

Studies on the characterization of partly hydrolysed derivatives of poly(vinyl acetate) and their red iodine complex

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Three samples of poly(vinyl acetate) 36% hydrolysed, respectively, by saponification, transesterification and acid-equilibrium have been characterized through the refractive indices and light-scattering properties of their solutions in 10% aqueous methanol at 25°C. The original poly(vinyl acetate) sample and its iodine/iodide complex have been similarly characterized, respectively, in methanol at 5°C and in 9.1% methanolic water over the range 5–15°C. The apparent weight-average molecular weights of the vinyl polymers show that the three hydrolytic processes degrade the 130 000 average molecular weight of the original poly(vinyl acetate) macromolecules hardly at all. It is suggested that values of the apparent second virial coefficient might be used as criteria for the characterization of hydrolysed poly(vinyl acetate) specimens which have otherwise identical degrees of hydrolysis and blockiness of their residual acetate groups, but contrasting polydisperse characteristics and surface-active properties. The apparent average root-mean-square radius of gyration of the poly(vinyl acetate) macromolecules is reduced to $\approx 33\%$ or less of its value on formation of the complex. The characteristics and structure of such complexes are discussed.

Keywords Poly(vinyl acetate); hydrolysed poly(vinyl acetate); iodine complex; molecular weight; second virial coefficient; radius of gyration; light-scattering

INTRODUCTION

The red complex formed between poly(vinyl acetate) and iodine is of value as a qualitative analytical test for this polymer and in its quantitative determination¹⁻⁷. The wavelength of maximum visible-light absorbance, λ_{\max} , is generally in the range 500–510 nm for this red complex, and it is of interest because it is so similar to the better-known, blue poly(vinyl alcohol)-iodine complex, which has $\lambda_{\max} \approx 700$ nm, yet it appears to be distinct. Curiously, the two types of complex, seemingly in equilibrium with one another, can be formed concomitantly from the same polymer in the case of certain water-soluble, partly hydrolysed poly(vinyl acetate) preparations⁸⁻¹⁰. Moreover, it has been shown recently that even pure poly(vinyl acetate) can partially form the blue complex in the presence of sufficient iodine if the iodide concentration is kept low enough, and it has been suggested that the two forms of complex may differ only in the sequence length of the iodine chain involved¹¹.

The red complex is generally prepared from water-insoluble, pure poly(vinyl acetate) polymers by dilution of a methanolic solution of the polymer and iodine in an excess of dilute aqueous potassium iodide. Approximately 20 two-carbon backbone units of the polymer are required to complex each iodine atom¹²; the complex most probably contains the I_3^- ion or sequences thereof¹³, and water appears to be a necessary component^{6,14}. The iodine evidently has a solubilizing effect on the polymer

which is otherwise insoluble in a highly aqueous alcoholic medium. From this, and the fact that the more concentrated highly aqueous solutions of the complex produce a red fibrous precipitate when agitated⁶, it may be inferred that such solutions may contain aggregates of iodine-complexed polymer molecules of very high molecular weight even in dilute solution. Definitive measurements of molecular weight and related parameters for this red complex do not appear to have been attempted. However, measurement by the light-scattering technique may afford evidence relating to both the molecular size and shape of complex polymers, and an attempt has been made to establish conditions under which light-scattering measurements on this highly coloured and probably aggregated molecular complex might be made with the conventional optical measurements available to the authors. It appeared likely that this might be accomplished for high dilutions of polymer and reagent, but at a low temperature which could ensure sensibly complete formation of the complex¹⁴.

A number of partly hydrolysed poly(vinyl acetate) samples derived from the same parent polymer were available¹⁵ and the molecular parameters of a small selection of these chosen for their contrasting structure yet similar degrees of hydrolysis were examined. Such polymers are of intrinsic interest, and published work on their molecular parameters has been scarce^{15,16}; moreover, further criteria for distinguishing specimens

with the same degree of hydrolysis, but prepared by different routes are highly desirable¹⁷. Accordingly, some of the properties of these polymers and their parent were examined during this study of the closely related iodine complex whilst the optical instruments were adjusted for critical use. Also, the study of these polymers was used to establish consistency of measurement prior to examination of the more complex system.

EXPERIMENTAL

Materials

Suspension-polymerized poly(vinyl acetate) in the form of free-pouring spheres with diameters in the range 0.1–1 mm (lot 99197), was obtained from ICN K & K Laboratories, Plainview, New York. Three specimens of modified poly(vinyl acetate), derived from this poly(vinyl acetate) sample, each $\approx 36\%$ hydrolysed by a different method and having contrasting properties, were selected from the products of a study published previously¹⁷. Iodine, potassium iodide, sodium thiosulphate, fluorescein, potassium dichromate and sodium hydroxide were BDH AnalaR-grade reagents.

Distilled water, methanol (Fison) and benzene (BDH) were each filtered through No. 3 sintered glass and distilled in a dust-free closed system. The first distillate was used to rinse the receivers, then dust-free solvent specimens were collected and the filled receivers were stored in a dust-free Perspex box. The methanol and water thus prepared were used as polymer solvent, and the benzene was used to fill the sample-cell thermostat vat of the light-scattering photometer.

AnalaR benzene (2 dm³) was refluxed over 1 mm diam. sodium wire (10 g) for 12 h. Then, the fraction (≈ 1 dm³) distilling at 80–80.5° was collected and refractionated from fresh sodium wire (2 g) through a 1500 × 40 mm diam. glass column packed with 4 mm diam. glass helices. The distillate was passed through a No. 3 sintered glass disc into a series of dust-free receivers. Aliquots (≈ 30 cm³) of the distillate were pipetted automatically into de-dusted polypropylene centrifuge tubes, and the capped tubes were centrifuged for 1 h at 15 000 rev min⁻¹ (22 500 G) in an M.S.E. High Speed 17 centrifuge. The upper 25 cm³ of clarified benzene were carefully withdrawn by hypodermic syringe and transferred to capped, dust-free light-scattering cells for use as the standard.

Solutions of polymers and the iodine complex

Complete dissolution of the poly(vinyl acetate) in methanol, and of its partly hydrolysed derivatives in 10% (vol/vol) aqueous methanol, was ensured by maintaining the solutions at 60–70°C under a reflux condenser for 1 h. The cooled solutions were diluted to accurately known concentrations in dust-free volumetric flasks. The solutions and solvent were centrifuged at 12 000 rev min⁻¹ (18 000 G) for 2 h and then filtered through a No. 3 sintered glass disc directly into dust-free cells immediately prior to optical measurements.

For each polymer, five solutions were prepared for spectrophotometric study of the variation of the amount of complex formed at various concentrations as a function of temperature. For example, respectively 1, 2, 3, 4 and 5 cm³ of methanolic poly(vinyl acetate) solution (3.90 g dm⁻³) were added in each case to 5 cm³ of methanolic

thiosulphate-standardized iodine solution (3.34×10^{-3} mol dm⁻³) and made up to 10 cm³ with methanol as necessary. One cm³ of each of these solutions was then carefully diluted with 25 cm³ of aqueous potassium iodide solution (0.0162 mol dm⁻³) while the mixing fluids were very gently swirled to produce homogeneous test solutions of the red complex^{5,6,17,18}. A reagent blank solution was also prepared in which the polymer was omitted. The test solutions and blanks were allowed to equilibrate for 2 h at the required temperature.

Test solutions of the complex intended for refractive index and light-scattering measurements were made up similarly, as follows. Various measured volumes of methanolic poly(vinyl acetate) solution (0.1505 g dm⁻³), in the range 0.5–5 cm³ were made up together with 1 cm³ volumes of methanolic iodine solution (7.067×10^{-3} mol dm⁻³) to 10 cm³ with methanol. 5 cm³ of each solution was then carefully diluted as previously with 50 cm³ of aqueous potassium iodide solution (0.0172 mol dm⁻³). This set of solutions was centrifuged at 12 000 rev min⁻¹ (18 000 G) for 90 mins and then filtered at 20° through No. 3 sintered glass discs to remove any polymeric gel and/or other debris. For the purpose of allowing for losses of complex on centrifugation, five standard solutions for comparative spectrophotometry were prepared in the same solvent as described previously, but without centrifugation, and containing finally (in equal steps) from 1.37×10^{-3} – 6.85×10^{-3} g dm⁻³ of reacted poly(vinyl acetate).

Spectrophotometry of the red complex

The visible-range spectra of test solutions and standards were scanned against appropriate reagent blanks at constant temperature in 1 cm cells from 400 to 700 nm. Pye-Unicam SPS-100 and Unicam SP-600 spectrophotometers were used which were fitted with thermostabilizing cell holders which allowed the temperature of the sample to be maintained constant within $\pm 0.1^\circ\text{C}$. Absorbances, the mean of three scans in each case, were measured as necessary at the wavelength of maximum absorbance, ≈ 510 nm, and at the wavelength of the mercury emission line used in the light-scattering studies on the complex, 546 nm. The absorbance scales of the instruments were calibrated with standard aqueous solutions of potassium dichromate.

Refractive index measurements

Absolute refractive indices were measured with a Hilger-Chance M-410 refractometer, the V-block of which could be maintained at constant temperature $\pm 0.1^\circ\text{C}$ in the range 5–25°C by means of water circulated from a thermostat. A ground glass cover to the sample compartment prevented contamination from the atmosphere and losses of solvent by evaporation. The light-source was a mercury vapour lamp fitted with filters to isolate the 546 nm and 436 nm emission lines. The mean of five settings of the apparatus was taken for each sample, and refractive indices were obtained to five decimal places from the calibration tables supplied with the instrument. Refractive index differences (Δn) were calculated between each solution and its solvent.

Refractive index differences were also measured directly by the fringe-shift method with a Jamin Interferometer (Bellingham and Stanley Ltd.). This was mounted on a large, optically stable base and housed in a dust and

draught excluding Perspex box equipped with hinged flaps to permit adjustments to the instrument. Solutions and solvent were compared in identical, stoppered fused-quartz cells of 1.8 cm path length (l) at temperatures held constant to $\pm 0.2^\circ\text{C}$. A point-o-light bulb housed behind a collimating lens and iris diaphragm was used as the light source in conjunction with filters to isolate the 546 nm and 436 nm regions of the spectrum and to reject infrared radiation. The interference fringes obtained between the light beams passing through the two cells were viewed by a telescope equipped with fine cross-wires. The instrument included two optically ground glass compensator plates of 0.8 cm thickness, which were mounted one in each beam and were rotatable both mutually and in unison to permit mechanical differentiation of the length of the light paths of the two beams. With pure solvent in both cells the instrument was calibrated by a plot of position of rotation of the compensator plates measured on a vernier scale against the (linear) movement of the interference fringes past the cross-wires. When the solvent in one beam was replaced by a polymer solution, the number of fringes displaced (m) was measured by the traverse on the compensator plate scale required to restore the achromatic band between the upper and lower sets of fringes to its original position corresponding to solvent in both beams. Values of Δn were calculated from the relation $\Delta n = m\lambda/l$, where λ is the wavelength of the light involved.

The values of Δn were plotted against polymer concentrations (c) and specific refractive index increments (dn/dc) were obtained by measurement of the gradient of the graphs in $\text{g}^{-1} \text{cm}^3$ units.

Preparation of light-scattering cells

Several identical cells, made of quartz in cylindrical shape, open at one end, 5 cm long and 2.5 cm i.d., were fitted into metal frame holders which were provided with dust-proof lids. Prior to use, the cells were allowed to stand overnight in chromic acid cleaning solution to destroy any possible dust or organic deposit, particularly on the surfaces of the cell in the operational optical path. The cells and lids were then washed thoroughly with distilled water. The cells were further treated (without lids) for 30 min in an apparatus in which a continuous jet of hot, filtered (No. 2 sinter) acetone was sprayed over their inner surfaces whilst their outer surfaces were similarly exposed to streaming hot acetone. The cells were then dried with filtered air and were transferred immediately, with their lids in place, to a small dust-proof box for storage until required for use. Great care was taken with these cells at all times to ensure that their surfaces were never marred in any way. All other manipulative apparatus was equally well cleansed and stored in a dust-proof box.

Light-scattering measurements

A model 42000 Sofica PhotoGonio Diffusometer was used. The sample-cell vat was filled with pure dust-free benzene for the calibration experiments, or else methanol, and was maintained within $\pm 0.1^\circ\text{C}$ at selected temperatures from 5 to 25°C . The prepared solutions of polymer and complex in their cells were equilibrated in the vat for 24 h before measurements were taken. The normal level and distribution of scattered light intensity (measured in arbitrary units by a galvanometer energized by the photocathode) was established with fluorescein

solution and with the specially purified benzene, and any necessary adjustment of the incident beam was made before measurements on each polymer sample or standard were commenced. Generally, scattering values were measured at angles of 30, 37.5, 45, 60, 75, 90, 105, 120, 135, 142.5 and 150° .

All measurements of the fractional decrease in intensity of the incident light due to scattering from unit length of the solution or solvent under examination at angle θ (the Raleigh ratio), were referred to the standard literature value¹⁹ for benzene at the 90° scattering angle, $R_{90^\circ(\text{b})} = 16.3 \times 10^{-6} \text{cm}^{-1}$ for 546 nm measured at 25°C . The response of the photocathode (galvanometer reading G_θ) was calibrated, accordingly, with the specially purified benzene at the 90° angle at all temperatures except 5°C for which a glass standard was used and a value for benzene at 5°C extrapolated from values for benzene and glass obtained at higher temperatures. Thus, values of the Raleigh ratio for the polymer sample solutions were obtained by the expression²⁰:

$$R_{\theta(\text{p})} = R_{90^\circ(\text{b})} \frac{G_{\theta(\text{p})}}{G_{90^\circ(\text{b})}} \left(\frac{n_p}{n_v} \right)^2 \left(\frac{\sin \theta}{1 + \cos^2 \theta} \right)$$

where n_p and n_v are, respectively, the refractive indices of the polymer sample solution and the vat fluid, and the squared term is the correction to R_θ required by refractive alteration in the volume of the incident light beam viewed by the photocathode when liquids of different refractive index are in the light path (calibration was with benzene in both cell and vat). The term $\sin \theta$ is the correction for the change in light-beam volume viewed by the photocathode for $\theta \neq 90^\circ$, and the term $1 + \cos^2 \theta$ corrects for the use of unpolarized incident light. Corrections for internal reflections at the interfaces between media of different refractive index in the light path were negligible, as were corrections due to depolarization. The sample solutions exhibited no detectable fluorescence when excited by the 546 nm mercury emission line in a Perkin-Elmer MPF-3 spectrofluorimeter, and no correction for fluorescence was necessary. The $R_{\theta(\text{p})}$ values were corrected in the case of the absorbing red complex solutions by multiplication by the factor 10^{4a} where A is the absorbance of the solution in a 1 cm cell and a is the path length of the light-scattering cell in $\text{cm}^{21,22}$.

R_θ , the 'excess Raleigh ratio' for a given polymer under examination, was calculated from $R_{\theta(\text{p})} - R_{\theta(\text{s})}$, where s refers to measurements for the pure solvent, and estimates of weight-average molecular weight were obtained by the procedure of Zimm²³, as follows. Values of the expression:

$$Kc/R_\theta = 2\pi^2(n_s)^2(dn/dc)^2c/\lambda_0^4NR_\theta$$

for different values of θ and c were plotted vertically against the expression $kc + \sin^2(\theta/2)$ where k , an arbitrary constant, was assigned (Table 2) to spread out the plotted points to form a characteristic grid of convenient size²³ (N is the Avogadro number and λ_0 the wavelength of the light used *in vacuo*). The grid lines were extrapolated simultaneously to $\theta=0$ and $c=0$ to obtain, in the case of each polymer system examined, an intercept on the vertical axis equal to $1/M_w$ where M_w is the weight-average molecular weight.

The line obtained by extrapolation of the experimental grid points to zero angle corresponds for low

concentration of polymer to the expression:

$$Kc/R_\theta = 1/M_w + 2A_2kc$$

From its slope, a value for the second virial coefficient (A_2) in the thermodynamic equation relating osmotic pressure and molecular weight was obtained.

The line obtained by extrapolation of the plotted experimental values to zero concentration corresponds, with validity for macromolecules of any shape as θ approaches zero, to:

$$Kc/R_\theta = (1/M_w)[1 + (16\pi^2/3\lambda^2)\langle r^2 \rangle \sin^2 \theta/2]$$

Here, the second factor, the 'reciprocal particle scattering factor', is the one by which the excess Rayleigh ratio must be multiplied to correct for destructive interference in the scattered light due to phase differences in light scattered from particles of size much greater than $\lambda/20$, where λ is the wavelength of the light in the scattering medium (λ_0/n_s). From the ratio of the initial slope of this line to its already-considered intercept, a value for $(4\pi/\lambda)^2\langle r^2 \rangle/3$ was obtained from which a value for the root-mean-square (z -average)²⁴ radius of gyration of the polymer molecules, $\langle r^2 \rangle^{1/2}$, was derived.

RESULTS AND DISCUSSION

Refractive and light-scattering properties of the partly hydrolysed poly(vinyl acetate) polymers in comparison with their parent

Table 1 lists typical refractive index differences obtained with the two instruments used and shows the range of concentrations linear with refractive index differences and the accuracy possible. Some results obtained with 436 nm

Table 1 Variation of refractive-index difference (Δn) with concentration of polymer (c) for light of wavelength 546 nm

Pure poly(vinyl acetate) in methanol at 5°C (by Hilger-Chance)		Transesterified poly(vinyl acetate) ^a in 10% aqueous methanol at 25°C (by Jamin)	
c (g cm ⁻³ × 10 ⁵)	Δn × 10 ⁵	c (g cm ⁻³ × 10 ⁵)	Δn × 10 ⁵
50	10	20.0	5.0
100	21	40.0	10.1
150	30	60.0	15.0
200	46	80.1	19.0
250	57		

^a 34.6 wt% hydrolysed

Table 2 Characteristics and molecular parameters for poly(vinyl acetate) and its derivatives

Type of poly(vinyl acetate)	Degree of hydrolysis (wt%)	Amount of water in methanol solvent (vol%)	Temperature of optical measurements (°C)	Specific refractive index increment, dn/dc (g ⁻¹ cm ³)	Assigned value of k in the Zimm plots	Apparent second virial coeff. × 10 ³ (cm ³ g ⁻² mol)	Apparent radius of gyration × 10 ⁶ (cm)	Apparent weight-average molecular weight × 10 ³ (g mol ⁻¹)
Saponified	37.6	35	25	0.204	3000	-53.0	3.1	120
Transesterified	34.6	10	25	0.250	300	-5.3	1.8	110
Acid-equilibrated	35.5	10	25	0.147	300	-9.1	3.1	100
Pure	0	0	5	0.220	200	-0.63	6.6	130
Iodine complexed	0	91	10	0.5 to 3.4 ^a	3 × 10 ⁵	+70 to 3500 ^a	2.1	≥140

^a Estimated accordingly as the molecular weight is assumed to range from 7 × 10⁶ to 1.4 × 10⁵

light, which was used as a check upon the technique, were in general agreement with the complete set of data which were obtained with 546 nm light. The set of dn/dc values used for the light-scattering studies is listed in Table 2. The values are within the normally expected range, but show no obvious correlation with polymer structure or origin. The accuracy of the dn/dc values is important, because the values of molecular weight derived from the anticipated light-scattering measurements depend inversely on the square of dn/dc (see Experimental). In this connection, it is reassuring that the independent measurement of dn/dc for pure poly(vinyl acetate) at 25°C in 10%-aqueous methanol gave a value of 0.13 g⁻¹ cm³, in agreement with the several similar values listed by Huglin²⁵ for this polymer and temperature with pure methanol as solvent.

The Zimm plots obtained for the three hydrolysed polymers were straightforward and showed only a slight scatter. Figure 1 shows, for example, the plot for the 34.6% transesterified sample of poly(vinyl acetate). The coincident intercepts of the zero angle and zero concentration lines were not markedly different for all three partly hydrolysed polymers. The angular variation in light intensity scattered at 5°C from three solutions of poly(vinyl acetate) in methanol is plotted in Figure 2. The concentration shift of the points is reasonably consistent for these solutions although there is a substantial scatter,

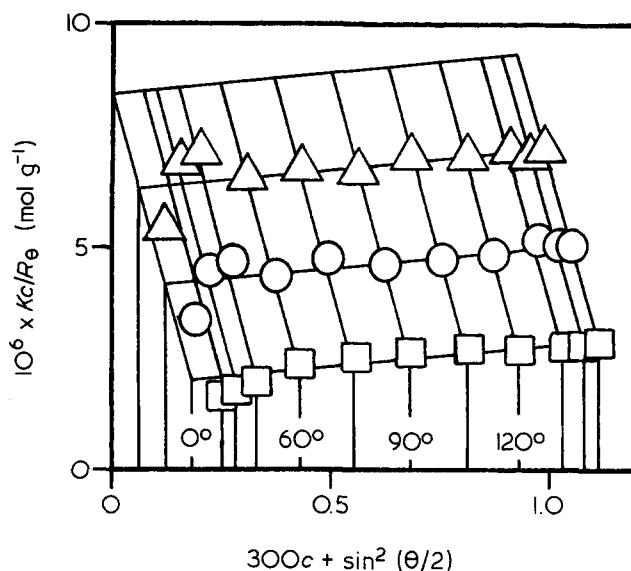


Figure 1 Zimm plot for a specimen of 34.6 wt% transesterified poly(vinyl acetate) dissolved in 10% aqueous methanol at 25°C. Wavelength of light used, 546 nm; light-scattering constant, $K=4.088 \times 10^{-7}$ mol g⁻² cm²; concentration of polymer, $10^4 \times c$ g cm⁻³: Δ , 2.00; \circ , 4.00; \square , 6.00

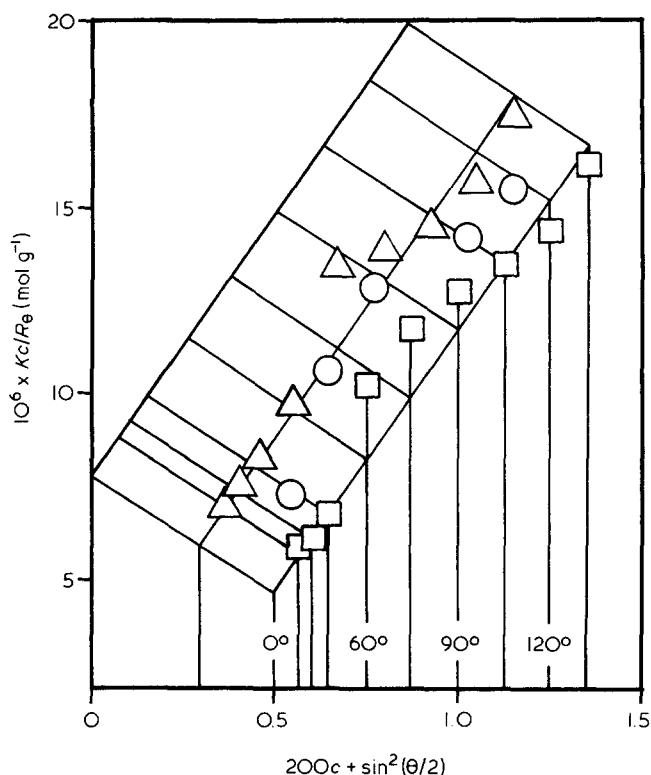


Figure 2 Zimm plot for a specimen of pure poly(vinyl acetate) dissolved in pure methanol at 5°C. Wavelength of light used, 546 nm; light-scattering constant, $K=3.213 \times 10^{-7} \text{ mol g}^{-2} \text{ cm}^2$; concentration of polymer, $10^3 \times c \text{ g cm}^{-3}$. Δ , 1.50; \circ , 2.00; \square , 2.50

particularly in the values for $c=0.002 \text{ g cm}^{-3}$, and a few points subject to gross error have been omitted for clarity. The amount of scatter observed in Figure 2 is disappointing and may possibly have been due to residual dust particles floating in the solution, or possibly partial gelation of some components of the solutions at the relatively low temperature of 5°C (which was used to obtain measurements on pure poly(vinyl acetate) under conditions similar to those for which sensible measurements on its iodine complex could eventually be made). Even so, the slope of the zero angle line in Figure 2 is well defined by the complete set of plotted points, and the extrapolations are clear.

The values found for the apparent weight-average molecular weights are accurate to within $\pm 10\%$. Accordingly the value of 130 000 obtained for the pure poly(vinyl acetate) is entirely consistent with the values obtained for the partly hydrolysed polymers when a factor of $\approx 70/86$ is allowed for the approximately uniform decrease of molecular weight which may be assumed to occur on $\approx 35 \text{ wt}\%$ hydrolysis of the acetate groups in pure poly(vinyl acetate). This agreement indicates that the simple Zimm treatment used on the results is almost certainly not greatly invalidated by the polydispersity of the polymers (which is discussed in more detail later). Furthermore, it appears most unlikely that there occurs any molecular association of the partly hydrolysed polymers into aggregates in the highly methanolic solvent at 25°C, as is apparently the case for similar polymers at temperatures $> 30^\circ\text{C}$ in water¹⁵.

Although the extrapolation involved in the Zimm procedure is open to an interpretation based on a range of gradients equivalent to approximately $\pm 20\%$ of the values quoted in Table 2 for the apparent second virial coefficients, the values obtained do cover two orders of

magnitude and require comment. In the case of the pure poly(vinyl acetate) examined in methanol as solvent, the value of $\approx 6 \times 10^{-4} \text{ mol cm}^3 \text{ g}^{-2}$ is similar, for example, to values observed for polystyrene in its known good solvent toluene²⁶. It is particularly noteworthy that the apparent A_2 value for the saponified polymer is much greater than the values for the other two partly hydrolysed ones. This may merely reflect the quantity of water in the methanolic solvent. However, A_2 values depend on many factors, and the results suggest the use of such values, albeit on an empirical basis, as a method for approaching the problem of characterizing apparently similarly hydrolysed poly(vinyl acetate) samples which possess contrasting surfactant properties in industrial applications²⁷⁻³¹. An explanation for these phenomena no doubt lies in the complex polydispersity of partly hydrolysed poly(vinyl acetate) specimens. Beresniewicz¹⁶ has discussed this phenomenon. Thus, higher-molecular-weight and, therefore, more highly branched poly(vinyl acetate) tends to be hydrolysed to a greater degree than the lower-molecular-weight components of polydisperse poly(vinyl acetate) owing, it has been suggested¹⁶, to preferential absorption of the hydrolysis catalysts being greater for the higher-molecular-weight material than for the lower. This phenomenon, as well as the degree of blockiness of the residual acetate groups^{17,18,32,33}, should differ with different catalysts. Hence, partly hydrolysed poly(vinyl acetate) appears to be polydisperse with respect to degree of hydrolysis, blockiness, branching, and no doubt also other structural subtleties among its various molecular weight fractions, to different extents as a result of the action of different hydrolytic catalysts. The general problem is further complicated by the effect of variable parameters (which are often difficult to control) in the industrial and laboratory polymerization of vinyl acetate, which may affect the polydisperse character of the poly(vinyl acetate) product^{7,34,35}. Schneider, Onu and Mihai³⁶ have noted that this is the reason for little agreement among the several relations between intrinsic viscosity and weight-average molecular weight which have been determined by various authors for 'pure' poly(vinyl acetate). Clearly, therefore, interactions of polymer coils of high and low molecular weight, which have differing structural spectra from specimen to specimen, may well lead to widely different apparent A_2 values, beside other properties, when there are the same overall analyses for seemingly similar partly hydrolysed poly(vinyl acetate) samples in evidence.

The slopes of the equal concentration lines in the Zimm plots are open to some latitude in interpretation, but they suggest the order of magnitude 10^{-6} cm for the apparent radii of gyration of these macromolecules, as is consistent with the random-coil configuration³⁷. Radii of gyration may not, in general, be determined accurately for macromolecules of M_w below $\approx 200\ 000$. However, Rao, Rao and Ralpagam³⁸ obtained an $\langle r^2 \rangle^{1/2}$ value of $5 \times 10^{-5} \text{ cm}$ for poly(vinyl acetate) of M_w 300 000 in ethyl acetate as solvent, presumably at room temperature (unstated), from which a value of 1.4 nm can be derived for the root-mean-square radius of gyration per polymerization monomer unit; and Schneider, Onu and Mihai³⁶ show a Zimm plot for poly(vinyl acetate) in cyclohexane as solvent at 25°C which allows $\langle r^2 \rangle^{1/2}$ to be estimated as $33 \times 10^{-6} \text{ cm}$ for a M_w of 2×10^6 , which gives again a value of 1.4 nm per unit. These values are mutually supportive, and the value here for the transesterified

polymer agrees exactly, and possibly fortuitously, with these. The values for the other two partly hydrolysed polymers are only slightly higher, in the range range 1.5–2 nm per unit. The value of $\langle r^2 \rangle^{1/2}$ for pure poly(vinyl acetate) in methanol as solvent at 5°C may be in error, i.e. high, because the fully extended molecules should have a mean end-to-end distance of $\approx 38 \times 10^{-6}$ cm, whereas the root-mean-square end-to-end distance calculated from the $\langle r^2 \rangle^{1/2}$ value is $\approx 17 \times 10^{-6}$ cm (which would mean that the macromolecules were swollen very close to their limit). The true value is most likely slightly lower here.

Iodine-complexing properties of the poly(vinyl acetate) and its partly hydrolysed derivatives

Two solvents were selected for work on the polymer-iodine complex: 3.8% (vol/vol) methanolic water, the high-yield solvent hitherto used for analytical examination of this polymer system⁵⁻⁷, and 9.1% (vol/vol) methanolic water which offered a more solubilizing medium for the complex, with less likelihood of the formation of locally-gelled fragments on the mixing of the reagents, whilst still permitting a reasonably high degree of complex formation (which decreases with increasing proportion of methanol in the aqueous solvent mixture⁵). In both solvents the broad, approximately Gaussian absorption band of the complex was clearly defined with λ_{max} near 510 nm. The ratio of absorbances at 546 nm and λ_{max} was ≈ 0.9 . A much lower concentration of iodine/iodide reagent than used previously^{6,7} was selected, because it was thought that high reagent concentration might promote absorption effects which would complicate the light-scattering studies.

Results of spectrophotometric measurements on the 3.8% methanolic solutions of the complex derived from pure poly(vinyl acetate) at various temperatures are listed in Table 3. The least-square lines for the eight sets of absorbance-concentration values shown had correlation coefficients ranging from 0.9950 to 0.9997, and the intercepts of the lines with the concentration axis were not significantly different from zero. The Beer-Lambert law, therefore, held reasonably for the conditions of these experiments which involved polymer concentrations not exceeding 0.075 g dm⁻³ of polymer (or 8.72 x 10⁻⁴ mol dm⁻³ of monomer/polymer units) so that an excess of iodine was always present. The variation of the extinction coefficient (*E*) with temperature has a sigmoid form^{5,14} and tends to the maximum value of 245 at low temperature (Table 3), which is consistent with previous observations on the maximum amount of the complex

which can form with a much larger excess of iodine at room temperature⁷. If it is assumed that an equilibrium constant may be formulated by the ratio of complexed polymer to non-complexed polymer, $E/(245-E)$, then the set of values listed in the last column of Table 3 is obtained. A plot of the log₁₀ of these values against the reciprocal of the absolute temperature yielded a reasonably straight line (correlation coefficient 0.994) confirming that the experimental conditions allowed equilibrium to be established³⁹.

As partly hydrolysed poly(vinyl acetate) polymers, especially acid-equilibrated ones, when examined under similar conditions show far less propensity to form complex than does pure poly(vinyl acetate)¹⁷, and also possess the polydispersity discussed previously, the best conditions for examining the light-scattering properties of the complex appeared to be with pure poly(vinyl acetate) well below room temperature under conditions in which the polymer-complex molecules would not be likely to show change in state of aggregation with concentration, i.e. extremely low concentration of polymer in as good a solvent as possible with adequate amounts of iodine and iodide to maintain sensibly complete formation of the complex. The solutions of poly(vinyl acetate) complex in the 9.1% methanolic aqueous solvent finally adopted were at least 10-fold more dilute in polymer than those discussed previously and yielded low absorbances which required very careful measurements. For example, for final iodine and potassium iodide concentrations identical with those shown in Table 3, poly(vinyl acetate) concentrations of 1.37, 2.74, 4.11, 5.48 and 6.85g x 10⁻⁶ cm⁻³ gave at 20°C maximum absorbances of 0.032, 0.045, 0.070, 0.095 and 0.120, respectively, in 1 cm cells. The values again confirm Beer's law for the system and yield an *E* value of 174, which is 13% less than the corresponding values at 20°C for the 3.8% methanolic solvent (cf. Table 3). This small reduction was considered acceptable, and sensibly complete formation of the complex could be expected for the temperature range 5–15°C by analogy with the results shown in Table 3. At the higher temperatures, various degrees of incomplete formation of the complex could be expected which would vary with the concentration of the polymer.

Refractivity and light-scattering properties for the poly(vinyl acetate)-iodine complex

In the case of the complex, there was too much absorbance with the 436 nm mercury emission line, even by the reagent blank, for worthwhile measurements of

Table 3 Spectrophotometric results for the red iodine complex formed by various concentrations (*c*, mg dm⁻³) of poly(vinyl acetate) in reaction with 6.42 x 10⁻⁵ mol dm⁻³ iodine and 1.56 x 10⁻² mol dm⁻³ potassium iodide mixed as described into 3.8% vol/vol methanolic water, as a function of temperature

Temperature (°C)	λ_{max} (nm)	Absorbance					Extinction coefficient ^a	Equilibrium constant
		<i>c</i> = 15	<i>c</i> = 30	<i>c</i> = 45	<i>c</i> = 60	<i>c</i> = 75		
5	520	0.353	0.704	1.050	1.461	1.808	240	48.0
10	520	0.327	0.645	1.025	1.403	1.655	230	15.3
15	512	0.316	0.638	0.945	1.232	1.610	212	6.42
20	510	0.291	0.625	0.863	1.190	1.492	198	4.21
25	510	0.262	0.515	0.834	0.950	1.211	161	1.92
30	498	0.206	0.398	0.589	0.736	0.931	123	1.01
35	498	0.106	0.215	0.293	0.357	0.438	57.5	0.307
38	496	0.074	0.142	0.184	0.229	0.295	37.8	0.182

^a For 1% solutions (wt/vol) in 1 cm cells

refractive index to be taken. Also, with the 546 nm line, whilst absorbance was much less, attempts to measure refractive index differences with the Jamin interferometer were not reproducible for all of the concentrations of the complex and all temperatures used. There are three possible reasons for this. Invisible striations of gelled complex may have formed when the solutions were handled in the cell of the instrument after the solutions had been centrifuged; the complex may have partially absorbed itself at the optical surfaces of the cell; and preferential absorption of one or both reagents, and/or one of the components of the solvent, by the macromolecules may not have been reproducible. The results in fact showed inconsistent variations of n with c , and an averaging of $\Delta n/c$ values for 5 and 10°C (the most consistent results) merely indicated a possible large dn/dc value between -5 and $6 \text{ g}^{-1} \text{ cm}^3$. Under these circumstances, as an expedient, the light-scattering study was attempted in terms of $Kc/R_\theta(dn/dc)^2$ as the dependent variable rather than Kc/R_θ .

For some concentrations of polymer not exceeding $2 \times 10^{-6} \text{ g cm}^{-3}$, the light-scattering measurements taken for the complex at 5, 10 and 15°C, and summarized in Figure 3, were sufficiently consistent to allow interpretation on a Zimm plot. For more concentrated solutions, the results were almost impossibly inconsistent owing presumably to uncontrollably irreproducible effects such as those noted previously. Nevertheless, the concentration shifts for the various light-scattering angles

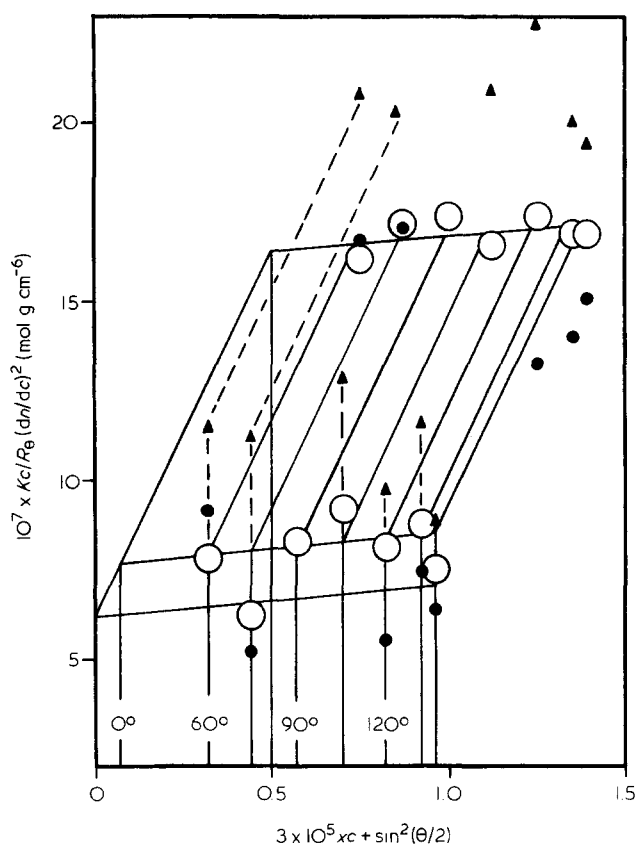


Figure 3 Zimm plot for the poly(vinyl acetate)-iodine complex dissolved in 9.1% methanolic water at: ●, 5; ○, 10; ▲, 15°C. Wavelength of light used, 546 nm; 'light-scattering constant', $K/(dn/dc)^2 = 6.572 \times 10^{-6} \text{ mol g cm}^{-6}$; concentration of polymer, $10^7 \times c \text{ g cm}^{-3}$; lower set of points, 2.28; upper set of points, 16.5. Concentration of I_2 and KI , 6.42×10^{-5} and $1.56 \times 10^{-2} \text{ mol dm}^{-3}$, respectively

shown in Figure 3, though generally very scattered, were all sufficiently parallel to define a gradient for the Zimm zero-angle line for the complex. The angular variation of scattered light was most regular for the data taken at 10°C, and the grid shown in Figure 3 was constructed by assigning a reasonable slope for the zero concentration line consistent with its extrapolation to a point coincident with the intercept of the zero angle line with the vertical axis. This slope defines the value for the radius of gyration of the complex listed in Table 2.

A typical formulation, e.g. $[(\text{CH}_2\text{CHOCOCH}_3)_2\text{OI}]_n$, would require an average molecular weight of $\approx 140\,000$ for an iodine complex derived from poly(vinyl acetate) of M_w 130 000 provided that the complex be assumed not to be aggregated in its 91% aqueous supporting solvent. This sets a lower limit for the molecular weight of the complex. By speculating that the complex may be aggregated to the point of precipitation, with a degree of swelling no greater than, for example, 2, then an upper limit for the molecular weight would be $\approx 7 \times 10^6$. With the assumption of these limits, it is possible to interpret the intercept and slope of the zero-angle line in Figure 3 in terms of possible ranges for dn/dc and A_2 , as shown in Table 2. A dn/dc value between 0.5 and 3.4 is plausible, because of the strong possibility of preferential absorption of one component of the solvent by the complex, which may lead to values of dn/dc as high as 0.8 in general⁴⁰; also, refractivity is relatively high in an absorption band, and an iodine-containing molecule would be expected to have a relatively high refractive index in any case. The positive values for A_2 appear to confirm that a complex was indeed formed. The results tentatively suggest that the complexed macromolecules may be aggregated to molecular weights $> 140\,000$ because the highest values in the estimated ranges for both dn/dc and A_2 appear improbable. If this is assumed, then the low value of $\langle r^2 \rangle^{1/2}$ which is observed for the complex (independently of dn/dc) indicates that the complexed macromolecules are considerably collapsed in their highly aqueous solvent compared to the parent poly(vinyl acetate) in its good solvent methanol.

CONCLUSIONS

The degree of collapse of the poly(vinyl acetate) macromoles on forming the complex would appear from the results to be by a factor of at least 3. Hence, a suitable model for the formation of the complex, as the methanolic iodine and poly(vinyl acetate) solution is poured into an excess of aqueous potassium iodide solution, is as follows. The influx of water and iodide into the iodine-permeated methanolic polymer causes a re-orientation and partial collapse of the polymer molecules around iodine chains, which is accompanied by development of the red/pink colour characteristics of the complex. The presence of water as the preponderant component of the final solvent evidently provides a thermodynamically favourable degree of collapse of the polymer molecules so that a complex can form which would otherwise not be stable in a solvent which would allow the polymer molecular more freedom to swell. The formation of the complex is commensurately temperature sensitive and decreases in amount with increases in the methanol content of the aqueous methanol solvent. The evidence found here for the constriction of the poly(vinyl acetate) molecules on formation of red complex is certainly not inconsistent

with the helical structure suggested for this complex by Hayashi and co-workers by analogy with the type of structure normally assumed to occur in the related blue complex following the suggestion of Zwick^{11,41}. The results obtained here very tentatively suggest some degree of aggregation of the red complex at the high dilutions at which the observations were necessarily made; and it is also perfectly plausible that the complexed molecules may aggregate further through mutual entanglement in the poor final solvent, to the point of precipitation at the highest concentrations⁶.

As noted in the Introduction, the same type of red/pink complex can easily be formed from the acetate-block parts of almost completely hydrolysed poly(vinyl acetate) specimens^{9,17}. Moreover, the presence of high iodide/iodine ratios displaces the equilibrium between the macromolecules and iodine toward formation of the blue complex which is normally thought of as being characteristic of their preponderant hydroxy-group sequences, whilst low iodide/iodine ratios favour the red complex^{8,10}. This is in sharp contrast to the recent report that very low iodide/iodine ratios (high iodine/iodide) favours the formation of a blue complex in the case of pure poly(vinyl acetate)¹¹. It is possible that the former result may be due to a preferential salt effect on a very polydisperse system, whereas the latter may be due to iodine acting as a bridging group in interlocking the acetate groups¹⁸ on the outside of relatively long complexed polymer helices which are wound around polyiodine chains. The formation of the blue complex from poly(vinyl alcohol) and also from partly hydrolysed poly(vinyl acetate) is certainly favoured by the presence of bridging groups such as boric and orthotelluric acids^{9,42}.

Finally, this work has shown that it is possible through light-scattering measurements to obtain a useful indication of the radius of gyration in the absence of refractivity measurements on a coloured complex polymer system. However, future use of a wavelength in the range 600–700 nm for the optical work (well clear of the maximum of the absorption band of the red complex), by means of a laser source⁴³, can be expected to lead to further improvements of this technique.

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