Partly alcoholized poly(vinyl acetate) polymers: kinetics of formation and reaction with iodine

D. P. Joshi and J. G. Pritchard
Department of Chemistry, North East London Polytechnic, Stratford, London, E15 4LZ, UK

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Methoxide-catalysed transesterification of poly(vinyl acetate) with methanol was examined kinetically. Polymer specimens were isolated at various stages of hydrolysis and the extent of their colourimetric reaction with iodine determined. Polymers with up to 60 mol % degree of hydrolysis can be prepared reproducibly by careful kinetic control of the reaction conditions. The analytical sensitivity for formation of the red I_2–PVA complex was consistent with a developing hydroxyl group block structure as transesterification proceeds.

INTRODUCTION

The Commercial products known as poly(vinyl alcohol) obtained by the hydrolysis of poly(vinyl acetate), have been extensively studied[1,2]. The base-catalysed replacement of acetate in PVAc by hydroxyl can be halted at points in the 70–100 mol % range of hydrolysis with reasonable predictability[3,4]. However, far less is known about poly(vinyl acetate–alcohol) polymers with degrees of hydrolysis in the range 0–60 mol %, because the more rapid earlier stages of the hydrolysis are less easily managed. Here, we have studied kinetically the methoxide-catalysed reaction and investigated properties of the products. In particular, the reaction with iodine is the basis of an analytical method for PVAc[5,6], and the mechanism of formation of the red PVAc–iodine complex is of interest[6–8]. Red complex formation has been reported for some specimens of PVAc hydrolysed to within the range 70–100%[9,10], and we present here a study of this phenomenon for the entire range.

EXPERIMENTAL

Materials

PVAc beads (lot 99197), molecular weight range 125 000–150 000, were supplied by ICN K & K Laboratories, Plainview, New York. Hopkin and Williams pure reagent grade methanol was dried and stored in closed flasks with anhydrous calcium chloride suspended above the surface of the solvent. The following were standard laboratory reagents: dioctyl phthalate; hydrochloric acid and sodium hydroxide; potassium iodide. Iodine was Analar. Analar sodium carbonate was dried at 130°C for 4 h and stored over anhydrous silica gel.

Methoxide-catalysed transesterification of PVAc

PVAc (1.2000g) was dissolved in methanol (25 cm^3) at 65°C. The stirred solution was thermostatically controlled at either 22° or 30° ± 0.1°C and exactly 0.5 cm^3 of a solution of sodium in dry methanol (5% w/v; 2.174 M) was added. The reaction was quenched after a specific time by neutralization with 1 M aqueous acetic acid. The solution was concentrated to about 8–10 cm^3 by evaporation of methanol and the polymer precipitated by distilled water. The precipitate was filtered off, washed with water, and then reprecipitated from methanol, rewashed and finally dried under vacuum at 22°C for 2 days over phosphorous pentoxide.

Saponification analysis

The dry, hydrolysed PVAc (~0.2 g, w) was completely dissolved in methanol (25 cm^3) and stirred at 60° ± 1°C under a reflux condenser. Aqueous sodium hydroxide (50 cm^3, 0.1 M) was added and stirring continued for 2 h. The solution was then cooled at 22°C. The stirrer and condenser were rinsed with water which was added to the main bulk of the solution, and this was titrated against 0.1 M aqueous hydrochloric acid until just acid to phenolphthalein. The titre was deducted from a blank titre (without polymer) to give v cm^3 of 0.1 M sodium hydroxide consumed by the saponification. The wt % (W) of vinyl acetate units, (molecular weight 86.09) in the polymer specimen is $86.09\ v/100\ w$, and assuming the remainder of the hydrolysed PVAc polymer to consist of polymerized vinyl alcohol units, (molecular weight 44,06), the mol % of vinyl acetate units (M) is given by $44.06 \times W/(86.09-0.4203W)$.

Dioctyl phthalate (1 g) was dissolved in methanol (25 cm^3). Sodium hydroxide (25 cm^3 of 0.5 M in 20% aqueous methanol) was added and the mixture refluxed for 3 h (after 30 min, 5 cm^3 of water was added to prevent precipitation of salt). The cooled solution was then titrated as above: 1.0060 g of ester required 7.42 cm^3 of 1.002 M aqueous hydrochloric acid, and 1.0110 g required 7.39 cm^3. Two blanks required 12.55 and 12.57 cm^3.

Iodine complex

5 cm^3 of 5 methanol solutions of each polymer (containing 1.909–9.547 g/l in equal steps) were added to 5 cm^3 aliquots of 0.02014 M methanolic iodine solution. 1 cm^3 of each of the resulting solutions was diluted with 25 cm^3 of 0.0161 M aqueous potassium iodide to give red–violet

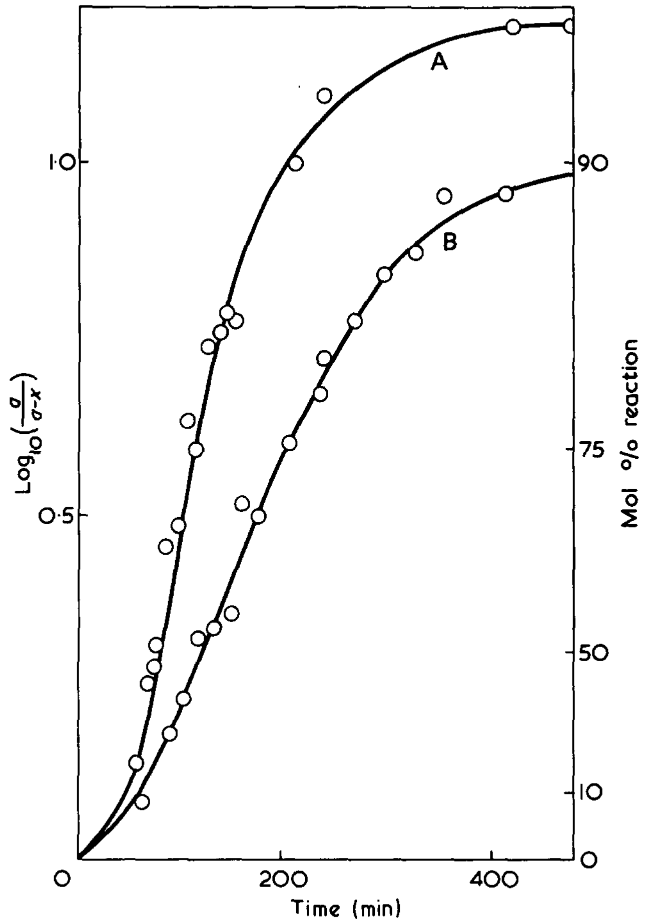


Figure 1 Kinetics of transesterification of PVAc: A, 30°C; B, 22°C; a = initial mol % concentration; x = concentration of acetate groups reacted (mol %)

colorimetric solutions. The blank contained 0.000386 M iodine and 0.0154 M potassium iodide.

The colorimetric solutions were allowed to stand for 2 h at 20°C to equilibrate (shorter times, 30–60 min, were adequate for pure PVAc). The visible spectra of the solutions at 20.0° ± 0.1°C were scanned against the blank on a Unicam SP700 spectrophotometer. The stock solutions for the 46.2 and 51.8 wt % hydrolysed PVAc samples were made up with 20% aqueous methanol, and those for the ~70% hydrolysed polymers were made up with water. Absorbances per mg/dm^3 at the wavelength of maximum absorbance were converted to absorbances per mmol of vinyl acetate units/dm^3 by multiplying the former by $100(44.06 + 0.4203M)/M$, where M is the mol % of vinyl acetate units in the poly(vinyl acetate–alcohol) polymer.

RESULTS AND DISCUSSION

Saponification analysis

The accuracy of the analytical procedure was checked by the duplicate results for the 'standard' pure ester dioctyl phthalate, which gave recovery values 100.05 and 99.97%. Six results on the non-hydrolysed sample of PVAc gave a mean of 99.49 wt % of vinyl acetate units ± 0.13% standard error.

Figure 1 shows the results for the mol % of hydrolysis of the partly hydrolysed PVAc samples *versus* transesterification time. The general scatter indicates that the reproducibility of our procedure cannot be guaranteed to better than ±3–5 mol % at ~10% reaction and ±2–3% at about 80% reaction. However, some experiments carried out carefully in duplicated pairs gave results agreeing within 1%.

Kinetics and mechanism of the transesterification reaction

Figure 1 illustrates the kinetics of the methoxide-catalysed transesterification of PVAc in methanol for two temperatures. The reaction shows an initial slow stage up to ~10% (apparent induction period), a pseudo-first order rate law for 10–85% of reaction, and a fall-off from the first order rate law after ~85%. For the 10–85% range the rate coefficients are 1.13×10^{-4} and 2.53×10^{-4} sec^{-1} for 22° and 30°C, respectively. The concentration of sodium methoxide catalyst was 0.0369 M, and so the second order rate coefficients are 3.54×10^{-3} and 6.84×10^{-3} dm^3/mol sec. These values yield 62 kJ/mol for the Arrhenius activation energy and –90 J/mol K for the entropy of activation. Such values are consistent with a simple bimolecular displacement mechanism since the bimolecular displacement of alkoxide groups from aliphatic esters by hydroxide ions in 15% aqueous ethanol, yield energies and entropies of activation which are in the ranges 60–70 kJ/ mol and –95 to –110 J/mol K[11].

No simple rate law has been observed previously for base-catalysed transformation of PVAc to the partly hydrolysed state, (although a pseudo-first order rate law has been reported for acid catalysis[12]), and mechanisms involving autocatalysis have been discussed[13–19]. The mechanism for the present reaction appears to be a simple bimolecular one, but the kinetics are complicated by changes in the degree of swelling of the polymer in the three stages noted. It has been suggested[20,21] that acetate groups surrounded by adjacent acetate groups are much more difficult to hydrolyse or transesterify off than acetate groups next to adjacent hydroxyl groups. This may be one reason for the initial slow phase of the reaction. Another is that diffusion of methoxide into the polymer coils is slow before sufficient hydroxyl substitution has occurred to expand the polymer coils into a more ionophilic phase. However, after this, the reaction is rapid and kinetically straightforward. The reaction rate is controlled by the rate of elimination of methyl acetate from low concentrations of the ions I and III, which are a known type of stable intermediate in the $B_{Ac}2$ mechanism as classified by Ingold[22]. Stabilization of III by nearest neighbour hydrogen bonding no doubt contributes to the higher rate for the middle phase of reaction compared to the first phase which proceeds to a greater extent through intermediate I. The ions II and IV very rapidly regenerate the catalyst. The fraction of polymer in the form of III is proportional to the quantity of non-hydrolysed acetate groups; hence, the reaction follows a first order rate law as long as the methoxide concentration is constant. Finally, the reaction slows down because the polymer rejects the alcoholic solvent and contracts until precipitation occurs[18]. Formation of sodium acetate may also contribute to the slowing of the final phase.

Iodine complex

Table 1 lists data for the polymers used to demonstrate the formation of iodine complex. In the presence of 0.000386 M iodine and 0.0154 M potassium iodide. The absorbance of the red complex formed per mg/dm^3 of polymer was linear with concentration of polymer over the range 0–200 mg/dm^3 examined. Gradients of the best straight lines through the absorbance concentration graphs (sensitivities) are listed in the last column of *Table 1*.

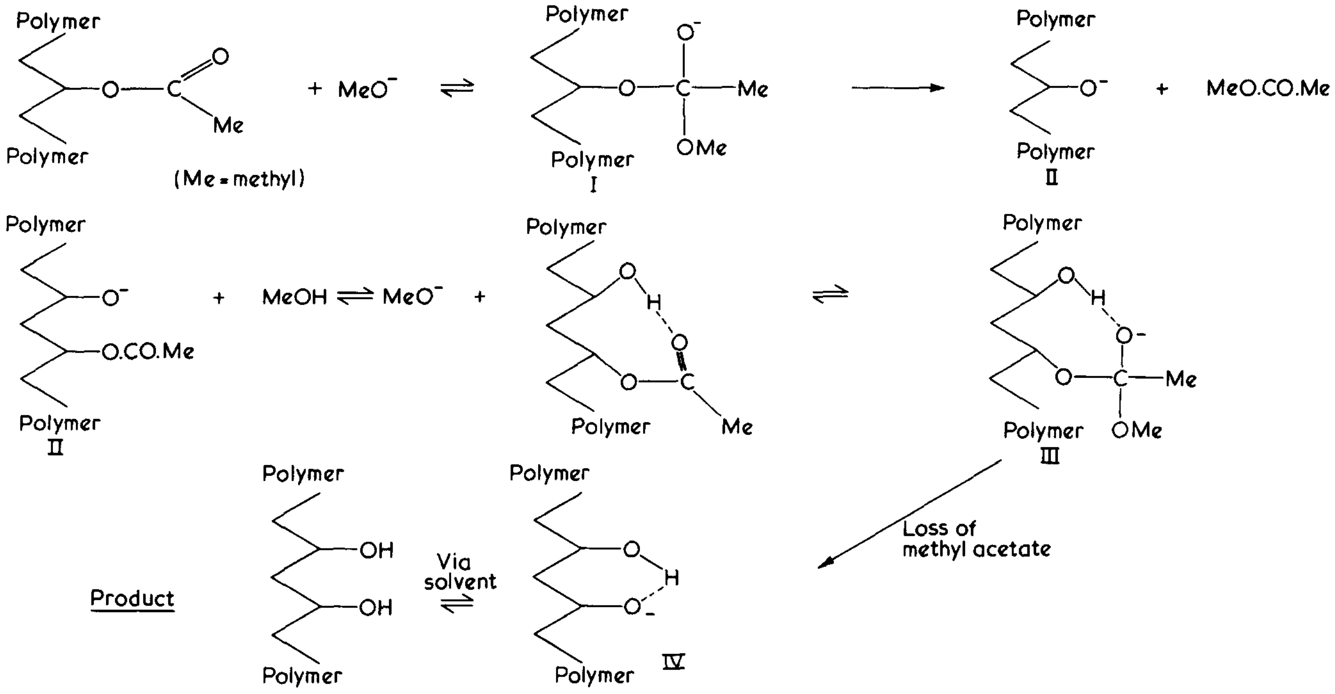


Table 1 Preparative and spectroscopic data for partly hydrolysed PVAc samples

Alcoholysis reaction time (min)	Alcoholysis reaction temperature (°C)	Vinyl acetate units (wt %)	Vinyl acetate units (mol %)	Wavelength of absorption maximum (nm)	Gradient of absorbance *vs.* concentration graph (abs. units × 10^2 per mg/dm^3)
–	–	99.5	99.0	520	2.383
–	–	96.1*	92.7	520[6]	2.2[6]
180	10	91.9	85.3	520	2.231
240	10	85.8	75.6	515	1.975
90	22	78.5	65.1	515	1.740
120	22	64.5	48.2	505	1.093
165	22	53.8	37.3	500	0.817
180	22	48.2	30.3	495	0.548
47	40	31.8	19.3	500	0.125
75	40	26.8	15.8	500	0.028

* Purity of a Monsanto *Gelva 7* PVAc polymer

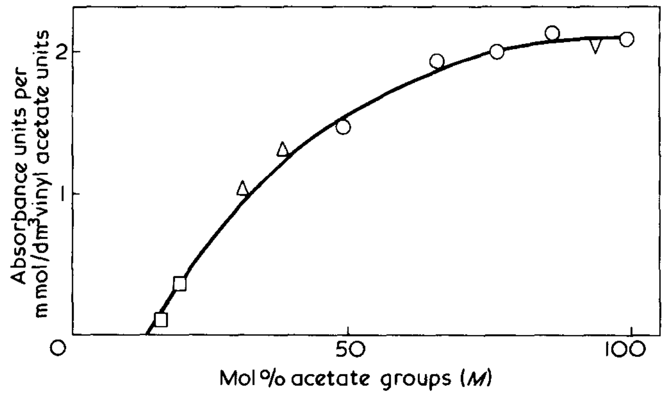
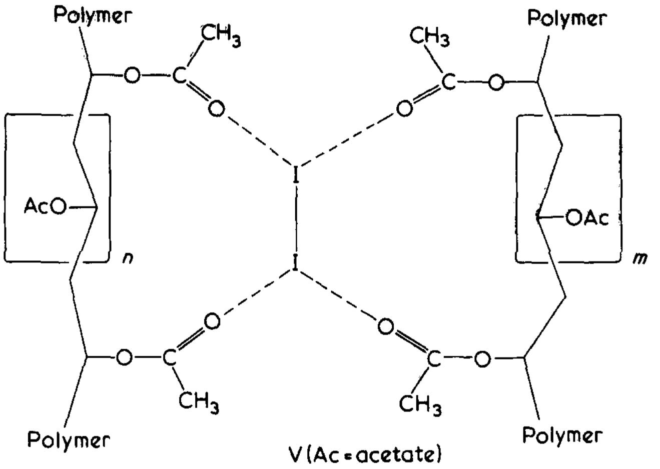


Figure 2 Sensitivity of red complex formation between partly hydrolysed PVAc and iodine. Final solvents: ○, 96% aqueous methanol; ▽, Pritchard and Serra[6]; △, 97% aqueous methanol; □, pure water

Figure 2 shows the variation of the sensitivities of the colorimetric solution with mol % of vinyl acetate groups in the polymer. A constant sensitivity (2.05) would be observed if the environment of the acetate groups in the copolymers remained unchanged throughout the 0–100% range. No change was observed in the level of complex formation for the 80–100% range of vinyl acetate content.

Formation of the red complex to the point of saturation of pure PVAc with iodine corresponds to not more than one iodine molecule for every 24 acetate groups, and PVAc films have been observed to swell to at least three times their original volume during chemisorption of iodine[8]. This leads us to suggest that p–d orbital interaction (V) is the basis of complex formation.

If the hydroxyl groups introduced into partly hydrolysed PVAc are randomly scattered, then it is plausible that structure (V) should tolerate 20 mol % replacement of acetate by hydroxyl, in the sequences *n* and *m* or in the remaining part of the polymer, without loss of sensitivity in iodine complex formation. When acetate groups are replaced beyond the 20 mol % point, however, we suggest that the hydroxyls increasingly form block sequences[16,23,24] which interfere with complex formation, until at about 80 mol % replacement hardly any complex is formed at all by the remaining scattered 20% of acetate groups which are unable to act in concert. The wavelength of maximum absorbance of the 'red' absorption band of the complex shows trends (*Table 1*) in accord with the three distinct compositional regions noted above (which is reminiscent also of the situation with the kinetics of formation). The nature of the substituent groups in the sequences *n* and *m* would clearly affect the ligand strength in the complex and its absorption band.



V (Ac = acetate)

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