

The influence of polymerization conditions on the tacticity of poly(*N*-vinyl-2-pyrrolidone)

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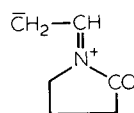
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The tacticities of polyvinylpyrrolidones prepared under various free radical polymerization conditions have been examined by ^{13}C n.m.r. at both 25 and 75 MHz. The spectra reveal, contrary to previous reports, that the polymerization solvent influences polymer structure to a small extent. Polymers prepared in water are slightly more syndiotactic than those prepared in organic solvents or in bulk. This difference is attributed to the influence of hydrogen bonding.

Keywords Polymerization; polyvinyl pyrrolidone; ^{13}C -nuclear magnetic resonance; tacticity; hydrogen bonding

INTRODUCTION

It is known that the free radical polymerization of monomers with ionizable groups, such as acrylic and methacrylic acid, is markedly influenced by the nature of the solvent^{1,2}, pH and ionic strength³. These variables affect monomer association^{1,2} and the degree of charge separation shown by the ionizable groups of the monomer and polymer radicals³, which in turn modify the propagation rate constant. As a result, polymerization rates and molecular weights depend on these parameters, which have also been shown to influence polymer tacticity^{3,4}. It has been established with other systems⁵⁻¹² that the propagation rate constant can be subject to a medium effect, even though the monomer and polymer radicals involved carry no ionizable groups. This has been attributed to a number of factors, such as monomer-radical and solvent-radical complexing⁵⁻⁷, hydrogen bonding⁸⁻¹¹ and other solvent effects¹². With *N*-vinyl-2-pyrrolidone (VP), for example, downfield shifts of the vinyl methylene hydrogen and carbon n.m.r. absorption peaks, observed in the presence of water¹³, can be attributed to the influence of hydrogen bonding on the resonance structure:



and correlated with the assignment of a less negative Alfrey-Price electrostatic e value to the monomer¹⁴. Thus k_p is greater in aqueous solution, which accounts for the increase in polymerization rate and polymer molecular weight, as well as the modified copolymerization behaviour, observed in this medium¹⁰. It seems reasonable to expect that the influence of water on the propagation constant for VP is paralleled by an effect on the tacticity of the poly(*N*-vinyl-2-pyrrolidone) (PVP)

formed. The work described in this paper was commenced to test this supposition.

Recently, two papers have been published concerned with the tacticity of PVP. In one of these¹⁵, triad and tetrad stereochemical sequences have been assigned, respectively, to three methine and five methylene chain carbon peaks observed in the ^{13}C -n.m.r. spectrum of PVP. The relative heights of the methine peaks and areas of the methylene peaks were found to approximate to a Bernoullian statistical model with $P_M=0.45$. Variation of the polymerization temperature of VP from -78° to 85°C in toluene is reported to have little effect on the tacticity of the PVP isolated, and polymer prepared in water at 100°C gave a similar ^{13}C -n.m.r. spectrum to that prepared in toluene. In the second publication¹⁶, the ^{13}C -n.m.r. spectrum of PVP prepared by radical polymerization was investigated, no other details of polymer preparation were disclosed. Triad stereochemical assignments were given to three carbonyl peaks whose areas conformed to Bernoullian statistics with $P_M=0.27$. On this basis, five methylene chain carbon peaks in the spectrum were assigned but these assignments differ from those proposed in the first publication¹⁵. Four methine carbon peaks were observed but no stereochemical assignments were made to these.

EXPERIMENTAL

The purification treatment of commercial VP has previously been described¹⁰.

Polymerizations were conducted with bulk monomer and 20% VP solutions in water, ethyl acetate, dimethyl sulphoxide, benzene and methanol, using 2-azobisisobutyronitrile ($0.2-2 \times 10^{-2} \text{ mol dm}^{-3}$) as the initiator. Reactions were induced either photochemically at 17°C or thermally at 70°C . Polymer precipitated as it formed from VP-ethyl acetate reaction-mixtures. After removal of reaction vessels from the thermostat, PVP was

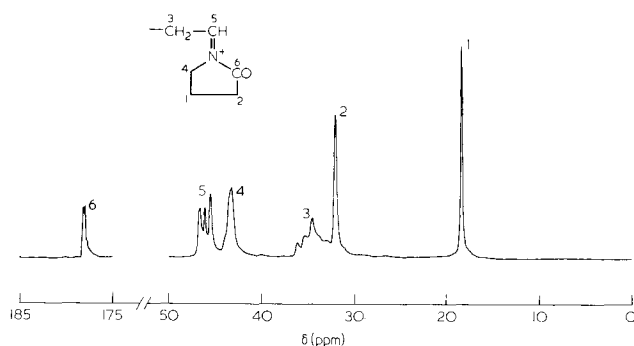


Figure 1 Complete 25 MHz ^{13}C n.m.r. spectrum for polyvinylpyrrolidone prepared in ethyl acetate at 17°C

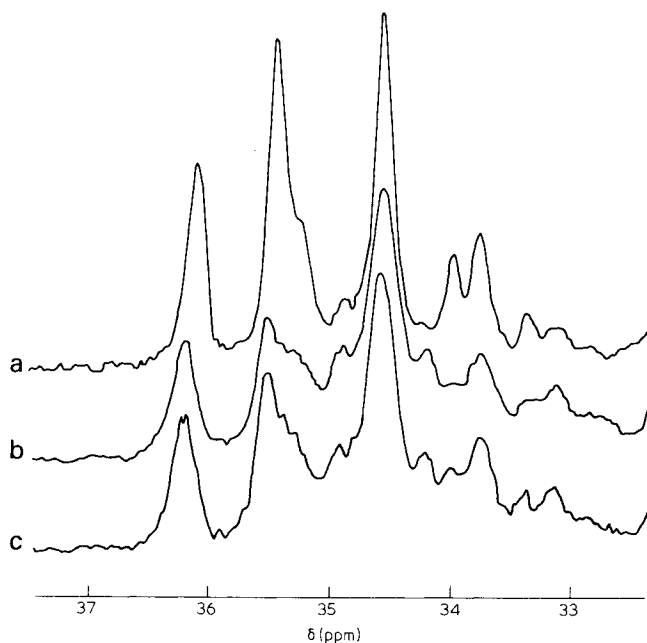


Figure 2 β -Methylene carbon signals recorded at 75 MHz for (a) PVP prepared in H_2O at 17°C , (b) PVP prepared in ethyl acetate at 17°C and (c) PVP prepared in ethyl acetate at 70°C

separated from residual monomer etc. by aqueous dialysis, or alternatively by repeated precipitation with acetone containing $\sim 1\%$ water. The polymer was finally isolated by freeze-drying from aqueous solution.

^{13}C -n.m.r. spectra of 10% w/v PVP solutions in D_2O at 90° were recorded on a Jeol FX100 spectrometer operating at 25.1 MHz. A 90° pulse was used with a 0.5 s repetition time and 5000 Hz sweep width. Broad-band irradiation was employed to remove the ^{13}C - ^1H couplings and the spectra were recorded using 4K data points, followed by zero filling to 8K. The spectra of six samples were also recorded under similar conditions using a Varian HR300 spectrometer operating at 75 MHz.

The resolution of the carbonyl peaks was found to be enhanced in D_2O at lower probe temperatures. Thus some carbonyl spectra were separately recorded at ambient temperature with the FX100, using a 90° pulse, 4.2 s repetition time and 500 Hz spectral width. All chemical shifts were recorded relative to internal TMS using dioxane as a secondary reference.

RESULTS AND DISCUSSION

Figure 1 shows the complete ^{13}C n.m.r. spectrum of PVP prepared in ethyl acetate at 17°C . Peak assignments given

are based on the results of single frequency off-resonance proton decoupling experiments and expected chemical shift relationships and are in agreement with those reported in previous publications^{15,16}. The relaxation times of carbon atoms 1-5, with the experimental conditions pertaining to Figure 1, were measured as 0.11, 0.08, 0.07, 0.07 and 0.11 s, respectively. Using appropriate 180° - τ - 90° pulse sequences, nulling of the resonances of carbon atoms 5 and 4 were achieved in turn. This procedure showed no evidence of any overlap of these resonances.

It is evident from Figure 1 that both the chain methylene and methine carbon resonances show resolvable stereochemical splittings. These splittings are particularly pronounced in the spectra recorded at 75 MHz, expansions of which are given in spectra (b) of Figures 2 and 3. These show five groups of methylene carbon peaks centered at 36.2, 35.5, 34.6, 33.8 and 33.1 ppm and three major methine carbon peaks at 46.7, 46.1 and 45.6 ppm, respectively. These peak positions are in good agreement with those found by Cheng *et al.*¹⁵ and Dubroveen and Panov¹⁶, whose assignments are given in Table 1. Figures 2 and 3 show expansions of the β - CH_2 , $-\text{CH}$, and CH_2N peaks also for PVPs prepared in ethyl acetate at 70°C (c) and in water at 17°C (a). Differences between the spectra of samples prepared under the different conditions are apparent, especially when the influence of the polymerization solvent is examined. This is contrary to the observations reported for PVP prepared in toluene and water¹⁵. From Figure 2 it is seen that the peaks at 36.2 and 35.5 ppm increase in intensity relative to the peak at 34.6 ppm when ethyl acetate is replaced by water as the polymerization solvent. In Figure 3 the shoulder and peak at 46.8 and 46.7 ppm, respectively, observed with PVP samples prepared in ethyl acetate, are reduced in intensity for polymer prepared in aqueous solution and two additional peaks, at 46.5(5) and 46.4 ppm, are apparent. The relative heights of the peaks at 46.1 and 45.6 ppm are also different and a minor peak is

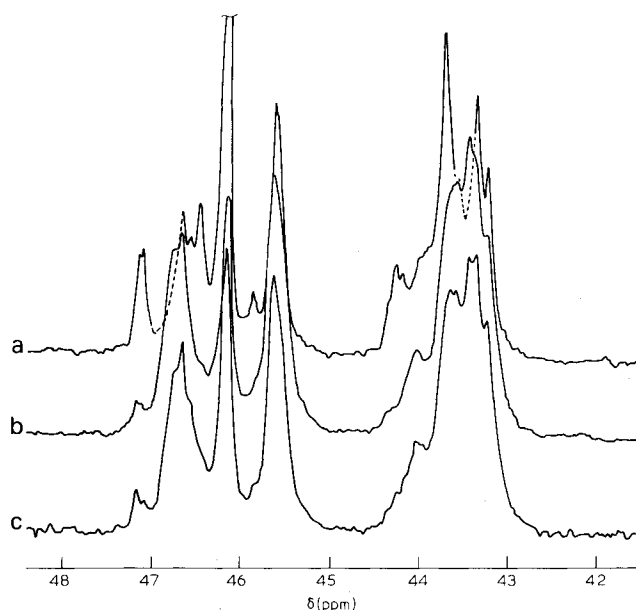


Figure 3 Methine and CH_2N carbon signals recorded at 75 MHz for (a) PVP prepared in H_2O at 17°C , (b) PVP prepared in ethyl acetate at 17°C and (c) PVP prepared in ethyl acetate at 70°C

observed at 47.1 ppm. This latter absorption is recognizable in the spectra of PVP prepared in ethyl acetate but is of lower intensity. Both sets of previous workers noted the presence of a small absorption ~ 0.2 ppm downfield from the principal peak at low field. Cheng, Smith and Vitus attributed this to an impurity; Dubroveen and Panov imply that it is part of a pentad/triad pattern.

Figure 3 also shows that the detailed shape of the $-\text{CH}_2-\text{N}$ absorption peak is influenced by the polymerization solvent. Parallel changes were also found in the carbonyl carbon resonances, as measured at room temperature, which involve four peaks (Figure 4). Dubroveen¹⁶ reported three carbonyl peaks at 178.5, 178.3 and 178.0 ppm which were assigned to the triads rr, mr and mm, respectively.

¹³C n.m.r. spectra of PVP samples prepared in DMSO solution at 70°C were virtually identical to those shown as (c) in Figures 2–4. Thus the polarity of the polymerization medium has no direct effect on the tacticity of the PVP formed. Minor differences only were noted in the spectra of PVP samples prepared in bulk and benzene solution compared with those of polymer prepared in ethyl acetate

at the same temperature. The spectra of PVP prepared in methanol, however, showed features intermediate between those arising from polymer prepared in ethyl acetate and water. This is evidence that hydrogen-bonding in the polymerization process, involving VP and possible PVP radicals, influences polymer microstructure. In general, the appearance of spectra was unaffected by the extent of polymerization conversion.

From Figures 2 and 3 and Table 2 it is seen that the change in PVP microstructure, when water is substituted for ethyl acetate as the polymerization solvent, parallels that observed when the polymer is prepared in ethyl acetate at a higher temperature, although in this latter case the change is much less pronounced. With some polymerizing systems it is known that increasing the temperature increases the preference for the formation, in the polymer chain, of meso diads^{17,18}. However this trend cannot be assumed to occur generally. Terrell¹⁹, for example, has recently shown that increasing the polymerization temperature of vinyl carbazole increases the preference for the formation of racemic diads. He accounts for this observation by suggesting that the activation enthalpy difference for meso and racemic diad formation is determined mainly by a difference in stabilization energy due to electronic interaction in the transition state, rather than a difference in repulsion

Table 1 Assignments and relative intensities of polyvinylpyrrolidone β -methylene and methine carbon signals as reported by (a) Cheng et al.¹⁵ and (b) Dubroveen et al.¹⁶

Chemical shift	Assignment		Relative intensity	
	(a)	(b)	(a)	(b)
Methylene carbon (C3)				
36.2	rrr	mnr	16	10
35.5	rrm	mrr	29	30
34.6	mnr + mrm	rrr	33	38
33.8	rmr	rrr	14	15
33.2	mmm	mrm	9	6
Methine carbon (C5)				
47.1	—	—	—	4
46.7	mm	—	24	22
46.1	mr	—	43	36
45.5	rr	—	33	38

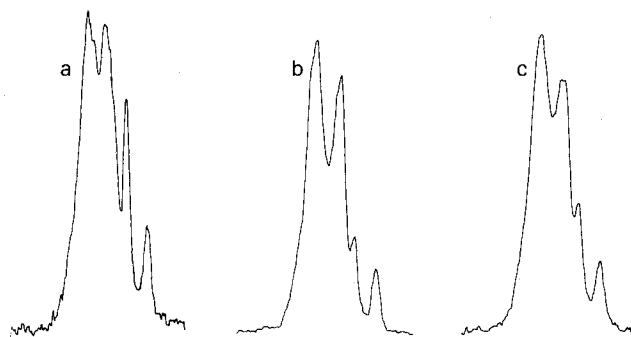


Figure 4 Carbonyl carbon signals recorded in DMSO at 20 MHz for (a) PVP prepared in H₂O at 17°C, (b) PVP prepared in ethyl acetate at 17°C and (c) PVP prepared in ethyl acetate at 70°C

Table 2 Relative intensities of β -methylene and methine carbon signals obtained in this work at 75 MHz for (a) polymerization of 20% VP in ethyl acetate at 17°C, (b) polymerization of 20% VP in ethyl acetate at 70°C, (c) polymerization of 20% VP in H₂O at 17°C, (d) polymerization of 20% VP in H₂O at 70°C, (e) VP polymerized in bulk at 17°C and (f) VP polymerized in bulk at 70°C

Methylene carbon (C3) PVP sample	36.6–35.8 ppm		35.8–35.0 ppm		35.0–34.1 ppm		34.1–33.5 ppm		33.5–32.5 ppm		
	20% VP/EA/17°C (a)	10	20	44	12	14	20% VP/EA/70°C (b)	11	22	41	14
20% VP/H ₂ O/17°C (c)	15	30	31	16	8	20% VP/H ₂ O/70°C (d)	15	29	32	15	10
VP/17°C (e)	11	20	41	14	14	VP/70°C (f)	12	24	40	14	10
VP/70°C (f)	12	24	40	14	10						
Methine carbon (C5) PVP sample	47.4–47.0 ppm		47.0–46.5 ppm		46.5–46 ppm		46–45 ppm				
	20% VP/EA/17°C (a)	2	31	27	40	20% VP/EA/70°C (b)	4	28	32	37	
20% /H ₂ O/17°C (c)	9	17	44	30	20% /H ₂ O/70°C (d)	8	20	39	33		
VP/17°C (e)	2	28	30	40	VP/70°C (f)	5	23	36	36		

energy due to steric hindrance. Terrell correlates the sign and magnitude of this activation enthalpy difference with the Alfrey-Price e value of the monomer. It is suggested that $-ve$ values of $(\Delta H^*_{S/I} - \Delta H^*_{I/S})$ (where S/I indicates isotactic diad formation when the previous diad was syndiotactic and I/S , syndiotactic diad formation when the previous diad was isotactic) are expected for monomers with very negative (< -0.8) and very positive (> 1.25) e values. Since e for VP is -1.14^{20} the inference, therefore, is that PVP prepared in water or methanol has a more syndiotactic-like structure than that prepared in ethyl acetate and other non hydrogen bonding solvents. It is interesting that poly(methacrylic acid) produced by free radical polymerization in aqueous solution has recently been shown to have a higher content of syndiotactic triads than the same polymer prepared in toluene⁴. ¹³C n.m.r. spectra of PVP prepared by the polymerization of bulk monomer showed the same trend with polymerization temperature as illustrated in Figures 2 and 3 for PVP prepared in ethyl acetate. In the case of PVP prepared in water, however, a smaller reverse trend occurred, as shown in Table 2. This can be attributed to the reduced effect of hydrogen bonding on aqueous polymerizations conducted at higher temperatures.

Peak area measurements on spectra obtained at 75 MHz were made using the method of cutting out and weighing. In the case of the chain methylene carbon, this was restricted to five ppm ranges, whose relative absorption intensities are shown in Table 2 and are directly comparable with the data of Cheng *et al.*, and Dubroveen and Panov, which is given in Table 1. From Tables 1 and 2 it is apparent that a similar distribution of methylene carbon peak intensities occurs with PVP samples prepared in the presence of water to that found by Cheng, but a different intensity pattern applies to PVP isolated from bulk monomer or ethyl acetate solution polymerizations. Also, with polymer formed in aqueous solution, the intensities of the absorptions at 36.6–35.8, 35.8–35.0 and 34.1–33.5 ppm are greater and those at 35.0–34.1 and 33.5–32.5 ppm are less than for polymer prepared in non-aqueous media. This is consistent with the assignments of Cheng (but not Dubroveen and Panov) and the interpretation that increasing the polymerization temperature in neat monomer or ethyl acetate, as well as polymerizing in water, produces a more syndiotactic polymer. Peak intensities for the methylene carbon were found to approximate to Bernoullian statistics with $P_M=0.44$ (predicts: rrr=17.6, rrm=27.6, mmm and mrm=32.5, rmr=13.8 and mmm=8.5) for polymer prepared in water, and $P_M=0.55$ (predicts: rrr=9.1, rrm=22.3, mmm and mrm=40.8, rmr=11.1 and mmm=16.6) for PVP prepared in bulk monomer or ethyl acetate at 17.0°C. Peak area measurements for the methine carbon were restricted to four ppm ranges. Since the peak at 46.4 ppm, clearly visible in the spectra of PVP prepared in the presence of water, increases with that at 46.1 ppm, it is considered to be a component of this and a mr pentad. If the absorption at 47.4–47.0 δ is discounted, the data in Table 2 give, for the PVP sample prepared in water at 17°C, mm=19, mr=48, and rr=33 which is in reasonable agreement with the relative intensities observed by Cheng (Table 1) and predicted from Bernoullian statistics with $P_M=0.44$ (mm=19.4, mr=49.3 and rr=31.4). With polymer prepared in ethyl acetate or bulk monomer, however, the measured mr and

rr peak intensities are lower and higher, respectively, than predicted with $P_M=0.55$ (mm=30.3, mr=49.5 and rr=20.3). The proportion of the rr peak is in fact greater than that observed for PVP prepared in aqueous solution. The reason for this inconsistency is not obvious, although with the resolution shown in Figure 3 and the absence of reliable assignments for the various peaks observed, comparison of triad intensities is necessarily approximate. Of particular interest is the origin of the peak at 47.1 ppm, attributed by Cheng and co-workers to an impurity. This conclusion appears unlikely since its proportion depends on the polymerization solvent and temperature. It may arise because of a defect structure in the polymer, although this would, perhaps, be expected to lead to anomalous peaks in the methylene carbon absorption regions of the spectrum also. Changes in the relative intensity of this peak with the different polymerization conditions employed parallel those observed with the 46.1 ppm peak. Thus, like the peak at 46.4 ppm, it could also be regarded as a pentad of mr.

Quantitative comparison of the relative intensities of the four carbonyl peaks of Figure 4, as well as the CH₂-N absorption region shown in Figure 3, with polymerization conditions is limited because of the poor resolution obtained. Nevertheless it is observed that the major carbonyl peak at the lowest field is reduced in relative area, whereas that at second highest field is increased, when PVP is produced in the presence of water. Based on comparative studies in the chain methylene absorption region this suggests that the former peak is most likely to be the mm triad and the latter a component of the mr or rr triad. However, as with the methine absorption peaks, analysis of the relative intensities of the carbonyl peaks from P_M values calculated from methylene peak intensities, may not be consistent. Thus the possibility exists that the peak at lowest field arises from the rr triad, as suggested by Dubroveen and Panov.

CONCLUSION

The work described in this paper has shown that the tacticity of PVP prepared by free radical polymerization in aqueous solution is different to that of PVP prepared in organic media, contrary to the observation of Cheng¹⁵. This effect is most likely to be due to the influence of hydrogen bonding on the polymerization propagation process in aqueous solution. The ¹³C n.m.r. spectra of polymer prepared in the presence of water shows chain methylene and methine carbon peak intensity distributions which are consistent with Bernoullian statistics and the tetrad and triad assignments, respectively, proposed by Cheng *et al.*, with $P_M=0.44$. In contrast, peak intensities found with PVP prepared in ethylacetate or bulk monomer are consistent with Bernoullian analysis only in the methylene absorption region, where $P_M=0.55$. The interpretation of the influence of temperature on the relative intensities of these peaks, by comparison with related studies made with poly(vinyl carbazole), supports the assignments given by Cheng.

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