Partly alcoholized poly(vinyl acetate) polymers: properties of polymers hydrolysed by different routes

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Several polymers have been prepared over the entire compositional range of poly(vinyl acetate—alcohol) intramolecular mixtures by each of three routes — saponification with alkali, base-catalysed transesterification with methanolic methoxide, and acid-catalysed equilibration with acetic acid and hydrochloric acid mixtures. The polymers prepared by the three routes showed contrasting behaviour in their reaction with iodine in the presence of iodide and in their melting. The results are interpreted in terms of a linear block structure of acetate groups being required for high efficiency in iodine-complex formation and an attendant linear block structure of alcohol groups being required for high crystallinity and high melting-point. The order of degree of block structure in the polymeric products by the three routes is as follows — saponification, high; transesterification, intermediate; acid-equilibrium, hardly any. The use of the iodine complex for the analytical determination of samples from this system is discussed.

INTRODUCTION

Poly(vinyl acetate) may be converted to poly(vinyl alcohol) by a variety of methods[1]. In a recent communication it was demonstrated that careful kinetic control of this conversion by methoxide-catalysed transesterification allows poly(vinyl acetate—alcohol) intramolecular mixtures to be prepared with predictable mole % conversion over the entire compositional range[2]. A typical set of such polymers was characterized by its sensitivity to formation of a red complex with iodine, in the presence of iodide, under specified conditions[3]. It was suggested that the sensitivity progressively decreased as the block sequence structure[4-11] of the acetate substituents was destroyed by hydroxyl substitution[2]. There is fragmentary evidence for variation of the iodine sensitivity with details of the method of acetate-alcohol conversion[7]. Hence a systematic study of this phenomenon over the complete range of polymer composition is presented for the most contrasting methods of converting the acetate into the alcohol.

EXPERIMENTAL

Materials

Pure poly(vinyl acetate), molecular weight range 125 000—150 000, was obtained from ICN K & K Laboratories, Plainview, New York. The following AnalR-grade reagents were used as received: methanol, acetone, acetic acid, hydrochloric acid (Fison's); sodium hydroxide, potassium iodide, iodine (BDH). AnalR anhydrous sodium carbonate (BDH) was dried at 130° for 4 h, and stored under vacuum at 22° over anhydrous calcium chloride.

Methoxide-catalysed transesterification of poly(vinyl acetate)[2]

The polymer was dissolved in methanol (2.4 g/50 cm³), which was held at 65—70° under a reflux condenser for 1 h.

The solution was then thermostatted at 22° with stirring[2]. Exactly 1 cm³ of freshly prepared sodium in methanol (0.015 g/cm³) was added and a stop watch started. For several such solutions, the transesterification was halted at a specific time by neutralization with 1 M aqueous acetic acid (external litmus). The reaction mixtures were then concentrated to 15—20 cm³ under vacuum at 35—45°. Water-insoluble polymeric products, with up to *ca.* 70 mole % replacement of acetate by alcohol groups, were precipitated with distilled water, washed, reprecipitated from methanol and re-washed, then dried under vacuum at 22° and stored over anhydrous calcium chloride for 3 or 4 days. Methanol-insoluble products, with degrees of hydrolysis in the 70—99 mole % range, were reprecipitated from aqueous solution by acetone, washed with acetone, and dried and stored as above.

Hydrolysis of poly(vinyl acetate) in acetone—water mixture[6,12]

The polymer was dissolved in a 3:1 (V/V) acetone-water mixture (2.5 g/50 cm³) which was held at 65—70° under a reflux condenser for 2 h. The solution was then thermostatted at 22° with stirring. A calculated amount of aqueous sodium hydroxide (40% W/V) was added to achieve a predetermined degree of hydrolysis, and the stirring was continued for 4h. Polymeric products with up to 70 mole % hydrolysis were precipitated by water and purified as for the transesterification products. Acetone-water insoluble proudcts (70—99 mole %hydrolysis) were in this case reprecipitated from water by methanol and then worked up as before. Methanol was used in the purification process because acetone was found to be ineffective in removing sodium acetate from the polymeric product.

Acid-catalysed equilibration of PVAc in acetic acid-water mixture[13]

The PVAc resin (2.5 g) was vigorously stirred under a reflux condenser at 90° with an acetic acid-water mixture (24 cm³) and concentrated hydrochloric acid (1 cm³) for 10 h. In the initial stages of the hydrolysis the polymer remained undissolved. The catalyst was neutralized with aqueous sodium hydroxide (40% W/V), and soluble polymeric products were isolated initially by precipitation with acetone. The products were then purified by reprecipitation as for the products of the transesterification experiments. The ultra-violet visible spectrum of methanolic solution of non-white polymer samples (5 g dm⁻³) were scanned in 1-cm cells at 20° against methanol as blank on a Unicam SP700 spectrophotometer.

Equilibrium concentrations for the reaction were determined as follows. Each of several acetic acid-water-hydrochloric acid mixtures containing 10% W/V of poly(vinyl acetate) were prepared in triplicate as described above and equilibrated at 90° for, respectively, 8, 24 and 52 h. The reaction mixtures were then cooled and, with the washings from condenser and stirrer, made up to 100 cm³ with distilled water. In those cases for which homogeneous solutions resulted, aliquots were titrated with 0.1 M aqueous sodium hydroxide to the neutrality point of phenolphthalein to establish the total acid content in the equilibrium mixture. The amount of hydrochloric acid present was then deducted from the total acid, giving values for the quantity of acetic acid at equilibrium. Polymers with less than *ca.* 85% hydrolysis gave inhomogeneous mixtures when their cooled reaction solutions were made up to 100 cm³, and these mixtures could not be titrated satisfactorily. The acetic acid content at equilibrium in these and the homogeneous cases was calculated from the amount added initially plus the amount generated by the hydrolysis. The water content of the reaction mixtures at equilibrium was calculated from the amounts added initially (as pure water and water in the hydrochloric acid) minus the amount consumed in the hydrolysis. Equilibrium values for the acetate and hydroxyl content of the isolated products were obtained from the mole % degrees of hydrolysis determined as detailed below. Apparent equilibrium constants were then calculated by treating the poly(vinyl acetate-alcohol) products as though they were mixtures of pure poly(vinyl acetate) and pure poly(vinyl alcohol), that is by multiplying together the equilibrium molar ratios of poly(vinyl alcohol) to poly(vinyl acetate) and the corresponding equilibrium molar ratios of acetic acid to water.

Saponification analysis of poly(vinyl acetate) and its partially hydrolysed products

The dry polymer (~0.1 g, w) was completely dissolved in an appropriate solvent, either methanol or aqueous methanol (12 cm³), and stirred at 60° under a reflux condenser. Aqueous sodium hydroxide (25 cm³, 0.1 M) was added drop by drop over 15 min and stirred for 2 h. The unreacted sodium hydroxide was titrated with 0.1000 M aqueous hydrochloric acid (phenolphthalein) according to the method previously tested[3]. The titre was deducted from the blank titre, obtained from an identical experiment with no polymer, to give v cm³ of 0.1000 M sodium hydroxide consumed by the saponification. The weight % (W) of vinyl acetate units (molecular weight 86.09) in the polymer is 86.09 v/100 w and, assuming that the remainder of the polymer consists of vinyl alcohol units (molecular weight 44.06),

the mole % of vinyl acetate units is 44.06 W/(86.09−0.4203 W). The analysis was carried out in duplicate for each polymer.

Iodine complex formation

Solutions of those polymers which were methanol soluble (12.17 g/dm³) were added in a series of 1 to 5 cm³ aliquots to 5 cm³ aliquots of methanolic iodine solution (0.02014 M). These solutions were made up uniformly to 10 cm³ with methanol. Each solution (1 cm³) was carefully diluted with (0.0162 M) aqueous potassium iodide solution (25 cm³) with a gentle swirling motion of the fluid to yield each colorimetric test solution[2,3]. Aqueous solutions of the methanol-insoluble polymers (12.17 g/dm³) were added in a series of 1 to 5 cm³ aliquots to 2 cm³ aliquots of aqueous iodine (0.00193 M) and potassium iodide (0.078 M) solution, and then diluted to 10 cm³ with distilled water[10]. The iodine and potassium iodide concentrations in the final mixtures were 0.000387 M and 0.0156 M, respectively. The maximum polymer concentrations in the final mixtures were: methanol-soluble polymers, 0.2340 g/dm³; methanol insoluble polymers, 6.085 g/dm³. To one additional polymer solution a four-fold molar excess of sodium acetate per polymer segment was added to test the effect of this on the absorbance of the polymer-iodine complex.

The test solutions were prepared at room temperature and were then thermostatted at 20° and allowed to stand for 2 h to reach equilibrium. Then their absorbances over the range 400–600 nm were scanned in 1 cm cells at 20° against a blank solution without polymer on a Unicam SP700 or Pye-Unicam SP8-100 spectrophotometer. The absorbance of both instruments was calibrated with standard dichromate solution. The values of absorbances per mg of polymer/dm³ at the wavelength of maximum absorbance (*ca.* 500 nm) were converted to absorbance units per mmol of vinyl acetate units in each polymer/dm³ by multiplication by the factor 100 (44.6 + 0.4203 M)M, where M is the mole % of vinyl acetate units in the poly(vinyl acetate-alcohol) polymer.

Melting characteristics of the polymers

The ranges of melting of the polymers were determined on a Perkin–Elmer DSC-1B differential scanning calorimeter. The samples (5–10 mg) were heated under nitrogen at 32° min⁻¹, and the reference compartment was left blank. The temperature recorder was calibrated at room temperature and at the melting-point of tin. The maximum of the thermogram recording the melting range was taken as the average melting-point. Polymers which initially gave no observable thermogram (owing to their low degree of crystallinity) were maintained at 100° under nitrogen for 1 to 2 h and were then scanned on the calorimeter.

RESULTS AND DISCUSSION

Products of methoxide-catalysed alcoholysis (transesterification) and their iodination

This reaction has the stoichiometry shown:
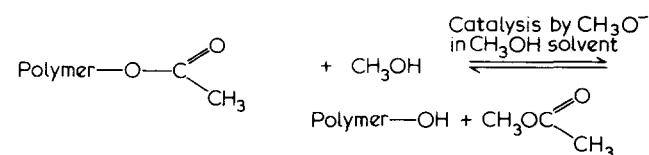
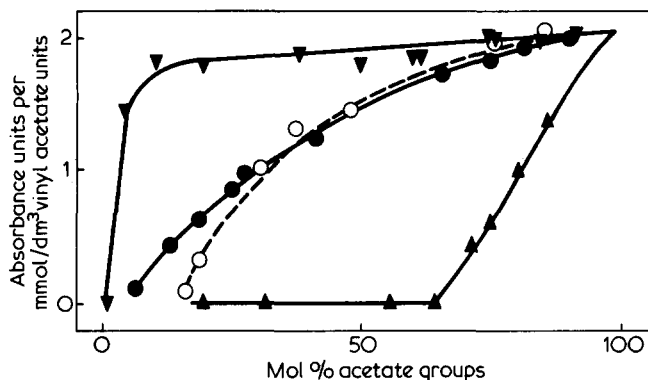The reaction followed the kinetic path prevously described

Figure 1 Sensitivity of red complex formation between partly hydrolysed poly(vinyl acetate) and iodine. Polymers prepared by saponification, ▼; methoxide-catalysed transesterification, ●, (Joshi and Pritchard[2], ○); acid-catalysed equilibration, ▲

— a slow initial stage, a rapid stage covering the 10–85 mole % alcoholysis range and a slow final stage[2]. The products obtained by halting the reaction at desired points within the entire 0–100 mole % alcoholysis range were all white powders; measurement of their mole % degrees of hydrolysis and spectrophotometry of their iodine complexes gave the central line in *Figure 1*. These results lie on a smooth curve, which indicates that the procedure of preparation, saponification, iodination and spectrophotometric analysis can generally be reproduced to within 1–2%. The results confirm the trend reported by Joshi and Pritchard (dashed line in *Figure 1*) for similar though less precisely controlled preparations[2].

Products of saponification with aqueous alkali (hydrolysis) and their iodination

$$Polymer—O—C\overset{O}{\underset{CH_3}{<}} + OH^- \longrightarrow Polymer—OH + CH_3CO.O^-$$
In 50%-acetone/water
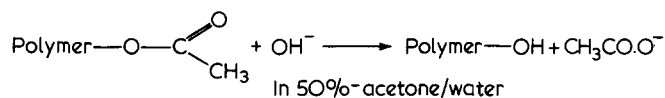
The degree of replacement of acetate by hydroxyl groups was conveniently pre-selected for this reaction by use of the appropriate stoichiometric quantity of alkali for each particular product. The kinetics of the reaction have been explored elsewhere and show three stages similar to the kinetics of the transesterification[7,11,15]. The products of the reaction were white powders over the entire hydrolysis range. Difficulty was experienced in removing sodium acetate from these polymers. It was demonstrated, however, that the presence of sodium acetate did not affect the absorbance of the iodine complex, nor the end point in the saponification analysis. The results of the iodination reaction show some scatter (upper curve, *Figure 1*), but clearly the hydrolysis causes only a comparatively minor diminution in the amount of complex formed, right up to about 90 mole % hydrolysis, and only as the last 10 mole % of the acetate groups are replaced by hydroxyl does the amount of complex fall rapidly to zero.

Products of acid-catalysed equilibration and their iodination

$$Polymer—O—C\overset{O}{\underset{CH_3}{<}} +H_2O \rightleftharpoons Polymer—OH + CH_3COOH$$
Hydrogen ion catalysis
(HCl)
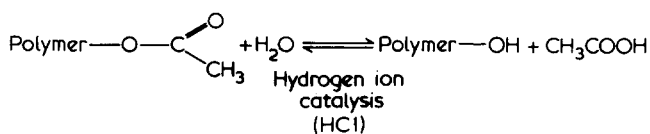
The reaction of pre-selected quantities of water, acetic acid and poly(vinyl acetate) for reaction times of 8, 24 or 52 h

resulted in essentially no difference (within ±0.5%) in the equilibrium point for the reaction at 90°. *Table 1* lists the final mole % hydrolysis values of the polymers at equilibrium for various initial ratios of acetic acid to water. When these values are plotted graphically they lie on a smooth curve. There is a slight scatter in the values at low % hydrolysis, but the data extrapolate accurately to zero % hydrolysis for 100% acetic acid. The experimental procedure is thus quite reliable. *Table 1* also lists the molar ratio of acetic acid to water at equilibrium, calculated from the extent of reaction indicated by the observed mole % of hydrolysis. These values were checked where practicable by titrimetric determination of the acetic acid at equilibrium, with agreement within 5–6% (*Table 1*). Apparent equilibrium constants for 90°, calculated from the molar equilibrium concentrations of the reacting components for the 20–90% hydrolysis range, lie within the range 1.84 ± 0.20, and are remarkably constant, considering that the medium changes over the range considered. (For 40° a value near 1 has been quoted[1,7].)

The colours of the polymeric products varied with the mole % degrees of hydrolysis as follows: >80% off-white; *ca.* 80% straw; 40–80% translucent brown; <40% dark brown. The brown colour could be lessened only slightly by charcoal in the work-up solutions (to absorb low molecular weight coloured products). The colour of the polymers therefore appears to be an unavoidable consequence of acid-catalysed dehydration and acetic acid elimination, which generates conjugated sequences of double bonds along the polymer chains[16]. The brown products in solution showed molar absorptivities in the range 5–10 at λ_{max} 276 nm, based on the mean molecular weight of the monomer segments in the polymer. There was, however, no significant absorbance over the range 450–550 nm, so that the brown colour did not interfere with the iodine test. The lower curve of *Figure 1* shows that the amount of iodine complex formed for these acid-equilibrated hydrolysis products decreases very rapidly as the % hydrolysis increases. Beyond 33 mole% hydrolysis there is essentially no coloration observable with iodine.

Table 1 Equilibrium data for the system: poly(vinyl acetate)-poly(vinyl alcohol)-acetic acid-water-hydrogen chloride (catalyst)*

Initial acetic acid concentration (volume %)†	Equilibrium degree of hydrolysis (mole %)	Equilibrium molar ratio of acetic acid/water	
		From titration of acetic acid	From degree of hydrolysis
0.0	97.7	0.0206	0.0207
16.0	94.3	0.0822	0.0862
20.0	93.9		0.108
24.0	92.5	0.122	0.129
32.0	90.5	0.175	0.183
36.0	89.2	0.207	0.216
54.0	80.5		0.431
68.0	68.2		0.770
78.0	52.1		1.28
84.6	46.0		2.05
93.5	35.6		6.28
94.8	28.3		7.75
95.4	24.8		9.91
95.6	19.6		10.3
96.0	14.2		11.2

* Equilibration of 10% w/v of poly(vinyl acetate) with 0.0110 M hydrogen chloride and various concentrations of acetic acid in water for not less than 5 h at 90°
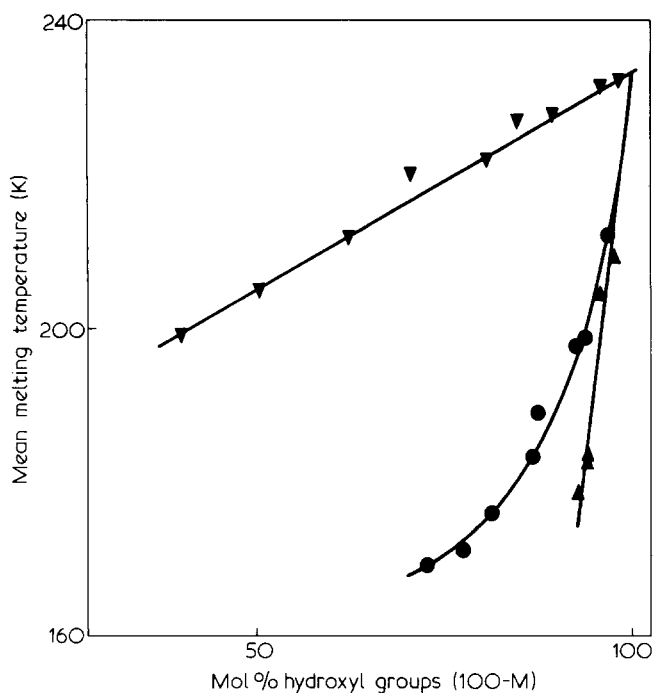† Made up before addition of vinyl acetate

Figure 2 Mean melting temperatures for partly hydrolysed poly(vinyl acetate) polymers — prepared by saponification, ▼; methoxide-catalysed transesterification, ●; acid-catalysed equilibration, ▲

This behaviour contrasts dramatically with the results obtained with the products prepared through the use of basic reagents.

Influence of acetate block structure on iodine complex formation of the polymers

The complete pattern of behaviour shown in *Figure 1* provides compelling evidence that formation of the iodine complex by the poly(vinyl acetate-alcohol) polymers depends upon their content of long acetate-block sequences, which varies with the method used for replacement of the acetate by alcohol groups. When basic reagents are used, the mechanism of this replacement reaction is currently believed to involve, as a major component, the auto-catalytic release of acetate groups by the already present hydroxyl groups[1], so producing an unzipping effect which can be halted only by chain branches or other chemical impurities in the vinyl polymer molecules[16]. The block replacement mechanism is evidently most completely operative for the saponification reaction. Although both reactions involving base are, in principle, reversible, it is plausible to expect the catalysed transesterification to permit measurable equilibration and concomitant randomization of the acetate and alcohol substituents, the more so as reaction time increases. In contrast, equilibration is generally considered to be much more rapid for acid-catalysed hydrolytic reactions[17]. In our case, at the 33 mole % hydrolysis point the acetate and alcohol group distribution has most likely become completely random, there being few acetate sequences longer than 2 or 3 units, i.e. no acetate block structure at all. No red iodine complex would be expected in this case because an average sequence length of at least 14 polymerized vinyl acetate units is required for the development of the red colour[18].

The contrasting behaviour shown in *Figure 1* is quite unlikely to arise from any other source such as, for example, any small differences there might be in the molecular weight of the polymers prepared by the different routes[18,19]. However,

some variations in degree of gelation of the polymers in the dissolution stages of the experimental work are difficult to foresee and control. It is likely that (invisible) partial gelation could give rise to variation in the block structure of the products of the hydrolysis reactions and, both dependently and independently, also in the extent of the iodination reaction. These effects are the likely causes of the observed scatter of points in *Figure 1*.

Significance of acetate block structure in analytical determinations

The iodination reaction, resulting in the formation of the characteristic red complex, has been used for many years for determination of poly(vinyl acetate)[3,20], and this reaction may also be applied to the determination of hydrolysed products of poly(vinyl acetate)[20]. It has now become evident that this is especially possible with high sensitivity for the products of saponification if they have not been hydrolysed to an extent greater than 90 mole %. However, it is clear from *Figure 1* that gross errors can arise in the interpretation of iodination analysis conducted on polymers of unknown preparative history and unknown block structure. This is particularly true for commercially hydrolysed poly(vinyl acetate) samples, most of which appear to have degrees of hydrolysis in the range 70–99 mol %. Only when the standard sample has strictly the same preparative history as the unknown samples may the method be safely attempted[20]. Moreover, iodination analysis offers a method for the determination of the likely preparative history of hydrolysed poly(vinyl acetate) samples of known mole % degree of hydrolysis.

Influence of hydroxyl-block structure on melting range of the polymers

Differential scanning calorimetry of the polymers prepared by the various methods showed clear, symmetrical peaks, corresponding to melting ranges of 20–30°, for the following ranges of mole % hydrolysis: saponification, 70–100%; transesterification, 80–100%; acid equilibration, none. The maxima of these peaks are plotted in *Figure 2*. Additional values for *Figure 2* were obtained from those noncrystalline polymers (outside the above ranges) which could be crystallised sufficiently at 100° in the course of 2 h to show distinct melting-range peaks in their thermograms thereafter. The remaining polymer preparations could not be crystallized at 100°; attempts to crystallize them at temperatures higher than 100° lead to partial decomposition and the matter was not pursued.

The relative average melting points shown in *Figure 2* offer additional evidence for the reaction controlled variation in the degree of block structure of the polymers. The melting points of the polymers prepared by each of the three routes increase smoothly as their acetate content decreases. The melting point is diminished by residual acetate substitution the more so, it is suggested by the authors, as this is more random. A relatively high melting point for a given acetate content, is thus achieved only by the products of the saponification reaction which, in accord with the results of iodination, retain a very high degree of hydroxyl group block strucutre. It is, of course, the crystalline block structure of CH_2CHOH units in pure poly(vinyl alcohol), usually present to the extent of ca. 50% of the polymer, which is responsible for the observed melting point of ca. 233°, the remainder of the pure polymer consisting of non-crystallizable, entangled molecular strands[16]. Partly hydrolysed poly(vinyl acetate)

polymers, in which substantial random equilibration of groups has occurred during the replacment reaction, are able to develop little hydroxyl block structure until the replacement of acetate groups is almost complete. Hence, in the case of the transesterified and acid-equilibrated polymers we observe melting points which increase rapidly towards a value of *ca.* 233° only as the final few mole % of acetate groups are withdrawn from the polymer system.

ACKNOWLEDGEMENT

REFERENCES

1 Noro, K. 'Polyvinyl alcohol – properties and applications' (Ed. C. A. Finch), Wiley, New York, 1973, Ch. 4
2 Joshi, D. P. and Pritchard, J. G. *Polymer* 1978, **19**, 427
3 Pritchard, J. G. and Serra, F. T. *Talanta* 1973, **20**, 541
4 Sakurada, I. *Gohsei Seni Kenkyu* 1942, **1**, 213
5 Hayashi, S., Nakano, C. and Motoyama, T. *Kobunshi Kagaku* 1963, **20**, 303; 1964, **21**, 304; 1965, **22**, 358
6 Tubbs, R. K. *J. Polym. Sci. A-I* 1966, **4**, 623
7 Noro, K. *Brit. Polym. J.* 1970, **2**, 128
8 Shiraishi, M. *Brit. Polym. J.* 1970, **2**, 135
9 Shiraishi, M. and Toyoshima, K. *Brit. Polym. J.* 1973, **5**, 419
10 Hayashi, S., Michihiro, T., Keneko, I. and Hojo, N. *Makromol. Chem* 1975, **176**, 3221
11 Nagai, E. and Sagane, N. *Kobunshi Kagaku* 1955, **12**, 195
12 Sakurada, I. *Kobunshi Kagaku* 1968, **17**, 21, 207
13 Nebel, R. W. *US Pat.* 2 657 201, 1953
14 Mann, F. G. and Saunder, B. C. 'Practical organic chemistry', Longmans, Green and Co., 1960, pp. 453–455
15 Sakurada, I. and Sakaguchi, Y. *Kobunshi Kagaku* 1956, **13**, 441
16 Pritchard, J. G. 'Poly(vinyl alcohol) – basic properties and uses', Gordon and Breach, New York, 1970, Ch 1–3
17 Gould, E. S. 'Mechanism and structure in organic chemistry', Henry Holt & Co., New York, 1959, pp 314–320
18 Morishima, Y., Fujisawa, K. and Nozakura, S. *Polym. Lett.* 1976, **14**, 467; *Polym. J.* 1978, **10**, 281
19 Hayashi, S., Kawamura, C. and Takayama, M. *Bull. Chem. Soc. Japan* 1970, **43**, 537
20 Hughes, J. M., Joshi, D. P. and Pritchard, J. G. *Talanta* 1979, (to be published)