

Poly(vinyl alcohol) Polymers with a Low Degree of Hydrolysis. I. Formation and Dissociation of Multimers in Aqueous Solution

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In aqueous solution poly(vinyl alcohol) polymers with a relatively high content of residual acetate groups were found to form associates of a micellar-like type. The associates dissociated on addition of ammonium laurate and reformed on removal of the tenside. The associating tendency and the tendency to form red complexes with iodine increased rapidly with an increase in the amount of residual acetate groups, suggesting that these phenomena were caused by the presence in the polymer molecules of poly(vinyl acetate) blocks. The results indicated that the hydrophobic blocks were unevenly distributed over the molecules. The cloud point temperature of aqueous solutions of these blocky polymers decreased on addition of vinyl chloride and increased on addition of ammonium laurate. This most likely was caused by interactions between these substances and the hydrophobic blocks of the polymer molecules.

Water soluble polymers obtained by partial or complete hydrolysis of poly(vinyl acetate) are commonly referred to as poly(vinyl alcohols), PVAL. Such polymers with a rather low degree of hydrolysis (a relatively high content of residual acetate groups) have recently attracted a growing interest as suspension stabilizers in the manufacture of poly(vinyl chloride), PVC, by the suspension process.¹ In the manufacture of suspension PVC resins, the choice of the suspension stabilizing system is rather important as it determines the product properties which are related to the size, shape and morphology of the resin particles. In practice, this makes the stabilizing system the single most important process variable.

The suspension stabilizing systems used in PVC production usually contain a water soluble polymer

as the main component. This is often combined with small amounts of a low molecular weight surfactant. The present knowledge of the mechanisms by which the suspension stabilizers control the resin properties is very sparse and mainly empirical.

The present work was carried out as part of a larger study aiming at a better understanding of the role of the suspension stabilizing system in PVC production. The PVAL polymers of primary interest in this work are soluble in cold water and their aqueous solutions tend to turn turbid on heating. This occurs with polymers having a degree of hydrolysis lower than about 75 mol % (75 % of the monomer units in the polymer have been converted to vinyl alcohol residues). PVAL polymers of this type have been the subject of very few studies as compared to those with a higher degree of hydrolysis, *e.g.* 85 %, which give stable solutions in cold as well as in hot water or to the almost fully hydrolyzed polymers (= about 99 %), which give stable solutions in hot water only.²

The present paper will deal with the phenomenon of self-association or multimerization³ of a number of commercial PVAL products. The effect of ammonium laurate, AL, and vinyl chloride, VCM, on this phenomenon will also be discussed. In a subsequent paper, a report will be given about the complexation of the same set of PVAL polymers with ammonium laurate and sodium lauryl sulfate.⁴ In a forthcoming paper the effect of PVAL with a low degree of hydrolysis on the interfacial tension at the VCM/water interface and on the stability of emulsions of VCM in water will be reported and compared with a cellulose derivative.⁵

Table 1. Commercial PVAL polymers used in the present study.

Trade name	Degree of hydrolysis %	Producer
Rhodoviol 5/270	71.5	Rhone-Poulenc
Mowiol LP 5.72	70.5	Hoechst AG
Polyviol M 05/290	74.7	Wacker Chemie
Alcotex 72.5 L	71.7	Revertex Ltd.
Alcotex 75 L	72.2	Revertex Ltd.
Elvanol 51-05	87.5	Du Pont
Elvanol 70-05	98.9	Du Pont

EXPERIMENTAL

Polymers. The commercial polymers used in this work are presented in Table 1. The values given for the degree of hydrolysis were determined by a method described by Finch.² Most of the experiments were carried out using Rhodoviol as an example of the PVAL's with a low degree of hydrolysis. In most cases the polymers were used without previous purification. Reference experiments with Rhodoviol purified by reprecipitation (water-acetone) or by ultrafiltration indicated that this could be done without introducing any errors in the self association studies.

Chemicals. AL was prepared by dissolution of lauric acid, LA, (BDH, specially pure) in dilute ammonia. Vinyl chloride was obtained from Kema-Nobel, Sweden. It was distilled from the steel cylinder prior to use. All aqueous solutions were prepared using distilled and then deionized water.

Gel permeation chromatography (GPC) experiments. The GPC or gel filtration experiments were carried out using thermostatted columns of the type provided by Pharmacia. Except where otherwise stated, the GPC experiments were carried out at 23 °C. The samples were added using a sampling valve. A peristaltic pump, a motor driven syringe or a reciprocating chromatography pump (Altex, model 110) were used for pumping the eluant. A differential refractometer was used as detector (Optilab Multiref 901 or LDC). In most cases a pre-column was used to eliminate pressure variations in the detector. The columns were calibrated using Dextran solutions with a broad molecular weight distribution, MWD, prepared by mixing fractions of Dextran T obtained from Pharmacia. The calibration was made according to the method developed by Abdel-Alim and Hamielec.⁶

Solubilization of vinyl chloride. The ability of PVAL polymers and AL to solubilize VCM was determined by vapour pressure measurements on aqueous solutions containing weighed amounts of VCM. The experimental arrangement used has been described in a previous paper.⁷

RESULTS AND DISCUSSION

Formation and dissociation of polymer associates. Preliminary ultracentrifugation runs on aqueous solutions of Rhodoviol 5/270 (Table 1) had indicated that this polymer contained two components; one with a high and one with a low sedimentation coefficient. In agreement with this observation the GPC results reproduced in Fig. 1 also indicated that this polymer contained two fractions; one with a high molecular weight (I), which was not fully resolved on the column used, and one with a much lower molecular weight (II). When fractions I and II, collected from a series of experiments were rerun on the same columns, the results shown in Fig. 2 were obtained. The fact that the two fractions gave quite different chromatograms, supported the indication that the MWD of the sample was bimodal. It had been observed, however, that the cloud point temperature of dilute solutions of this polymer

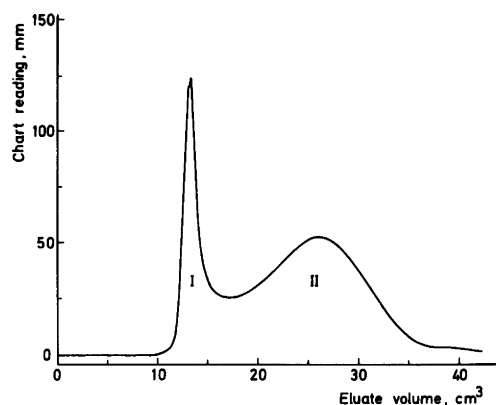


Fig. 1. GPC of Rhodoviol 5/270 (0.3 cm³ of a 1% solution) on Sepharose Cl-6B. Column: 15 × 220 mm. Elution: Water, 044 cm³/min.

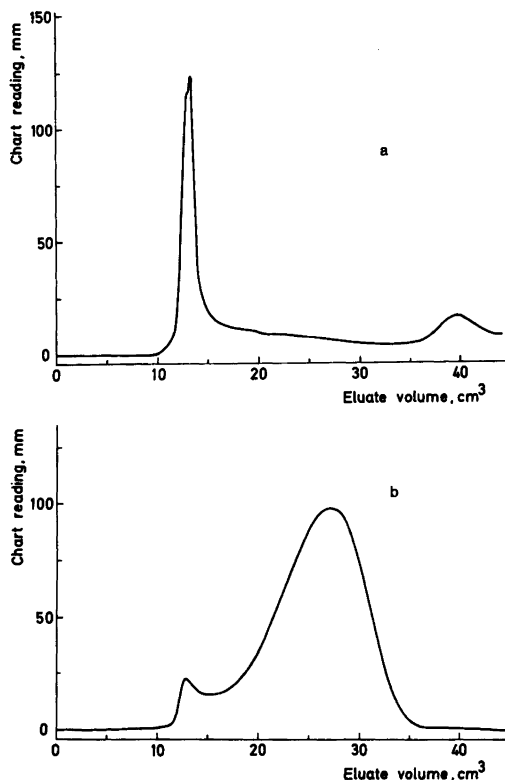


Fig. 2. GPC of fraction I (a) and II (b) from Rhodoviol 5/270 on Sepharose Cl-6B. Column: 15×220 mm. Elution: Water, $0.44 \text{ cm}^3/\text{min}$.

increased (in these systems the cloud point is reached by heating from room temperature) rapidly on addition of AL. This initiated GPC experiments

in which dilute solutions of AL were used as an eluant instead of pure water. Results from such an experiment are given in Fig. 3. The peak at 40 cm^3 in this figure corresponds to the excess amount of AL in the sample solution and has no relation to the polymer. As can be seen, in the presence of AL the high molecular weight fraction seems to have disappeared. As will be shown below, this effect of AL was reversible. This means that the difference between results in Figs. 1 and 3 cannot be ascribed to a hydrolysis of the polymer in the weakly alkaline laurate solution. Instead, the difference must be interpreted to show that in pure aqueous solution this polymer to a large extent associates and forms multimers with a high apparent molecular weight. These associates dissociate on addition of a small amount of AL.

The results in Fig. 4 were obtained using 0.1 M NaCl as an eluant instead of water. Although the shape of the chromatogram was affected by the presence of salt, the multimers did not dissociate. This means that the dissociative effect of AL on the PVAL associates was due to a selective interaction between the soap and the polymer and not the result of nonspecific electrolyte interactions. The influence of NaCl on the shape of the chromatogram will not be discussed here. It should be pointed out, however, that the total effect of NaCl includes that on the separation properties of the Sepharose gel.

The question could be raised whether the association of the polymer as observed in pure aqueous solution was an equilibrium property of the solution or not. To test this, the following experiments were made. To an aqueous solution of Rhodoviol was added AL. The mixture was then placed in an ultra filtration cell and the laurate was washed out

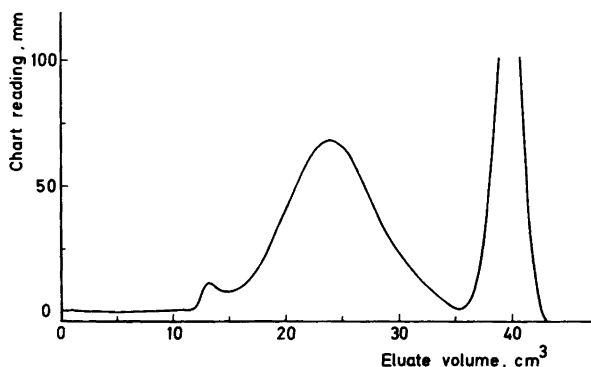


Fig. 3. GPC of Rhodoviol 5/270 (0.3 cm^3 of a 1% solution containing 0.5% AL) on Sepharose Cl-6B. Column: 15×220 mm. Elution: 0.1% AL, $0.44 \text{ cm}^3/\text{min}$.

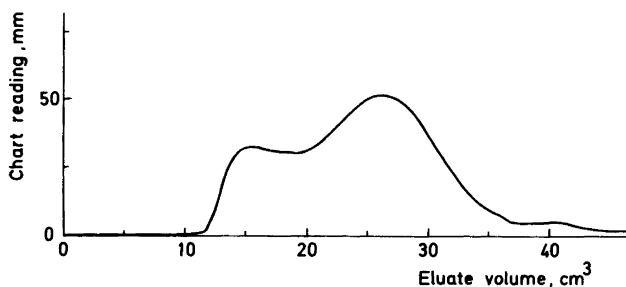


Fig. 4. GPC of Rhodoviol 5/270 (0.2 cm^3 of a 1 % solution containing 0.1 M NaCl) on Sepharose Cl-6B. Column: $15 \times 220 \text{ mm}$. Elution: 0.1 M NaCl, $0.44 \text{ cm}^3/\text{min}$.

with water. Results from a GPC run on the resulting polymer solution (Fig. 5) showed that reassociation had occurred on removal of the laurate. The association observed in pure water thus must be an equilibrium property of the polymer solution.

Association of commercial products with different degrees of hydrolysis. Fig. 6 is based on results from GPC studies on a set of commercial PVAL products. In this case 0.01 M NaCl was used as eluant in order to suppress the possible effect of charged groups on the polymers (*i.e.* initiator fragments). In preparing this figure the area under peak I was measured as the total area up to the eluate volume corresponding to the minimum between the two fractions. The diagram shows that the relative amount of associated molecules increased rapidly with a decrease in the degree of

hydrolysis. No tendency to form aggregates was observed for sample 6 (degree of hydrolysis 87.5 %). The results for sample 7 (degree of hydrolysis 99.8 %) was obtained in an experiment in which the sample solution was heated before the run in order to dissociate the molecular aggregates which form when solutions of highly hydrolyzed PVAL polymers are kept at room temperature (*cf.* Ref. 2). These types of aggregates were observed in GPC runs on old solutions of sample 7.

Structural requirements for association. The results in Fig. 6 strongly suggest that the observed aggregation of PVAL polymers with a low degree of hydrolysis depends on association between polymer segments having a high content of residual acetate groups. This in combination with the fact that fraction I of Rhodoviol could be isolated and rechromatographed without the appearance of a

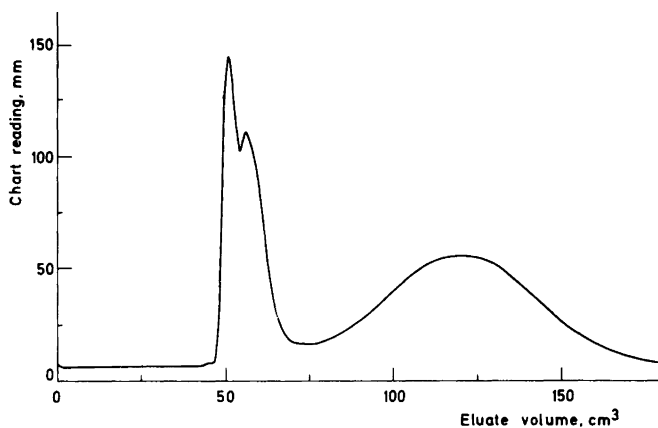


Fig. 5. GPC on Sepharose Cl-6B of a solution obtained by washing with water, pH 9.3, in a membrane filter cell a solution containing 1 % Rhodoviol 5/270 and 0.1 % AL. Column: $25 \times 400 \text{ mm}$. Elution: Water, $1.33 \text{ cm}^3/\text{min}$.

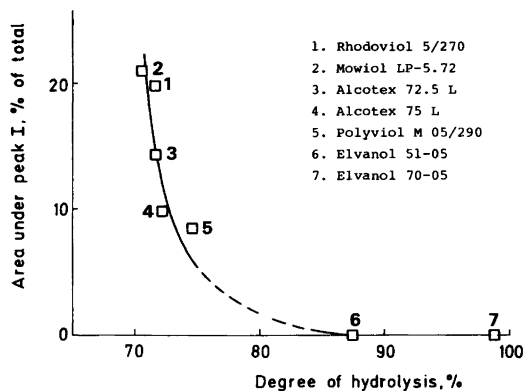


Fig. 6. Relative size of fraction I as determined by GPC experiments with commercial PVAL polymers on Sepharose Cl-6B. Column: 15 × 230 mm. Elution: 0.01 M NaCl, 1.3 cm³/min.

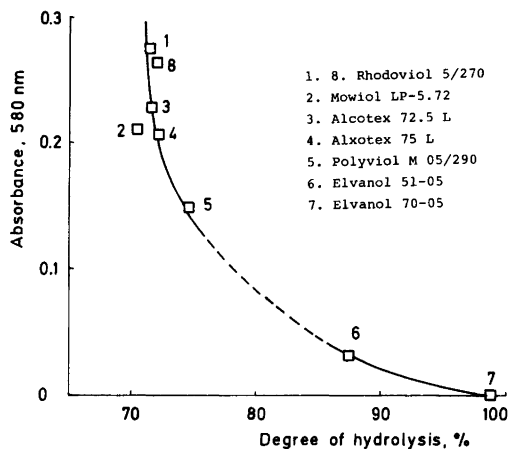


Fig. 7. Absorbance at 580 nm of solutions containing 100 ppm of PVAL polymers and 50 ppm of I added as the I₂-KI complex.

a large fraction of dissociated molecules (*cf.* Fig. 2), a fact which could not be expected if the association were governed by the law of mass action, indicated that fractions I and II differed in their chemical constitution. Direct analysis of fractions I and II collected from a number of runs with Rhodoviol confirmed this. The average degree of hydrolysis of fraction I was 65 % and that of fraction II 73 %. This difference in the composition of the fractions was paralleled by a difference in cloud point. At a concentration of 0.3 %, a solution of fraction I on heating became turbid at 30 °C and then clear again at 90 °C, whereas a solution of fraction II became turbid at 45 °C and was not cleared on further heating to the boiling point. Fractions I and II also differed in their tendencies to form complexes with iodine. In the presence of borate, with fraction II, the well-known blue complex⁸ often used for the determination of poly(vinyl alcohol) dominated, whereas with fraction I a large contribution from the red colour ascribed to a complex between iodine and acetate groups⁹ was evident.

Fig. 7 shows that for the PVAL polymers studied, the absorbance of the red iodine complex (in this case borate was not present) increased as the degree of hydrolysis decreased. The increase in the absorbance was much faster than in proportion to the concentration of acetate groups. This indicated that the formation of the iodine complex required the presence of blocks of vinyl acetate residues in the polymer. This has recently been confirmed by

Pritchard and Ahmed by measurements on poly(vinyl acetate-co-vinyl alcohol) polymers prepared by different routes.¹⁰ The shapes of the curves in Figs. 6 and 7 were rather similar. This strongly suggested that the tendencies to self-associate and to form red complexes with iodine were due to the same factor. It can thus be concluded that the self-association of PVAL polymers observed in this work was due to interactions between polymer segments containing blocks of residual acetate groups. The tendency of these hydrophobic blocks to associate was dramatically reduced by selective binding of AL.⁴ With reference to the results in Fig. 2, the vinyl acetate blocks responsible for association were unevenly distributed over the polymer molecules. This, of course might be a consequence of the occurrence of a two-phase system during the hydrolysis of the parent poly(vinyl acetate). Because of such a phase separation different conditions during the hydrolysis may give rise to large differences in the properties of the partly hydrolyzed products.

The size of the polymer aggregates. To learn more about self-association of PVAL with a low degree of hydrolysis, GPC experiments were carried out on Rhodoviol at various temperatures using a Sepharose Cl 4B column. This column had a higher exclusion limit than for those previously used. It was calibrated with Dextran T fractions. The chromatograms were resolved into two fractions as shown in Fig. 8, assuming fraction II to be

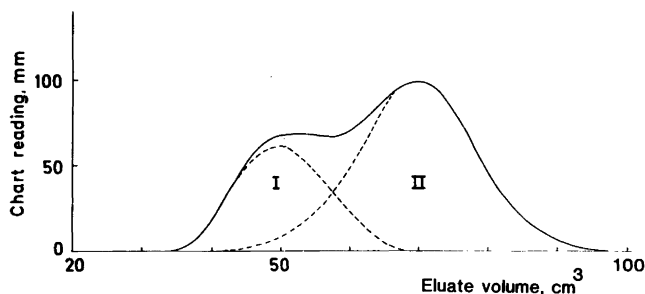


Fig. 8. Resolution of a GPC chromatogram obtained by running Rhodoviol 5/270 on Sepharose CI-4B at 24.8 °C. Column: 15 × 500 mm. Elution: 0.01 M NaCl, 0.8 cm³/min.

symmetrical and the results are given in Table 2. As can be seen, the relative amount of fraction I increased with an increase in temperature. There was also a slight increase in the relative amount of fraction I when the concentration of the sample solution was increased. The MWD found for fraction II agreed well with that for the whole polymer as determined after complete hydrolysis. This justifies the method used for resolution of the chromatograms. With the fully hydrolyzed sample the following data were obtained: $\bar{M}_n = 18 \times 10^3$ g/mol, $\bar{M}_w = 45 \times 10^3$ g/mol, and $\bar{M}_w/\bar{M}_n = 2.5$. As can be seen, the apparent molecular weight and the heterogeneity index (\bar{M}_w/\bar{M}_n) for fraction I seemed to be almost independent of the conditions. The results suggested that, on the average, the multimers contained about ten polymer molecules. The value for \bar{M}_w/\bar{M}_n for fraction I was close to the value expected on the assumption that all aggregates contained an equal number of polymer molecules.³

Assuming the MWD of fraction II to be representative for that of the unassociated molecules, this would give 1.2 instead of 1.3 as actually found. These results suggest a micellization type of association. The possibility of such a type of association in solutions of polymers having both hydrophilic and hydrophobic groups has been discussed previously (cf. e.g. Ref. 11).

Influence of VCM and AL on the solution behaviour of PVAL. As mentioned previously, small amounts of AL were found to produce a large increase in the cloud point temperature of aqueous solutions of Rhodoviol. Thus, the addition of 0.05 % AL to a 0.5 % solution gave an increase in the cloud point from 35 to 75 °C. Experiments with VCM showed that this substance had the opposite effect. In Fig. 9 the cloud point is given as a function of the relative pressure of VCM over the solution, P/P_0 , where P_0 is the saturation pressure. Considering the fact that the solubility of VCM in

Table 2. Influence of temperature and sample solution concentration on the relative amount of fraction I (the associated molecules) and on the MWD for fractions I and II from Rhodoviol 5/270 as determined in GPC experiments (conditions as given in the text to Figure 8).

Temp. °C	Conc. of PVAL in sample %	Size of fraction I % of total	$\bar{M}_w(I)$ $\times 10^{-3}$ g/mol	$\bar{M}_n(II)$ $\times 10^{-3}$ g/mol	$(\bar{M}_w/\bar{M}_n)_I$	$(\bar{M}_w/\bar{M}_n)_{II}$
4.8	1	11.8	180	19	1.3	2.6
10.2	1	15.4	180	21	1.4	2.4
14.0	1	23.0	160	16	1.4	2.7
20.2	1	28.1	180	18	1.3	2.6
24.8	1	32.3	210	22	1.3	2.5
20	0.50	26.4	170	18	1.3	2.8
20	1.0	28.0	150	14	1.3	2.8
20	2.0	32.0	150	14	1.4	2.7
20	3.0	34.6	130	13	1.5	2.7

Table 3. Solubilization of VCM by PVAL polymers as determined on aqueous solutions at 35 °C and at a relative VCM pressure of 0.9.

Polymer	Degree of hydrolysis	VCM solubilized (mg/g polymer)
Rhodoviol 5/270	71.5	86
Elvanol 51-05	87.5	25
Elvanol 70-05	98.9	1

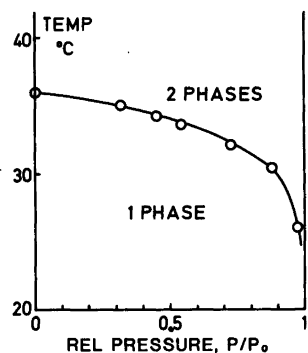


Fig. 9. The influence of VCM on the cloud point temperature of a 0.5 % solution of Rhodoviol 5/270.

water is less than 1 %, ⁷ the large decrease in the cloud point temperature as the saturation limit was approached indicated a highly specific interaction. As seen from the data in Table 3, small amounts of VCM were solubilized by PVAL polymers with a low degree of hydrolysis. Experiments with Rhodoviol at different temperatures showed that the solubilization was weakly exothermic ($\Delta H = -13$ kJ/mol).

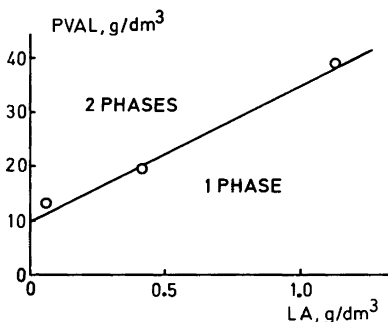


Fig. 10. Influence of AL on the phase separation at 35 °C in solutions of Rhodoviol 5/270 almost saturated with VCM ($P/P_0 = 0.99$). Concentrations in % by weight.

The phase separation in Rhodoviol solutions induced by VCM could be prevented by adding fairly small amounts of AL. Fig. 10 shows that the amount of laurate required increased with the concentration of Rhodoviol. In these experiments the partial pressure of VCM was kept just slightly below the saturation pressure. Obviously, AL had a stronger tendency to bind to the hydrophobic segments of the polymer than had VCM. Although it was found that VCM could be solubilized in AL micelles (0.34 g/g at $P/P_0 = 0.9$), very little extra VCM was solubilized in a Rhodoviol solution containing AL if the concentration of the latter was lower than the critical micelle concentration. The results obtained in these experiments with VCM and AL point out the high complexity of the practical systems in which the PVAL polymers are used.

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