Vinyl alcohol–vinyl propionate copolymers: sequence distribution and glass transition

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^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy was used for the determination of the sequence distribution in vinyl alcohol–vinyl propionate (VAL–VP) copolymers prepared by two different methods: by partial alkaline hydrolysis of poly(vinyl propionate) and by partial esterification of poly(vinyl alcohol). The ^{13}C n.m.r. spectra of the methylene carbons in the main chain show three split peaks, whose intensities change with copolymer composition. These peaks can be assigned to the three dyad sequences. The results obtained show that vinyl propionate units have an alternating tendency in VAL–VP copolymers prepared by esterification and a block distribution in VAL–VP copolymers prepared by hydrolysis. The T_g values of VAL–VP copolymers prepared by the two different methods are influenced by both the overall copolymer composition and the monomer sequence distribution.

(Keywords: vinyl alcohol–vinyl propionate copolymers; copolymer composition; sequence distribution; ^{13}C nuclear magnetic resonance; glass transition temperature)

INTRODUCTION

It has been well established that, in general, the sequence length distribution of comonomers has a large influence on the chemical and physical properties of copolymers and may exert an important influence on the practical uses of the polymer. The importance of the sequence distributions of vinyl acetate and vinyl alcohol units with respect to the surface activity has been recognized for a long time[1]. Recent advances in nuclear magnetic resonance (n.m.r.) spectroscopy, which have led to a more exact characterization of copolymers, include determinations of monomeric unit distribution[2–4]. On the other hand, the effect of copolymer composition and monomer sequence distribution on glass transition temperature, T_g, has been investigated for several copolymers[5–7].

This paper is concerned, first, with the dyad sequence distribution of vinyl alcohol–vinyl propionate (VAL–VP) copolymers prepared by two different methods: by partial esterification of poly(vinyl alcohol) (PVAL) and by partial alkaline hydrolysis of poly(vinyl propionate) (PVP) and, secondly, with the sequence distribution effects on T_g in VAL–VP copolymers.

EXPERIMENTAL

Materials

The PVAL used was a commercial product (Gohsenol AH-22) thoroughly hydrolysed. Its molecular weight, as measured by osmometry, was 49 500 g mol^{-1} and the purification was performed by a conventional reprecipitation method using a water–methanol mixture as solvent–precipitant system. The purified polymer was dried *in vacuo* to constant weight in the presence of phosphorus pentoxide. Propionyl chloride (Merck) was purified by distillation under normal pressure immediately before use. Pyridine (C. Erba) was purified by a conventional method[8] and dried for a few days with a C. Erba 4 Å molecular sieve. *N*-methyl-2-pyrrolidone (Fluka) was vacuum distilled and dried for a few days with a C. Erba 4 Å molecular sieve.

Preparation of VAL-VP copolymers

Partial esterification. Equimolar concentrations of propionyl chloride and pyridine were reacted at 10°C with 4 g (0.091 mol OH) PVAL using 200 cm^3 *N*-methyl-2-pyrrolidone as solvent. The extent of modification was controlled by the amount of propionyl chloride used. Different precipitants were used to isolate the copolymers, depending on the extent of modification. Distilled water appeared to be the best for the highly modified polymers. Methanol, isopropyl alcohol and diethyl ether were used as precipitants for the less modified polymers. All samples were purified by reprecipitation, then dried *in vacuo* in the presence of phosphorus pentoxide.

Partial hydrolysis. A poly(vinyl propionate) previously obtained by total esterification of the commercial sample of PVAL (Gohsenol type) was used as starting material.

The hydrolysis experiments were done as follows: 4.0 g (0.04 mol) of PVP were dissolved in a mixed solvent of pyridine–water. Then an aqueous solution of potassium hydroxide (10 g/100 cm^3) was added under stirring. At the end of the hydrolysis the composition in pyridine–water was 80:20 (v/v) and the polymer was kept soluble throughout the process. The reaction time was 24 h at 30°C. The extent of hydrolysis was controlled by the amount of aqueous solution of potassium hydroxide used. Cold water, ethyl acetate and diethyl ether were used to isolate the copolymers.The samples were purified by reprecipitation, then dried *in vacuo* in the presence of phosphorus pentoxide.

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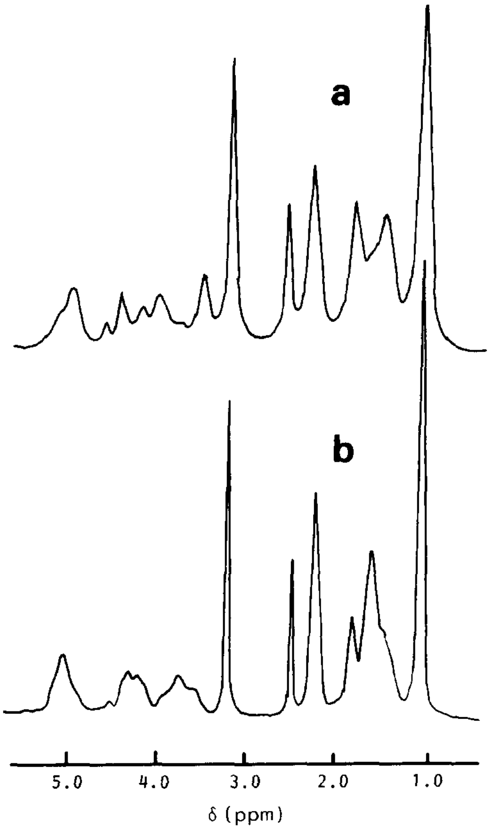

Figure 1 ^{1}H n.m.r. signals of: (a) VAL–VP copolymer (54.8 mol% VP units) prepared by partial alkaline hydrolysis of PVP; (b) VAL–VP copolymer (39.0 mol% VP units) prepared by partial esterification of PVAL

Methods

The ^{1}H n.m.r. spectra were registered in dimethyl sulphoxide at 70°C (internal reference hexamethyl disilane) using a 200 MHz Bruker AM-200 spectrometer. Deuterated acetone (45°C) and D_2O-deuterated pyridine (70°C) were used as solvents for the VAL–VP copolymers in the ^{13}C n.m.r. experiments according to their solubilities. The samples of approximately 10% (w/v) concentration in 10 mm tubes were observed at 20.15 MHz with a Bruker WP 80 SY spectrometer. Spectra were generally obtained after accumulation of 15000 scans, using a pulse width of 1.6 μs (pulse angle 40°) and a repetition time of 1 s. Spectral widths of 1000 Hz were chosen for the quantitative determinations.

The signal areas of the spectra were determined by spectral integration as well as by tracing over the peaks with a planimeter.

The amount of propionate groups in VAL–VP copolymers was determined by means of alkaline hydrolysis at 60°C with a standard solution of sodium hydroxide and back titration of the unreacted base with 0.1 M hydrochloric acid in the presence of phenolphthalein. Samples of 0.1–0.2 g were taken for the titration.

Glass transition temperatures of the copolymers were measured using a Perkin–Elmer DSC-4 differential scanning calorimeter, which was calibrated with standard materials. An initial scan was made to produce a uniform thermal history in all samples. Measurements were made at 10°C min^{-1} using dry copolymer tightly packed into an Al sample pan. All operations were carried out in N_2 atmosphere. To determine the T_g values we followed the criteria of $T_{\frac{1}{2}}$, which is the temperature of the mid-point of the line drawn between the tangents before and after the changes of c_p with T[9].

RESULTS AND DISCUSSION

Figure 1 shows the ^{1}H n.m.r. spectra of two VAL–VP copolymer samples, one prepared by hydrolysis of PVP and the other by esterification of PVAL. Using the assignments made for PVAL, PVP and vinyl alcohol–vinyl acetate one can straightforwardly assign all resonances of the spectra of VAL–VP copolymers. However, in the present discussion we focus our attention on the differences in the spectral region of the methylene protons in the main chain and the propionate substituted protons.

Two peaks, centred at 1.50 and 1.82 ppm, are observed in the methylene proton resonances of spectrum (a), corresponding to a VAL–VP copolymer prepared by hydrolysis of PVP. These two lines can readily be assigned to the methylene protons in VAL–VAL and VP–VP dyads, respectively, as has previously been indicated for vinyl alcohol–vinyl acetate copolymers[4,10]. On the contrary, in spectrum (b), corresponding to a VAL–VP copolymer obtained by esterification of PVAL, a very strong band is observed at 1.63 ppm together with a band at 1.82 ppm and a slight shoulder at 1.50 ppm. The stronger line located at 1.63 ppm between the methylene proton lines of VP–VP and VAL–VAL dyads may be assigned to the methylene protons of VAL–VP dyads.

In spectrum (a), the methine proton resonances of VP units show a peak centred at 4.87 ppm, which can be assigned to methine protons in VP units flanked by two VP units[3,4]. In spectrum (b) the band which appears at 5.05 ppm can be attributed to methine protons in VP units adjacent to VAL units.

All these spectroscopic results clearly indicate qualitatively that the two types of VAL–VP copolymer, prepared by hydrolysis and by esterification, show a different dyad distribution.

Figure 2 shows ^{13}C n.m.r. spectra in the region of the methylene carbon resonance of the main chain corresponding to the VAL–VP copolymer samples mentioned above. The ^{13}C n.m.r. spectra of PVAL and PVP are shown for comparison. Three methylene carbon signals are observed at 40.17, 43.15 and 45.0 ppm. The chemical shifts of the highest and lowest field peaks agree with those of the homopolymers, whereas the centre peak appears characteristically for the copolymer. Accordingly, these three peaks were assigned as dyads, that is, VAL–VAL, VAL–VP and VP–VP from the lower field.

Assuming essentially equal enhancements due to the nuclear Overhauser effect among the three methylene carbon peaks[11], the mole fractions of the three dyads can be accurately determined from the intensities of the lines. The results obtained are shown in *Tables 1* and *2*, where the value of η is also shown. The block character[12], η, is a measure of the departure from random character. It is given by the expression:

$$\eta = \frac{[\text{VAL–VP}]}{2[\text{VAL}][\text{VP}]} \qquad (1)$$

where [VAL–VP] is the mole fraction of VAL–VP dyads, [VAL] and [VP] being the mole fractions of VAL and VP

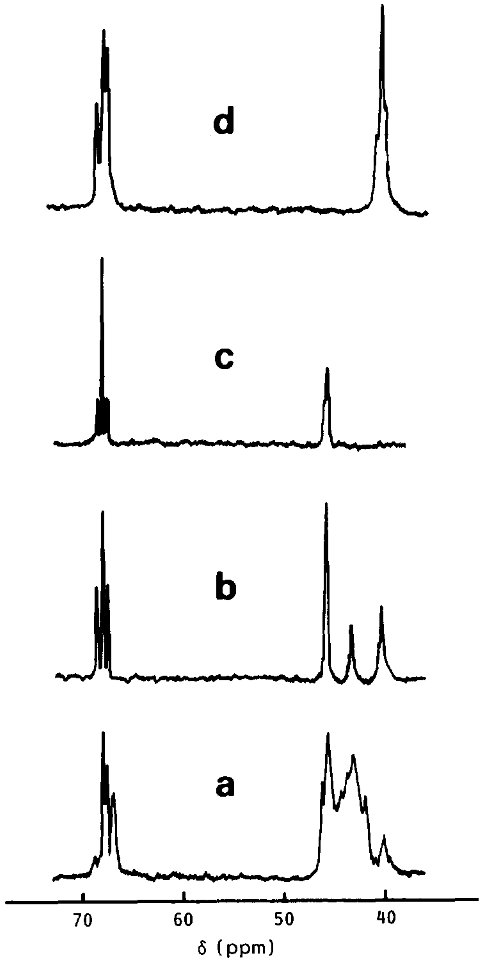

Figure 2 Partial ^{13}C n.m.r. spectra of: (a) VAL–VP copolymer (40.4 mol% VP units) prepared by partial esterification of PVAL; (b) VAL–VP copolymer (39.3 mol% VP units) prepared by partial alkaline hydrolysis of PVP; (c) PVAL; (d) PVP

Table 1 Composition, mole fractions of dyads and parameter η of VAL–VP copolymers prepared by partial alkaline hydrolysis of PVP

	Composition (mol%)		Dyad content (mol%)			
Sample	VAL	VP	VAL–VAL	VAL–VP	VP–VP	η
1	9.6	90.4	5.0	13.0	82.0	0.7
2	19.6	80.4	11.0	18.9	70.1	0.6
3	26.0	74.0	15.5	22.6	61.9	0.6
4	36.9	63.1	25.6	24.5	49.9	0.5
5	45.2	54.8	34.1	24.4	41.5	0.5
6	60.7	39.3	50.1	20.5	29.4	0.4
7	70.6	29.4	60.0	18.5	21.5	0.4
8	86.0	14.0	80.5	10.4	9.1	0.4

units, respectively. $0 \leqslant \eta < 1$ reflects more block character and $1 < \eta \leqslant 2$ means more alternating tendency of the copolymer than expected from random distribution; $\eta = 1$ means a completely random distribution.

As can be seen from *Table 1*, the η values obtained for the VAL–VP copolymers prepared by hydrolysis of PVP are between 0.4 and 0.7. These results mean that the sequence distribution involves blocks to a greater extent. The η values obtained for the VAL–VP copolymers prepared by esterification of PVAL (*Table 2*) are between 1.0 and 1.2, which reflects the alternating tendency of monomeric units in the copolymers.

Figures 3 and *4* show the mole fractions of dyads as a function of the mole fraction of VP in VAL–VP copolymers prepared by hydrolysis of PVP and by esterification of PVAL, respectively.

The dependence of the glass transition temperature on copolymer composition cannot in many cases be

Table 2 Composition, mole fractions of dyads and parameter η of VAL–VP copolymers prepared by partial esterification of PVAL

	Composition (mol%)		Dyad content (mol%)			
Sample	VAL	VP	VAL–VAL	VAL–VP	VP–VP	η
1	12.0	88.0	0.0	23.3	76.6	1.1
2	18.6	81.4	0.0	38.1	61.8	1.2
3	33.3	66.7	8.9	50.6	40.4	1.1
4	38.6	61.4	13.0	53.1	33.9	1.1
5	43.9	56.1	19.2	54.6	26.2	1.1
6	51.8	48.2	26.0	54.5	19.5	1.1
7	59.6	40.4	33.9	52.0	14.1	1.1
8	65.0	35.0	42.8	49.6	8.4	1.1
9	84.2	15.8	68.9	31.0	0.0	1.1
10	92.9	7.1	86.0	14.0	0.0	1.0

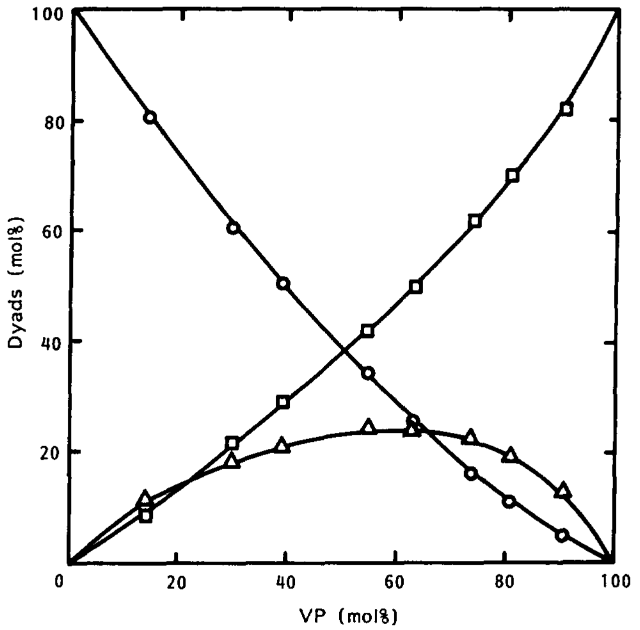

Figure 3 Mole fraction of VAL–VAL (○), VAL–VP (△) and VP–VP (□) dyads *versus* mole fraction of VP in VAL–VP copolymers prepared by partial alkaline hydrolysis of PVP

Table 3 Comparison of experimental and calculated glass transition temperatures T_g of VAL–VP copolymers prepared by partial alkaline hydrolysis of PVP

			T_g (°C), predicted by	
Sample	VP content (mol%)	T_g (°C) (expt.)	Barton[a]	Johnston[b]
1	90.4	20.5	20.2	22.7
2	80.4	22.0	22.9	25.1
3	74.0	23.0	24.9	25.8
4	63.1	26.0	28.6	29.3
5	54.8	30.5	31.7	33.2
6	39.3	32.0	37.3	33.9
7	29.4	35.0	41.8	34.9
8	14.0	52.0	51.4	48.8

[a] Calculated using equation (2), $T_{g,AB} = 37°C$
[b] Calculated using equation (3), $T_{g,AB} = 39°C$

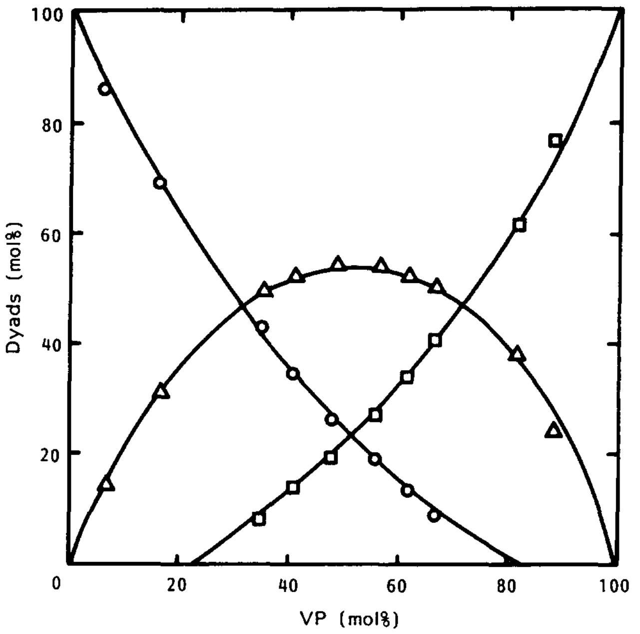

Figure 4 Mole fraction of VAL–VAL (○), VAL–VP (△) and VP–VP (□) dyads *versus* mole fraction of VP in VAL–VP copolymers prepared by partial esterification of PVAL

Table 4 Comparison of experimental and calculated glass transition temperatures T_g of VAL–VP copolymers prepared by partial esterification of PVAL

Sample	VP content (mol%)	T_g (°C) (expt.)	T_g (°C), predicted by Barton[a]	T_g (°C), predicted by Johnston[b]
1	88.0	23.0	20.7	20.5
2	81.4	27.0	23.3	24.0
3	66.7	29.5	28.6	31.3
4	61.4	28.0	30.3	31.6
5	56.1	39.0	33.3	39.0
6	48.2	42.0	36.1	39.1
7	40.4	40.0	39.0	38.5
8	35.0	43.0	42.1	45.8
9	15.8	51.5	51.6	54.2
10	7.1	53.0	57.1	56.9

[a] Calculated using equation (2), $T_{g,AB} = 37°C$
[b] Calculated using equation (3), $T_{g,AB} = 39°C$

predicted by simple additive relations such as the Fox equation[13]. The curvatures observed in the dependence of the T_g of random copolymers on their overall chemical composition have been explained by Barton[14] and Johnston[15]. Both authors suggested equations which describe the effect of the sequential distribution of monomeric units of a linear copolymer on its T_g.

Barton's approach can be considered as an extension of the Di Marzio–Gibbs theory[16] and is expressed as follows:

$$T_{g,c} = n'_{AA} T_{g,AA} + n'_{BB} T_{g,BB} + n'_{AB} T_{g,AB} \quad (2)$$

where $T_{g,c}$ is the glass transition temperature of the copolymer and n'_{ij} ($i,j = $ A or B) is the mole fraction of rotatable bonds corresponding to the dyads ij. $T_{g,AA}$ and $T_{g,BB}$ are the glass transition temperatures of the corresponding homopolymers; $T_{g,AB}$ is the T_g of the alternating copolymer.

Johnston suggested the equation:

$$\frac{1}{T_{g,c}} = \frac{w_A p_{AA}}{T_{g,AA}} + \frac{w_A p_{AB} + w_B p_{BA}}{T_{g,AB}} + \frac{w_B p_{BB}}{T_{g,BB}} \quad (3)$$

which can be considered as a generalization of the Fox equation[13].In equation (3), w_A and w_B are the weight fractions of the two monomeric units which have the probabilities p_{AA}, p_{AB}, p_{BA} and p_{BB} of having various linkages contributing T_gs of $T_{g,AA}$, $T_{g,AB}$ and $T_{g,BB}$ to the copolymer.

In this work we compare the Barton and Johnston correlations given by equations (2) and (3), respectively, with the experimental results obtained for VAL–VP copolymers prepared by hydrolysis of PVP and by esterification of PVAL (*Tables 3* and *4*).

On the basis of Barton's interpretation[14], from a plot of

$$T' = T_{g,c} - n'_{AA} T_{g,AA} - n'_{BB} T_{g,BB}$$

versus $n'_{AB} + n'_{BA}$ (*Figure 5*), considering both types of VAL–VP copolymer, we obtained a value for $T_{g,AB}$ of 310 K. The mole fractions n_{ij} corresponding to each type of dyad were calculated from the copolymer composition and *Figures 3* and *4*.

With the Johnston approach, applying a linear regression program to equation (3), a $T_{g,AB}$ parameter of 312 K was obtained for the two types of VAL–VP copolymer. The values of p_{ij} of the ij dyads were obtained from the copolymer composition and *Figures 3* and *4*.

Figure 6 compares the experimental T_gs of VAL–VP copolymers, prepared by hydrolysis of PVP, with those predicted by equations (2) and (3). The experimental data show a satisfactory correlation with the Barton and Johnston theory. Both correlations give similar results, a behaviour that has also been observed with other copolymers[7–17].

Figure 7 compares the experimental T_gs of VAL–VP copolymers, prepared by esterification of PVAL, with

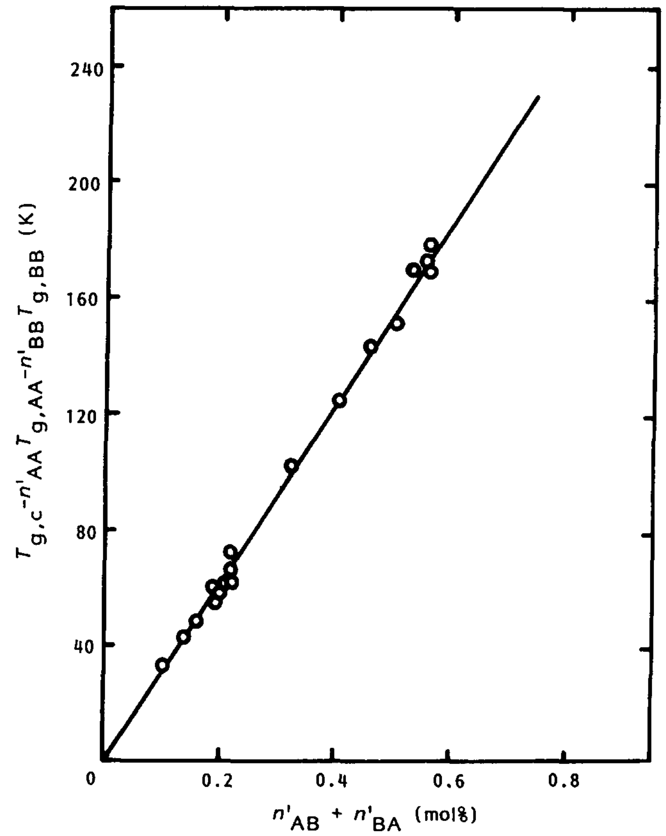

Figure 5 $T_{g,c} - n'_{AA}T_{g,AA} - n'_{BB}T_{g,BB}$ *versus* $n'_{AB} + n'_{BA}$ according to equation (2) for VAL–VP copolymers (hydrolysis and esterification)

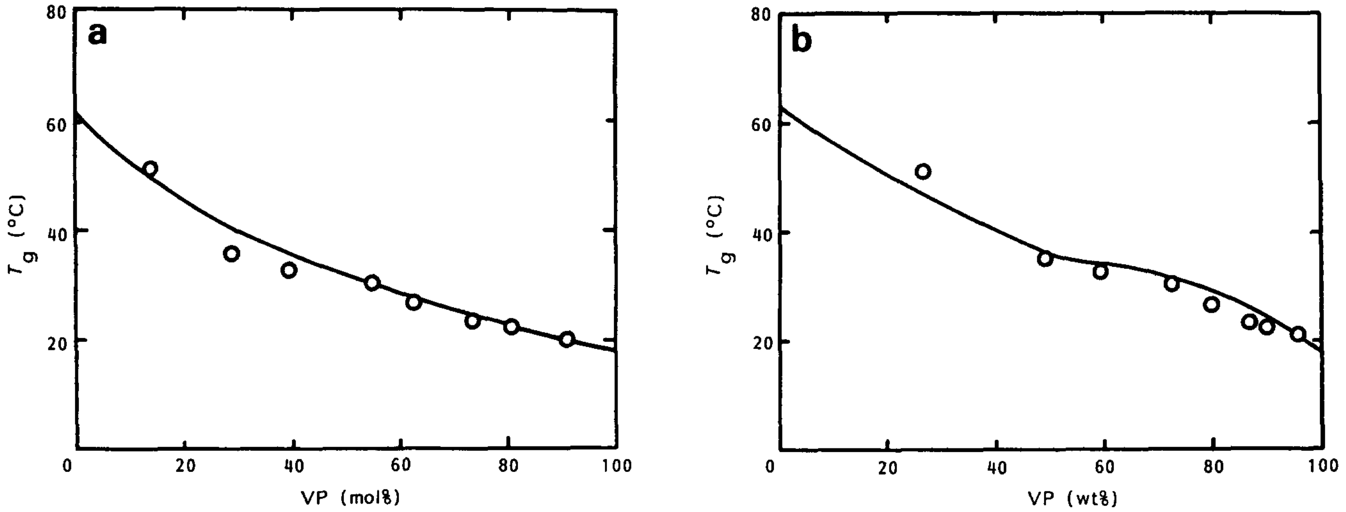

Figure 6 Dependency of glass transition temperature on the VP content of VAL–VP copolymers prepared by partial alkaline hydrolysis of PVP. (a) ——, Barton's approach; ○, experimental data. (b) ——, Johnston's approach, ○, experimental data

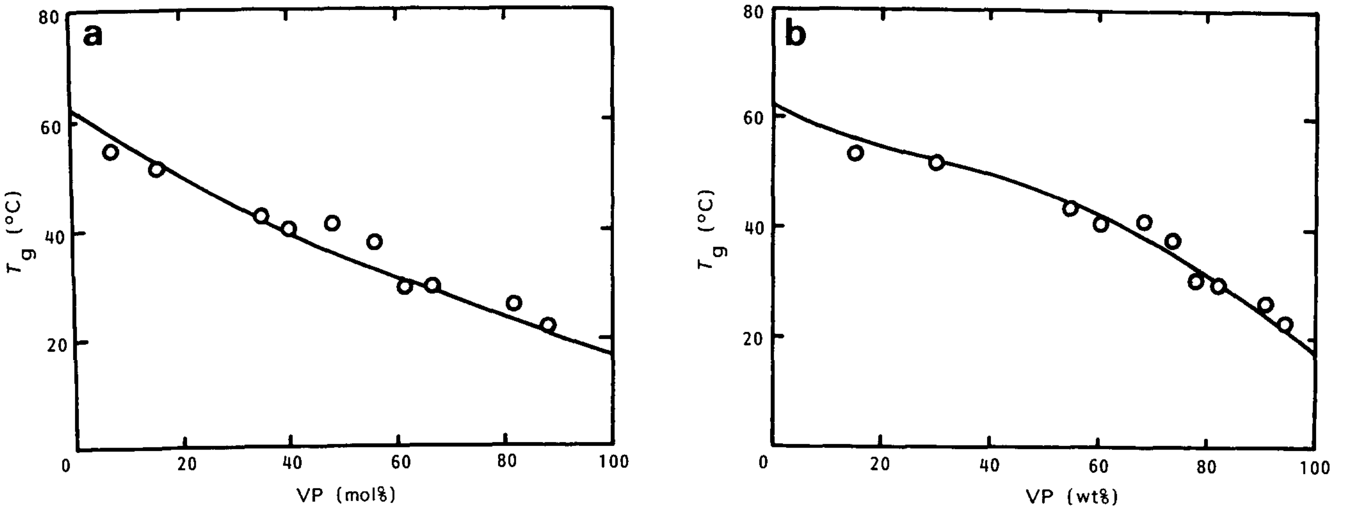

Figure 7 Dependency of glass transition temperature of the VP content of VAL–VP copolymers prepared by partial esterification of PVAL. (a) ——, Barton's approach; ○, experimental data. (b) ——, Johnston's approach; ○, experimental data

those predicted from the Barton and Johnston correlations. The experimental data also show a good correlation with those calculated.

Most of the authors using sequence distribution–T_g approaches have invoked steric and/or polar interactions between adjacent monomeric units to explain the influence of the sequence distribution on the glass transition temperature[14,15]. In the systems under investigation it is assumed that polar effects exert an important influence. Thus, the hydrogen bonding interaction between VAL vicinal units must be very different from the interaction between VAL and VP units.

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