

The glass transition temperature of poly(*N*-vinyl pyrrolidone) by differential scanning calorimetry*

D. T. Turner

Dental Research Center and Department of Operative Dentistry, University of North Carolina, Chapel Hill, NC 27514, USA

and A. Schwartz

Becton Dickinson and Company Research Center, PO Box 12016, Research Triangle Park, NC 27709, USA

(Received 6 February 1984; revised 5 July 1984)

Previously a wide range of values have been reported for the glass transition temperature, T_g , of poly(*N*-vinyl pyrrolidone), PVP, and it was suggested that lower values are due to variable uptakes of water caused by the hygroscopic nature of the polymer. Now it has been found that there are large variations in T_g , even in carefully dried specimens of PVP. Other factors found to influence T_g are residual monomer and the molecular weight of PVP. Polymers prepared by bulk polymerization, either by γ -irradiation or by heating with 2-azobisisobutyronitrile, have much lower values of T_g than dried ones prepared containing 30% water. The difference is mainly due to depression of T_g by residual monomer which, in the absence of water during polymerization, fails to react completely because of conversion to a glassy state. An unexplained observation is that even when all residual monomer has been removed, polymers prepared by bulk polymerization still have a lower T_g than would be expected from their molecular weight.

(Keywords: glass transition temperature; poly(vinyl pyrrolidone); differential scanning calorimetry; influence of water on polymerization)

INTRODUCTION

As many as eight literature references have been cited to show that a wide range of values have been reported for the glass transition temperature, T_g , of poly(*N*-vinyl pyrrolidone)[†], PVP, ranging from 54°C to 175°C¹. Generally, too little information was given about sample preparation or the method of measuring T_g to form an opinion about the reason for such a wide range of values. However, Tan and Challa suggested that the hygroscopic nature of PVP is responsible, following an experimental demonstration that water depresses T_g by a normal diluent effect¹. They pointed out that '*careful drying at the highest temperature possible, preferably under a nitrogen blanket, is necessary in order to obtain correct T_g values*'. This advice was followed in the present work but, nevertheless, a wide range of T_g values was still observed. Therefore, because of the increasing applications of PVP²⁻⁴, the influence of other variables on T_g was investigated. This included the effect of radiation polymerization with presence of water which, for hydrophilic polymers in general^{5,6}, is important in the synthesis of hydrogels for biomedical applications.

Subsequently, after present work on this aspect had been completed, it was learned that a decrease in T_g with

decreasing molecular weight of PVP had been reported by Sanner, Straub and Tschang⁷.

EXPERIMENTAL

Commercial samples of PVP were obtained which differ in nominal molecular weight K90 (360 000), K30 (40 000) and K15 (10 000) from GAF Corporation, New York. These are fine off-white powders which are specified as having maximum values of 5.0% moisture and 1% unsaturation (calculated as residual monomer). Similar preliminary results were obtained on several batches and on a sample, here designated A, with a nominal molecular weight of 10 000 (Polysciences, Warrington, PA). For some experiments, polymers were purified by dialysis against distilled water, using dialysis tubing with a 6000–8000 molecular weight cut off (Spectra/Por, Los Angeles).

Inhibitor was removed from *N*-vinyl pyrrolidone, VP (Aldrich, Milwaukee, Wisconsin), and from tetraethylene glycol dimethacrylate, TEGDM (Polysciences), by shaking with Amberlite IRA45 (Polysciences). For some experiments, VP was fractionally distilled giving a product which melted at 18°C. Only a single component was detected in both distilled and undistilled VP by thin layer chromatography, using variable mixtures of *n*-hexane and ethyl acetate as solvent. Monomer, either alone or mixed with water (30%), was polymerized under nitrogen. The reaction was initiated either by Co-60 γ -irradiation for 20 h at 0.1 Mrad/h or by overnight heating at 60°C with 2-

* Presented, in part, at the 2nd World Congress on Biomaterials, Washington, DC, USA, 27 April 1984.

† Poly[1-(2-oxo-1-pyrrolidinyl)ethylene].

azobisisobutyronitrile, AIBN (1%). The latter samples were heated for a further 1 h at 100°C and had a light yellow coloration. Samples prepared in water were rubbery because of plasticization. They were allowed to dry in air, or over anhydrous calcium sulphate (Drierite, Hammond, Ohio) to yield glassy off-white products.

To effect crosslinking during polymerization, the monomer mixture included TEGDM (2 wt%). The mixture was used immediately after preparation to avoid any spontaneous polymerization such as has been reported for mixtures of VP and methyl methacrylate⁸. To effect crosslinking after polymerization, samples were exposed, in nitrogen at 35°C, to γ -rays from a Cs-137 source (0.8 Mrad/h). No gel fraction was formed up to the maximum dose investigated, of 18 Mrad. However, gelation did occur in the same samples plasticized by addition of water. Gel fractions were determined gravimetrically and the gel swelling ratio, q_w , expressed as the ratio of the weight of the swollen sample to the weight of the residue left after drying.

Samples were dissolved in water and filtered through lens tissue paper for measurements in a Cannon-Fenske capillary viscometer at 25°C. Limiting viscosity numbers, $[\eta]$, were obtained by extrapolation of values of reduced viscosity to zero concentration. Values of viscosity average molecular weight, M_v , were calculated from $[\eta]$, ml/g, using equation (1). A few samples were checked in methanol, at 25°C, using equation (2)⁹.

$$[\eta] = 5.65 \times 10^{-2} M^{0.55} \quad (1)$$

$$[\eta] = 2.3 \times 10^{-2} M^{0.65} \quad (2)$$

Samples (2–4 mg), in powder form or as fine cuttings, were scanned from room temperature to 200°C by differential scanning calorimetry (d.s.c.) using a thermal analyser (DuPont 990, Wilmington, Del.). Samples were promptly quenched to room temperature, with the aid of liquid nitrogen, using a 'quench cooling can' provided with the apparatus. Preliminary experiments conveniently gave similar results in air as in nitrogen. Nevertheless, all the results to be reported here were obtained in dry nitrogen. In some cases larger samples (10 mg) were monitored in order to follow weight changes due either to heating or to storage in a humid atmosphere.

RESULTS AND DISCUSSION

PVP can be dried by prolonged contact with drying agents such as anhydrous copper sulphate or by heating in vacuum, but samples prepared in this way tend to give initial d.s.c. scans which are too noisy to allow unequivocal identification of a glass transition. A better procedure is to dry samples by preliminary runs in the d.s.c. apparatus. Generally, a first run on a sample with a large surface to volume ratio shows a pronounced endotherm with a peak between 110°C and 120°C (Figure 1). Previous related work on various polypeptides revealed similar peaks between 105°C–130°C which were attributed to removal of water^{10–12}. This suggestion, which was substantiated by findings that enthalpies of vaporization are close to the value for water^{11,12}, is adopted to explain the present observations. Consistently, in a second run the endotherm is not evident (Figure 1) but does redevelop if the sample is left to stand in the atmosphere. An

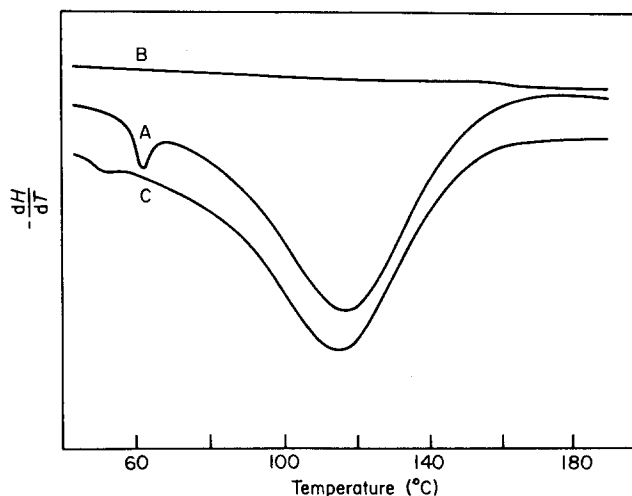


Figure 1 Major and minor endothermic peaks observed in a moist sample. Curve A: 1st run on K30; curve B: 2nd run, after quenching; curve C: 3rd run after reconditioning same sample for several days in its reagent bottle

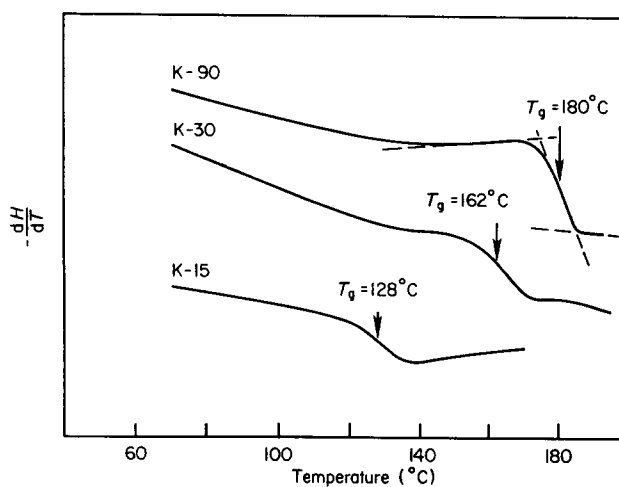


Figure 2 Definition of T_g after 3rd run, at maximum sensitivity

endothermic peak of just the same area is reproduced if, after run 2, the sample is conditioned for several days in the bottle of PVP from which it was obtained originally (Figure 1). From changes in weight, it was found that an endotherm of this magnitude corresponds to a few per cent water.

After run 1, subsequent runs usually revealed a characteristic and reproducible transition from a glass involving an increase in heat capacity. A value of T_g may be taken from the onset of this change, as in ref. 1, but here an alternative convention was adopted in which T_g is defined by the mid-point of the change of the y-coordinate (Figure 2). This latter convention is preferable when experiments are to be extended to include crosslinked networks¹³. In some runs the choice of base lines is somewhat subjective. One uncontrolled factor is the appearance of an endotherm towards the end of the transition. In work on other polymers an effect of this kind has been attributed to frozen-in strains¹⁴. In the present work this effect was minimized by making further runs until, fortuitously, simple scans gave values of T_g which agreed within one or two degrees. In this respect it was found, in experiments on K-90 and K-30, that as many as 15 runs could be made without any significant change in values of T_g . Only prolonged heating at 200°C, under nitrogen, of samples

K15 and A resulted in an increase in T_g . By confining attention to runs 3 to 5 the value of T_g was reproducible within a few degrees.

The glass transition is a rate process, and it is often desirable to extrapolate data obtained in conveniently rapid scans to zero heating rate. In the present experiments advantage was taken of the small rate of thermal changes of PVP to make a limited number of consecutive runs on a single sample beginning and ending at 20°C/min. It was found that values of T_g were rather insensitive to heating rate in the programmed range available which gave traces suitable for analysis (Figure 3). Possibly this insensitivity to heating rate results from the use of fine particles, in view of a previous report that very small samples are not rate dependent¹⁵. Because of this insensitivity, subsequent runs were confined to 20° min⁻¹, which was conveniently rapid and which generally gave best reproducibility when the apparatus was operated at maximum sensitivity.

A minor feature of the first run of a moist sample is a small endothermic peak near 62°C. Following resorption of water a less intense peak was observed at a lower temperature (Figure 1). It was not reproducible in subsequent runs, either after the usual quenching procedure or after slow cooling overnight. A similar endothermic peak was observed in all the commercial samples but not in any sample synthesized in the laboratory. Moreover, it was never observed in commercial samples after dialysis. A trivial explanation of the above observations would be that the commercial samples contain an impurity which is removed by dialysis, but this seems unlikely in view of the long recognized need for careful analysis and control of

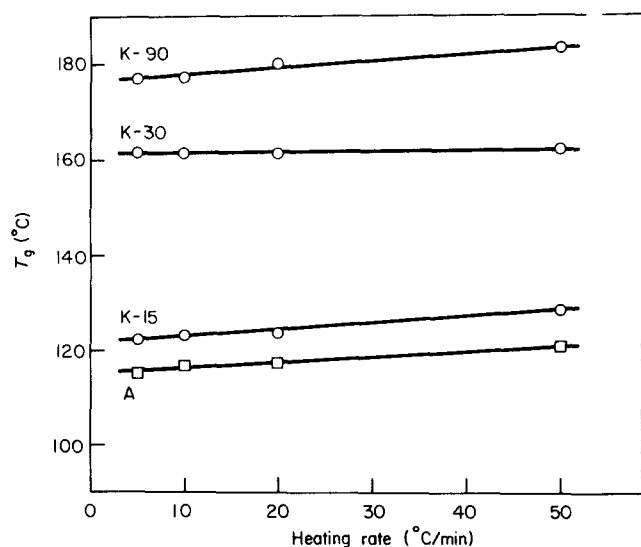


Figure 3 Influence of heating rate on T_g

Table 1 Properties of commercial PVP samples

Samples	M (nom.)	$[\eta]$ g ⁻¹ ml	M (calc.)	T_g (°C)
A	1×10^4	8	8.5×10^3	118–124
K-15	1×10^4	8	8.5×10^3	120–128
K-15 (dial.)	—	10	1.3×10^4	163
K-30	4×10^4	16	2.9×10^4	162
K-30 (dial.)	—	20	4.4×10^4	174
K-90	3.6×10^5	68	3.9×10^5	180
K-90 (dial.)	—	126	1.1×10^6	180

dial. = dialysed samples; M (nom.) = nominal molecular weight; M (calc.) = viscosity average molecular weight.

PVP as a drug product¹⁶. A second possibility that a transition occurs due to side chain relaxation of pyrrolidone groups, analogous to relaxations in poly(methyl methacrylate)^{17,18}, cannot be sustained because the effect is not reproducible in consecutive runs. A third, and more plausible possibility, is that the commercial samples are under internal stress resulting from their method of preparation. Previously sub- T_g endothermic peaks have been reported in a number of glassy polymers, but not in PVP, in which internal stress had been generated either by vitrification under pressure or by deformation below T_g .¹⁹

One variable which may affect the T_g of a polymer is its molecular weight^{20–22}. Equation (1) was used to calculate M from $[\eta]$, following the recommendation of Levy and Frank⁹. The values obtained in this way are somewhat lower than those specified by the manufacturers in the case of the samples of lower molecular weight, i.e. up to K-30 (Table 1). The relationship recommended in the Polymer Handbook²³, also obtained by Levy and Frank⁹, gives values which are still lower (72% of the values obtained using equation (1)). It has been pointed out²⁴, and emphasized²⁵, that there are some unexplained features concerning the use of such equations for aqueous solutions of PVP. For this reason a few additional estimates were made using methanol as solvent. These confirmed the trend of the results reported in Table 1. Particular attention was given to one of the sample of lowest molecular weight and the same value of M obtained in methanol as in water (K15: $M = 8500$).

PVP can be classified as one of those polymers for which T_g increases with molecular weight towards a limiting value (of 180°C) but theoretical predictions cannot yet be made for comparison. However, in line with the Gibbs–DiMarzio theory^{26,27}, PVP has been included in empirical correlations between T_g and the chain stiffness parameter, σ , as calculated from measurements of limiting viscosity number under theta conditions. It was found that all the linear polymers considered could be assigned to four series with various values of the parameters A and a in equation (1).

$$T_g = A(\sigma - a) \quad (1)$$

PVP was included in one of the series, using as coordinates $T_g = 80^\circ\text{C}$ and $\sigma = 2.46$.²⁸ On the basis of the present work, PVP should be reassigned using the correct value of $T_g = 180^\circ\text{C}$. However, this reassignment is complicated because variable values of σ have been reported for PVP ranging from 1.66 to 2.45, depending on choice of solvent²⁹.

The value of T_g decreases with a decrease in viscosity average molecular weight (Table 1). A more detailed functional analysis requires knowledge of number ave-

rage molecular weights^{30,31} but these cannot be derived from present data because of variations in the molecular weight distribution of PVP. In previous work, measurements of T_g have been made on better characterized samples of PVP but it is difficult to make a comparison because results were presented only schematically⁷.

Both vinyl pyrrolidone and PVP are miscible with water, and polymerization in aqueous solution is a common method of synthesis^{2,3}. It was found that polymers prepared by γ -irradiation in water (30 wt%) have a much higher T_g (176°C) than ones prepared from the monomer alone ($T_g = 132^\circ\text{C}$). Any special effects which might be attributed to use of high energy radiation are

ruled out by the observation that a similar difference was obtained when polymerization was initiated by thermal decomposition of AIBN: with water, $T_g = 167^\circ\text{C}$; without water, $T_g = 113^\circ\text{C}$ (Table 2). The polymers prepared using AIBN were both soluble and it was found that the one formed in water had a much higher limiting viscosity number ($273 \text{ g}^{-1} \text{ ml}$) than the one formed from monomer alone ($42 \text{ g}^{-1} \text{ ml}$). Previously evidence that presence of water during polymerization does, indeed, yield polymers of higher molecular weight was reported in studies of the polymerization of vinyl pyrrolidone by AIBN³². In confirmatory work, a case was made that water forms a complex with VP which results in an increase in the rate constant for propagation, k_p .³³ Thus, qualitatively, the

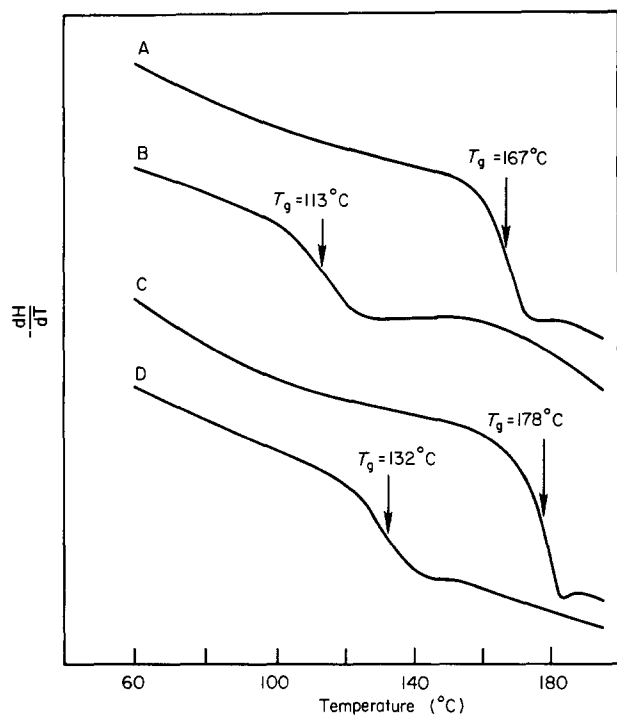


Figure 4 Influence of dialysis on d.s.c. scans. K30 before dialysis: Curve A: 1st run; curve B: 3rd run (maximum sensitivity). K30 after dialysis: curve C: 1st run; curve D: 3rd run (maximum sensitivity)

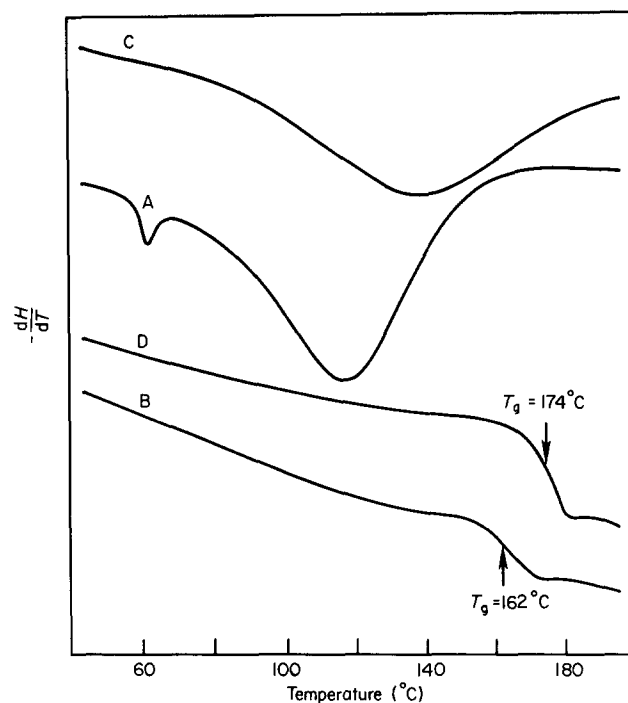


Figure 5 Influence of presence of water during polymerization on T_g . Initiation by AIBN: Curve A: 30% water and dried; curve B: no water. Initiation by γ -rays; curve C: 30% water and dried; curve D: no water

Table 2 Properties of PVP samples synthesized in bulk and in water

Sample	[η] $\text{g}^{-1} \text{ ml}$	M (calc.)	Gel fraction (swelling ratio, q_w)	T_g ($^\circ\text{C}$)	
				Whole sample	gel
Bulk, No TEGDM					
γ -rays	86	6×10^5	0	132	—
AIBN	42	1.7×10^5	0	113	—
AIBN (purified VP)	52	2.4×10^5	0	98	—
AIBN (purified VP, PVP heated only at 60°C)	80	5.2×10^5	0	116	—
Bulk, 2% TEGDM					
γ -rays	—	—	0.14 (36)	115	169
AIBN	—	—	0	145	—
30% H_2O, No TEGDM					
γ -rays	—	—	0.92 (14)	176	183
AIBN	273	4.8×10^0	0	167	—
30% H_2O, 2% TEGDM					
γ -rays	—	—	0.85 (20)	173	180
AIBN	—	—	0.44 (>100)	155	175

lower value observed after bulk polymerization might be attributed to a lower molecular weight. Quantitatively, however, this explanation is quite inadequate because the samples prepared by bulk polymerization have sufficiently high molecular weight to be expected to have values of T_g approaching 180°C (c.f. Tables 1 and 2).

A factor which could account for low values of T_g is residual monomer. VP was detected in bulk polymerized samples by thin layer chromatography. Under conditions in which PVP was stationary; using an elution mixture of n-hexane (60%) and ethyl acetate, $R_f=0.51$ for VP. An attempt to remove residual monomer by γ -irradiation under nitrogen was unsuccessful (Table 3), although this procedure had been used successfully with other glassy polymers having lower values of T_g . In order to find how to remove monomer conveniently, a mixture was made of PVP ($T_g=160^\circ\text{C}$) with 8% VP. It was found that T_g increased from 138°C on heating at 200°C, under nitrogen, and eventually levelled off near 168°C after several hours. Marked increases in T_g to a plateau value, were also observed when bulk polymerized samples of PVP were similarly heated (Table 3). Presumably such samples contain large amounts of residual monomer because the polymerization reaction virtually stops when the glassy state is reached. This type of trapping of monomer is particularly well documented in studies of the free radical polymerization of methyl methacrylate³⁴. Presumably an important role of water in the polymerization of VP is to prevent the formation of a glass and thereby allow the reaction to approach completion. As already mentioned, samples prepared with 30% water are rubber-like at room temperature before drying.

Another factor which affects T_g in some polymers is stereoregularity. This seems unlikely in PVP for two reasons. First, samples of PVP prepared under a variety of free radical reaction conditions show only minor differences in ¹³C n.m.r. spectra³⁵. Second, it has been suggested that variations in stereoregularity in vinyl polymers, with the repeat unit $-\text{CH}_2-\text{CHR}-$ (for PVP, R=pyrrolidone), have negligible influence on the value of T_g .³⁶ Despite these contraindications a test was devised to check any influence of stereoregularity. The test depends on removal of all components of low molecular weight. Such removal is difficult to effect by standard polymer methods because of the solubility of PVP in such a wide range of solvents³⁷. Therefore, the method used was to isolate the PVP molecules of highest molecular weight by radiation crosslinking³⁸ followed by gel partition. It is argued that the influence of crosslinking in such lightly

crosslinked gels would have negligible influence on T_g and that low values would be indicative of structural irregularities such as stereoregularity or head-to-head placement of repeat units. In fact the high values of T_g observed in the gel fractions indicate that effects due to structural irregularity are small (Tables 2 and 3). The lowest value observed ($T_g=169^\circ\text{C}$: Table 2) is for a case in which T_g may be depressed because of inclusion of TEGDM which, previously, had been shown to depress T_g when copolymerized with methyl methacrylate³⁹.

The above experiments still leave unexplained the low values of T_g (153° and 164°) obtained for bulk polymerized samples even after removal of residual monomer (Table 3). The molecular weight of these samples is too high for this factor to be invoked (Table 2). An apparently similar problem has been encountered in studies of polyvinyl chloride (PVC). In this case, uncomplicated by problems of hygroscopicity and residual monomer, the problem is to explain why PVC polymers prepared by free radical polymerization at higher reaction temperatures have lower values of T_g .⁴⁰ Molecular weight was shown not to be the controlling factor⁴⁰ and variations in stereoregularity were considered to be unimportant in light of the structural rule mentioned above (for PVC, R=Cl). It was suggested that variations in the degree of branching may be responsible³⁶. At present this suggestion cannot be evaluated in the case of PVP because branching has not been investigated experimentally (see ref. 41).

CONCLUSIONS

- 1 Commercial samples of poly(*N*-vinyl pyrrolidone) can be dried in the course of d.s.c. runs to give reproducible values of T_g .
- 2 With increase in molecular weight, T_g increases to a limiting value of 180°C.
- 3 Polymers prepared by bulk polymerization of monomer alone, either by γ -irradiation or by heating with AIBN, have much lower values of T_g than ones prepared with presence of 30% water.
- 4 Lower values are due mainly to residual monomer which fails to polymerize in the glassy state, i.e. in absence of water as plasticizer.
- 5 Even after complete removal of residual monomer from samples prepared by bulk polymerization, the value of T_g still remains lower than would be expected from values of molecular weight calculated from limiting viscosity numbers.

Table 3 Properties of bulk polymerized samples (AIBK) after various treatments

Monomer	Treatment of polymer	T_g (°C) (whole sample)	Gel fraction	q_w	T_g (°C) (gel)
Distilled VP	Heated only at 60° C	116	0	—	—
Distilled VP	18 Mrad	112	0	—	—
Distilled VP	3½ h at 200° C	153	0	—	—
VP + H ₂ O (34%)	2 Mrad	—	0.45	—	172
VP + H ₂ O (47%)	13 Mrad	118	0.56	25	182
VP	Usual 1 h at 100° C	98	0	—	—
VP	Usual, then 18 Mrad	115	0	—	—
VP	Usual, then 3½ h at 200° C	164	—	—	—
VP + H ₂ O (57%)	Usual, then 13 Mrad	118	0.56	25	182

VP — monomer shaken with Amberlite IRA45

6 Gel fractions, prepared by radiation crosslinking, gave high values of T_g and from such observations it is argued that any variations in stereoregularity could not account for low values of T_g in the whole sample, i.e. in gel plus sol fractions.

ACKNOWLEDGEMENT

We thank Ms Jane Graper for synthesis of PVP samples. One of us (D.T.T.) was supported by NIH Grants DE-02668 and RR-05333.

ADDENDUM

Molyneux, P. 'Water-Soluble Synthetic Polymers: Properties and Behavior', CRC Press, Baton, Florida, 1983, Vol. I, p. 179.

After completion of this manuscript, the above book appeared in which Molyneux pointed out the need for further studies to clarify discrepancies in the literature about T_g values for PVP.

REFERENCES

- 1 Tan, Y. T. and Challa, G. *Polymer* 1976, **17**, 739
- 2 'PVP, Polyvinylpyrrolidone, Annotated Bibliography', General Aniline and Film Corporation, New York, 1971
- 3 Sidelkovskaya, F. P. 'The Chemistry of *N*-vinylpyrrolidone and its Polymers' (in Russian), Izdatelstva Nauka, Moscow, 1970
- 4 'Proceedings of the International Symposium on Povidone', (Eds. G. A. Digenis and J. Ansell), University of Kentucky College of Pharmacy, Lexington, Kentucky, 1983
- 5 Tighe, B. J. in 'Macromolecular Chemistry', (Eds. A. D. Jenkins and J. F. Kennedy), RSC Specialist Periodical Report, London, 1980, Vol. I
- 6 Huglin, M. B. and Zakaria, M. B. *J. Appl. Polym. Sci.* 1983, **28**, 2451
- 7 Sanner, A., Straub, F. and Tschang, C. H. 'Chemistry, Structure and Properties of Polyvinylpyrrolidone', ref. 4, p. 20
- 8 Tamura, H., Tanaka, M. and Murata, N. *Bull. Chem. Soc. Japan* 1969, **42**, 3042

- 9 Levy, G. B. and Frank, H. P. *J. Polym. Sci.* 1955, **17**, 247
- 10 Morita, H. *Biopolymers* 1966, **4**, 215
- 11 Bulgin, J. J. and Vinson, L. J. *Biochim. Biophys. Acta* 1967, **136**, 55
- 12 Puett, D. *Biopolymers* 1967, **5**, 327
- 13 ten Brinke, G., Karasz, F. G. and Ellis, T. S. *Macromolecules* 1983, **16**, 244
- 14 Wunderlich, B. *J. Therm. Anal.* 1973, **5**, 113
- 15 Miller, G. W. *J. Appl. Polym. Sci.* 1971, **15**, 2335
- 16 Levy, G. B., Caldas, I. and Fergus, D. *Anal. Chem.* 1952, **24**, 799
- 17 Deutsch, K., Hoff, E. A. W. and Reddish, W. J. *Polym. Sci.* 1954, **13**, 565
- 18 Sinnott, K. M. *J. Polym. Sci.* 1959, **35**, 273
- 19 Prest, W. M. and Roberts, F. J. 'Structure and Mobility in Molecular and Atomic Glasses', (Eds. J. M. O'Reilly and M. Goldstein), Ann. N.Y. Acad. Sci. 1981, **371**, 67
- 20 Ke, B. J. *J. Appl. Polym. Sci.* 1962, **6**, 624
- 21 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303
- 22 Turner, D. T. *Polymer* 1978, **19**, 789
- 23 Kurata, M., Tsunashima, T., Iwama, M. and Kamada, K. in 'Polymer Handbook' 2nd Edn. (Eds. J. Brandrup and E. H. Immergut), Wiley and Sons, New York, 1975, IV-20
- 24 Graham, W. D. *J. Pharm. Pharmacol.* 1957, **9**, 230
- 25 Molyneux, P. in *Water*, Vol. 4 (Ed. F. Franks), Plenum Press, New York, 1975, pp. 657-658
- 26 Gibbs, J. H. and DiMarzio, E. A. *J. Chem. Phys.* 1958, **28**, 373
- 27 DiMarzio, E. A. and Gibbs, J. H. *J. Chem. Phys.* 1958, **28**, 807
- 28 Privalko, V. P. and Lipatov, Yu. S. *J. Macromol. Sci.-Phys.* 1974, **B(9)3**, 551
- 29 Meza, R. and Gargallo, L. *Eur. Polym. J.* 1977, **13**, 235
- 30 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
- 31 Fox, T. G. and Flory, P. J. *J. Polym. Sci.* 1954, **14**, 315
- 32 Breitenbach, J. W. and Schmidt, A. *Monatsh. Chem.* 1952, **83(5)**, 1288
- 33 Senogles, E. and Thomas, R. A. *J. Polym. Sci. Polym. Lett. Edn.* 1978, **16**, 555
- 34 Horie, K., Mita, I. and Kambe, H. *J. Polym. Sci. A-1* 1968, **6**, 2663
- 35 Cheny, H. N., Smith, T. E. and Vitus, D. M. *J. Polym. Sci. Polym. Lett. Edn.* 1981, **19**, 29
- 36 Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1968, **1**, 537
- 37 Bond, J. and Lee, P. I. *J. Polym. Sci. A-1* 1971, **9**, 1775
- 38 Charlesby, A. and Alexander, P. *J. Chim. Phys.* 1955, **52**, 699
- 39 Loshaek, S. J. *Polym. Sci.* 1955, **15**, 391
- 40 Reding, F. P., Faucher, J. A. and Whitman, R. D. *J. Polym. Sci.* 1962, **57**, 483
- 41 Molyneux, P. 'The Physical Chemistry and Pharmaceutical Applications of Polyvinylpyrrolidone', ref. 4, p. 1