892	10.813	130.915	4.230

(F.S.) = Fresh solution (E.A.) = Extent of association.

Table 2: Values of intrinsic viscosity $[\eta]$, weight average molecular weight (M_w), radius of gyration $(R_g^2)^{1/2}$ and supermolecular dimension for PVA-water system (sample B) after various system.

Days	$[\eta]$	$M_w \cdot 10^{-5}$	$(R_g^2)^{1/2} \cdot 10^3$ (E.A)	
F.S	0.988	1.265	142.740	-
10	0.994	1.315	144.882	2.142
20	1.021	1.359	147.792	2.910
30	1.041	1.439	151.627	3.835
40	1.063	1.509	155.107	3.480
50	1.108	1.586	159.899	4.792
80	1.145	1.630	163.141	3.242

(F.S) = Fresh solution (E.A) = Extent of association

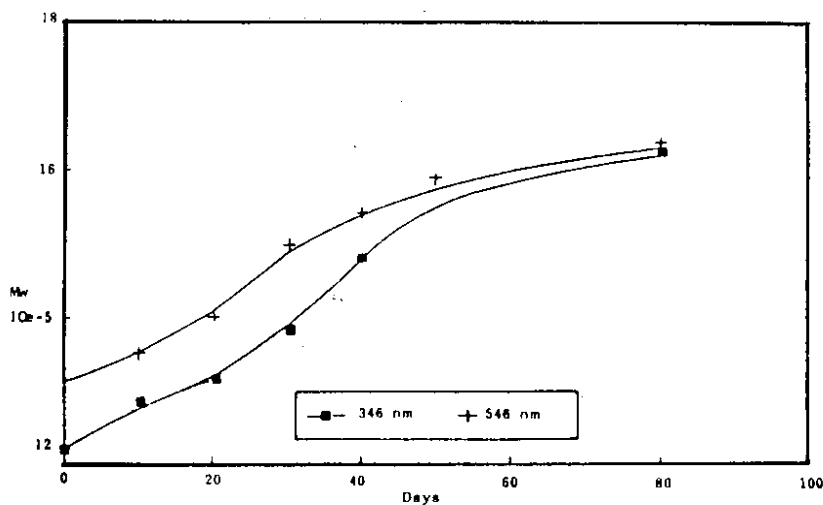


Fig. 3: Variation in molecular weights of sample B with time (days).

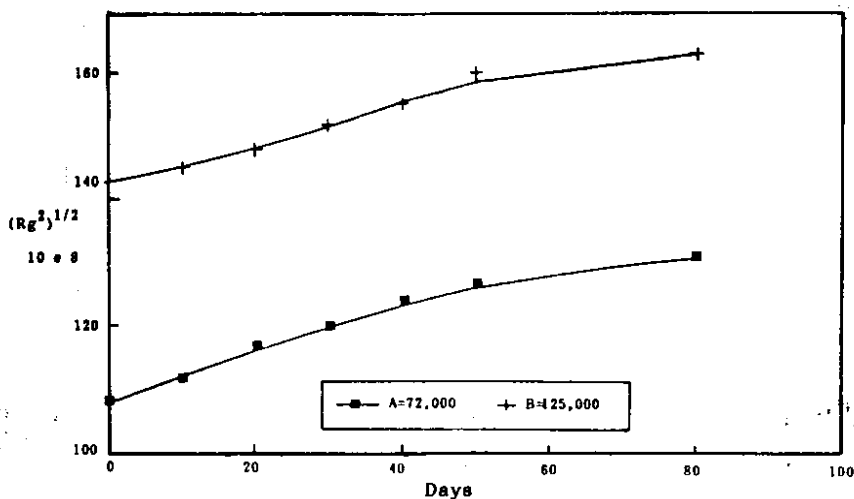


Fig. 4: Variation of the radius of gyration of samples A and B with time.

showing increase in Mw occurs between 60-80 days. The predominant factor which causes this, is the weight fraction of supermolecular particle [13].

The $(Rg^2)^{1/2}$ values of aged solutions give the dimension of the supermolecular formation alone, Fig. (4) indicates the radius of gyration for the two samples. The data in the table shows that $(Rg^2)^{1/2}$ increases with polymer molecular weight and also with time which shows formation of larger sized particles of the polymer molecules with time [14]. The extent of association or the dimension of the

supermolecule after various days of aging are obtained from the $(Rg^2)^{1/2}$ values of the aged solution minus $(Rg^2)^{1/2}$ of the fresh solution. These values are given in the last column of the Tables (1 & 2). The values show that the dimension of supermolecule increase rapidly upto 50 days after which the increase becomes slower upto 80 days. This can be explained by the decrease in polydispersity of the supermolecular structure with aging of the solutions [6,15]. So it may be concluded that aging is a process in which supermolecular formation arises, irrespective of the concentration of the solution,

where the predominant part of the polymer remains in the nonaggregated form. If the interpenetration of polymer chains takes at the same time, they become linked, thus, inturn give rise to the gel system [16]. The bond between the macromolecule are of physical nature and their existence is related probably with considerable crystallization ability of PVA. By this behavior the aging PVA-water system in many ways resemble polymer lattice with out surface charge [17].

Experimental

I. Polymer samples

Two samples of fully hydrolyzed poly (vinyl alcohol) PVA, manufactured by BDH chemical Ltd. England ($A = 7.2 \times 10^4$ and $B = 1.25 \times 10^{-5}$) were used. Solutions of PVA were prepared at 80 °C in triply distilled water. The concentration range for the aging solutions were 2-10g/dL with interval of 2g/dL. The solutions were aged at room temperature (approx 23°C). Before measurements, the aged solutions was diluted to concentration less than critical concentration C^* [10].

II. Methods

a) Viscometry

Viscosity was measured at 25 °C with calibrated Ostwald viscometer. The intrinsic viscosities of the two samples for various concentrations were obtained from the intercept of the plot of Huggin's equation [11].

b) Light scattering

These measurements were carried out on Brice Phoenix Universal light scattering photometer [12], using blue and green light of wave lengths 436 nm and 546 nm respectively. Due to the low molecular weight of the samples angular dependence of the scattered light was not possible so the turbidity method was employed for molecular weight determination instead of the Zimm method. The intensities of the scattered light were measured at 0° and 90° angle to the incident radiation of unpolarized light at room temperature. The molecular weight was determined by plotting HC/τ versus concentration according to Debye equation

$$HC/\tau = 1/Mw + 2A_2 C$$

Where C is the concentration in gram per cubic centimeters and A_2 is the second virial co-efficient. H is the optical constant, and is given by

$$H = 32 \pi^3 n_0 (dn/dc)^2 / 3 N_0 \lambda^4$$

n_0 = refractive index of solvent,

N_0 = Avogadro's number,

dn/dc = variation of refractive index of the solution with concentration,

λ = wave length of light in vacuum.

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