

UNUSUAL INFLUENCES OF TEMPERATURE AND MEDIUM ON THE TACTICITY OF RADICALLY POLYMERISED POLY(*N*-VINYL IMIDAZOLE)

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Abstract—The tacticities of radical poly(*N*-vinyl imidazole)s prepared in several organic solvents, in water and at various values of pH and temperature have been investigated by ^1H and ^{13}C -NMR. It seems most likely that high temperatures favour racemic placements over meso placements but that, at low pH, meso placements are favoured. Thus the changes in polymerisation rate with pH noted by others for this system are accompanied by changes in the stereochemistry of the resulting polymer.

INTRODUCTION

Rates of radical polymerisation of *N*-vinyl imidazole in water have been shown to be affected by pH, being significantly higher at low pH than at high pH with a region of transitional behaviour [1]. It has been suggested that this effect arises from protonation of the monomer and propagating radical at low pH leading to increased reactivity. There is evidence also for a strong monomer–water interaction which contributes to other anomalies; there are no comparable effects when dimethylformamide (DMF) or ethanol (EtOH) are used as solvents. Our main objective was to see whether or not the nature of the solvent, and in particular the pH, could affect also the tacticity of poly(*N*-vinyl imidazole). It has been established already, for example, that poly(methacrylic acid)s and poly(*N*-vinyl 2-pyrrolidone)s prepared with radical initiators in aqueous solutions are slightly more syndiotactic than those prepared in organic solvents [2, 3]. It will also be relevant to consider the published effects of polymerisation conditions, in particular of temperature, on the tacticity of radically polymerised poly(*N*-vinyl carbazole) [4]. To date there have been no reported measurements of the tacticities of poly(*N*-vinyl imidazole)s although there have been brief comments on the possible significance in terms of tacticity of peak splittings within some ^1H -NMR spectra [5].

EXPERIMENTAL

Materials

N-vinyl imidazole (Fluka AG) was dried over molecular sieves type 4A, distilled twice under vacuum, partly pre-polymerised with azobisisobutyronitrile (AIBN) and then redistilled just prior to use, following essentially the procedures of Bamford and Schofield [1]. A sample of *N*-vinyl imidazole selectively deuteriated in the 2-position was prepared also by the methods of Bamford and Schofield and shown to be 90 mol% isotopically enriched by ^1H -NMR [6].

The initiators AIBN and benzoyl peroxide (BPO) were purified by standard procedures; ditertiary-butyl peroxide (DTBP) and 4,4'-azobis(4-cyanopentanoic acid) (ACPA)

were used as received. All organic solvents were dried and then distilled by the usual procedures before use; water was deionised and then distilled.

Polymerisations

Radical polymerisations of *N*-vinyl imidazole (1 mol/l) were carried out at 70° in EtOH, methanol (MeOH), MeOH acidified with HCl, DMF and in water at *ca* pH 7 (no buffer), pH 1.7 (potassium tetroxalate buffer) and pH 8.9 (borax buffer). Mainly AIBN and BPO were used as initiators in the organic solvents and ACPA was used in water. Some polymerisations were carried out also in EtOH at 0, 40, 60, 80, 100 and 130°, using AIBN/365 nm at 0°, BPO at 100°, DTBP at 130° and AIBN at the remaining temperatures.

A few polymers were prepared for end-group studies using AIBN labelled in the methyl groups with ^{13}C (20 mol% isotopic enrichment after dilution with unlabelled AIBN). The preparation of this initiator has been described elsewhere [7]. Some polymers were prepared also from the 2-deutero-*N*-vinyl imidazole.

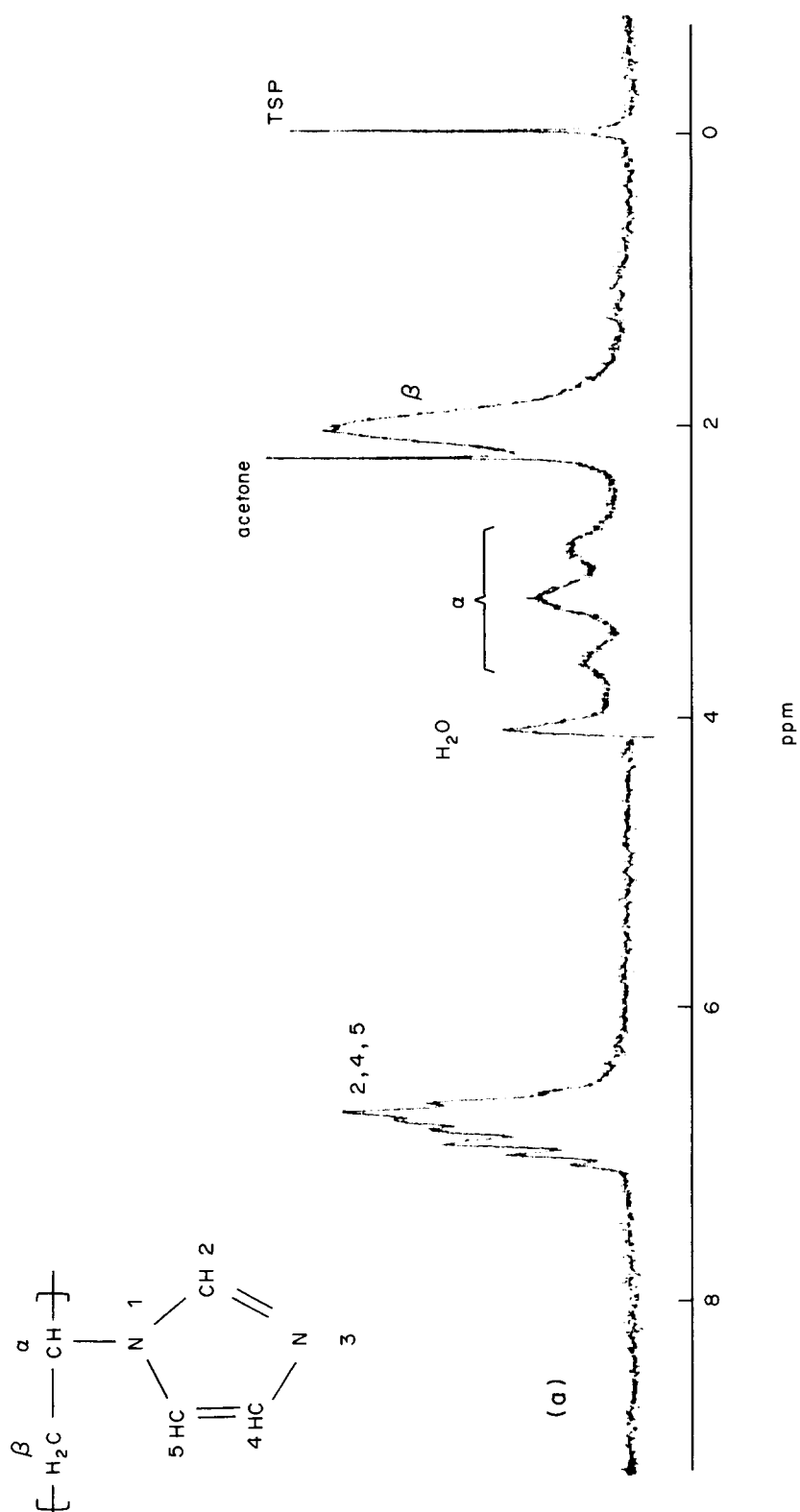
All polymerisations were performed under vacuum with initiator concentrations of around 8 mM and were taken to conversions no higher than 15%. Polymers were recovered by precipitation in acetone and reprecipitated in acetone from solutions in the polymerisation solvent. Prior to characterisation, all polymer samples were dried to constant weight under vacuum (usually for at least 140 hr) at 70°.

NMR spectra

High resolution ^1H -NMR spectra of the polymer samples were recorded at 99.6 MHz on solutions in D_2O (10% w/w) at 90° using a Jeol FX100 Fourier transform NMR spectrometer. Relevant operating parameters were: pulse width, 6 μsec (corresponding to a nuclear tip angle of 42°); spectral width, 1000 Hz (10 ppm); acquisition time, 0.4 sec; additional pulse delay, 2 sec; and number of pulses, 4. The spectra were accumulated with 4 K data points and then zero-filled to 16 K data points before plotting. A line-broadening of 0.2 Hz was applied prior to transformation to improve slightly the signal-to-noise ratio of the resulting spectrum.

High resolution ^{13}C -NMR spectra were recorded at 25.05 MHz also on 10% w/w solutions in D_2O at 90° on the FX100 spectrometer. Relevant operating parameters were: pulse width, 11–15 μsec (66–90°); spectral width, 5000 Hz (200 ppm); acquisition time, 0.4–0.8 sec with 1 sec intervals between pulses; and number of pulses, 10–100 K depending on sample availability. Broad-band proton decoupling was

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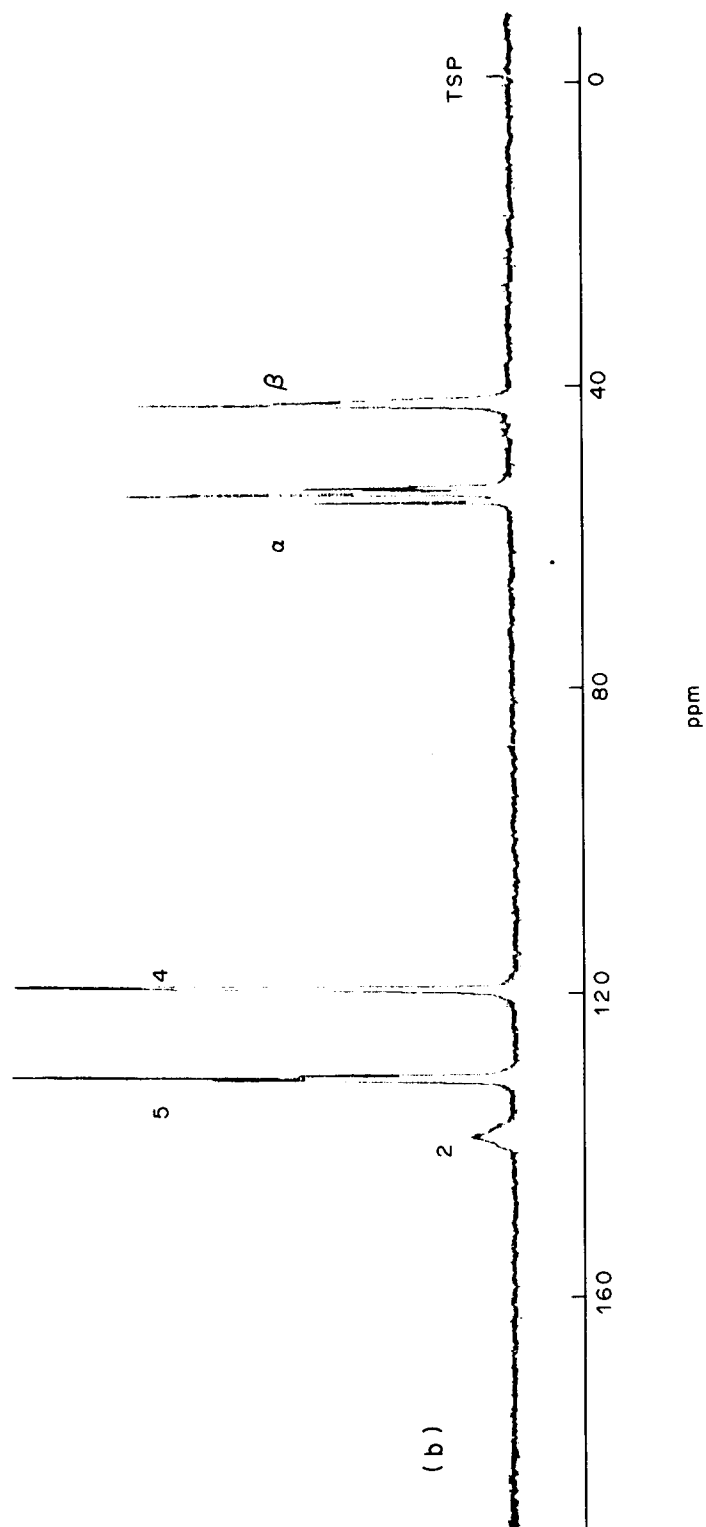


Fig. 1. Complete (a) ^1H and (b) ^{13}C -NMR spectra for poly(*N*-vinyl imidazole) prepared with AIBN in EtOH at 80°C.

Table 1. Assignments of proton and carbon NMR signals for poly(*N*-vinyl imidazole)

| Proton/carbon | Chemical shift (ppm) |
|---------------|----------------------|
| H α | 2.5–3.8 |
| H β | 1.7–2.4 |
| H2 | |
| H4 | 6.5–7.2 |
| H5 | |
| C α | 53.5–56.5 |
| C β | 42.0–44.0 |
| C2 | 137.5–140.5 |
| C4 | 119.5–120.5 |
| C5 | 130.5–132.5 |

applied to remove the ^{13}C – ^1H couplings. The spectra were recorded using initially 4 or 8 K data points and then zero-filled to 16 K or 32 K prior to transformation. Most ^1H and ^{13}C spectra were referenced to the pulse frequency which in turn was referenced to TMS as secondary reference via the known resonance position of dioxane in D_2O ; some later spectra were referenced to internal TSP-d4. Normally a line-broadening of 0.3 Hz was used for smoothing; where signal-to-noise ratio was inadequate, a negative exponential window was applied to produce resolution enhancement equivalent to a line-narrowing of *ca* 0.2 Hz.

Relative areas of NMR signals were assessed usually by the tracing, cutting and weighing method (sometimes following peak deconvolution on a Du Pont 310 curve resolver).

RESULTS

Complete ^1H and ^{13}C -NMR spectra for the sample of poly(*N*-vinyl imidazole) prepared with AIBN in EtOH at 80° are shown in Figs 1(a) and 1(b) respectively. The assignments of the groups of signals are indicated in the figures and are given rather more completely in Table 1. The overall assignments of the ^1H signals have already been reported elsewhere [5].

All the carbon signals and many of the proton signals show splittings related to the tacticity of the sample; of particular interest are the methine proton and methine carbon signals, both of which are split into three main groupings. For the proton signals, these groupings are centred around 2.8, 3.2 and 3.6 ppm respectively and the central grouping has previously been assigned to heterotactic (h) triads with the implication that the two remaining groups are assignable to isotactic (i) and syndiotactic (s) triads, although the decision as to which is which was not then taken [5]. The splittings of the methine carbon signals are even more pronounced with groupings centred around 54, 53 and 52 ppm (A, B and C). The signal at 53 ppm is further split into two components at 53.0 and 52.8 ppm respectively (B1 and B2) whilst that at 52 ppm is split into three at 52.3, 52.1 and 51.9 ppm respectively (C1, C2 and C3). Expansions of the methine carbon signals for several of the poly(*N*-vinyl imidazole) samples are shown in Fig. 2 and small but significant differences in the relative proportions of the peak components can be seen. The significance of these differences is discussed below.

Expansions of the methyl carbon end-group resonances for polymers prepared in DMF at 70° and in MeOH/HCl at 70° using the AIBN labelled in the methyl groups with ^{13}C are shown in Fig. 3. The resonances have major components at 26.8, 26.7, 26.0

and 25.9 ppm. Here too there are small but significant differences between samples.

DISCUSSION

The relatively simple splitting of the methine carbon signals for the poly(*N*-vinyl imidazole) samples into three main groups (A, B and C) suggests that these signals are primarily sensitive to steric triads. However, the assignment of these signals is not unequivocal. It seems safe to assign the central component (B) to heterotactic triads but the assignments of A and C cannot be made with certainty although between them they probably represent the isotactic and syndiotactic triads. The relative proportions of A, B and C for the polymer prepared with AIBN in EtOH at 70° are 22, 48 and 30%, whilst the relative proportions of the components of the similarly split methine proton signals are 20, 51 and 29% in order of increasing field. Thus, even if only the central component is assigned (to heterotactic triads), it is clear that the tacticity of the sample does not differ much from the perfect atactic situation where isotactic, heterotactic and syndiotactic triads are in the proportions 25:50:25. However, our inclination is to go further and to assign the upfield components of both the methine carbon (C) and the methine proton signals to syndiotactic triads and thus the downfield components (A) to isotactic triads. Our reason for making the assignments this way around is that, of the radical polymers for which tacticities have been elucidated by NMR, the vast majority have been shown either to be more syndiotactic than isotactic or to be merely atactic (even those from monosubstituted olefins where steric preferences are expected to be less marked), i.e. the probability of meso placement, P_m , has, in general, been found to be less than, or equal to, 0.5. For example, for polystyrene, $P_m \sim 0.46$ [8], for poly(vinyl chloride), $P_m \sim 0.45$ [9], for polyacrylonitrile, $P_m \sim 0.5$ [10] and for polyacrylamide, $P_m \sim 0.43$ [11]. Among the few exceptions appears to be *N*-vinyl pyrrolidone which, when polymerised with radical initiators in ethyl acetate, gives polymers with P_m close to 0.55; however, in water, this monomer also gives polymers which are more syndiotactic than isotactic ($P_m \sim 0.44$) [3].

For the sample of poly(*N*-vinyl imidazole) prepared with AIBN in EtOH at 70°, the relative areas of peaks A, B and C, with the assignments to triads given above, are close to those expected for Bernoullian statistics with $P_m = 0.46$ (i.e. 21:50:29). Table 2 gives triad fractions determined from the methine proton and methine carbon peak areas for poly(*N*-vinyl imidazole)s prepared at the various temperatures and also for samples prepared in different media; it was expected that raising the temperature would make the polymer more atactic and thus aid the assignment of peaks. At first sight it appears that changing the temperature has little effect on the tacticities of the polymers and that changing the medium similarly has little effect; with the exception of the sample prepared in MeOH/HCl, the i:h:s ratio deviates only slightly from 20:50:30. However there is one unusual feature evident amongst most of the results and that is that the

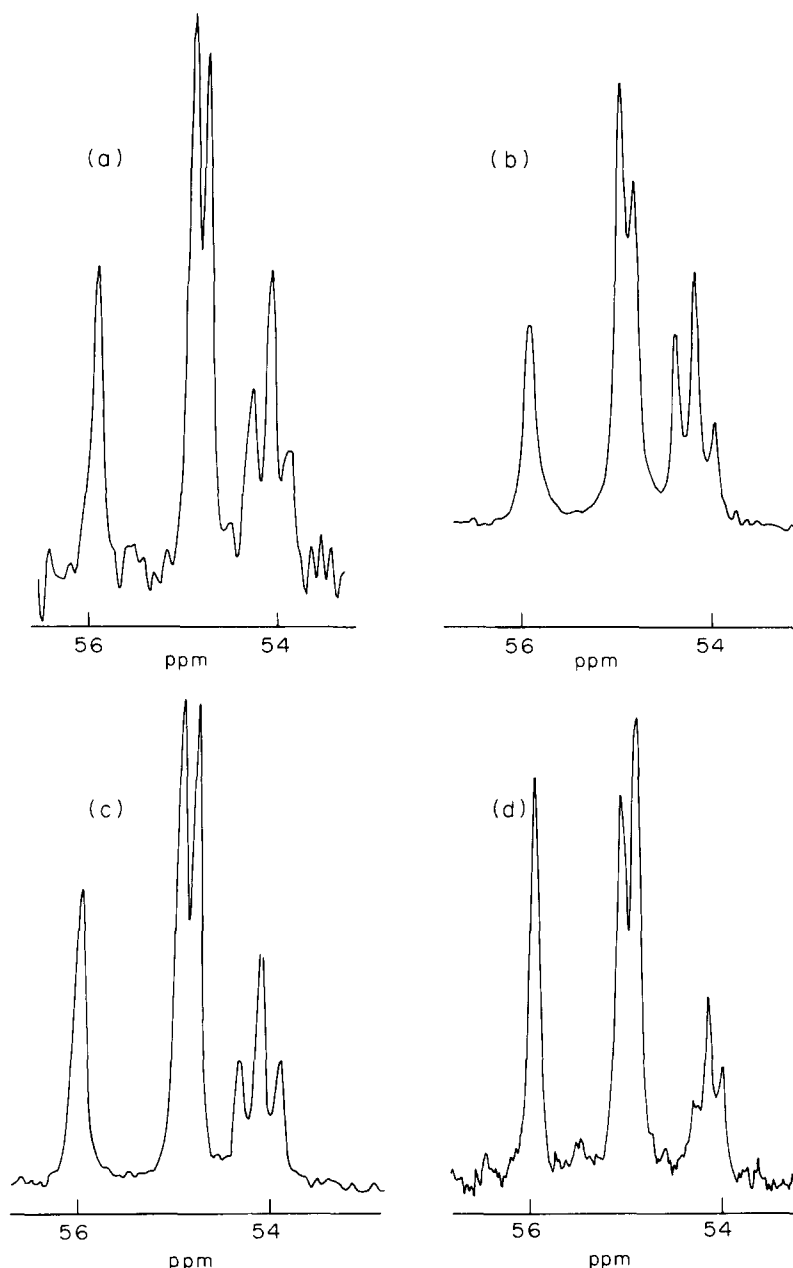


Fig. 2. Expansions of the methine carbon signals for poly(*N*-vinyl imidazole)s prepared in (a) EtOH with AIBN/365 nm at 0°, (b) EtOH with DTBP at 130°, (c) H₂O/pH 7 with ACPA at 70° and (d) MeOH/HCl with AIBN at 70°.

proportion of heterotactic triads is slightly greater than 50%; this can only arise in situations where the statistics governing the generation of tactic sequences is of an order greater than zero, e.g. first, or higher, order Markov rather than Bernoullian. It is possible, however, that this feature is an artifact arising from a systematic error in deconvoluting the peaks and measuring their areas and we do not attach much importance to it.

More revealing than the relative areas of the major methine peak groupings A, B and C are the relative areas of the sub-groupings B1, B2, C1, C2 and C3. If it is accepted that the main groupings reflect steric triad fractions, then it is reasonable to infer that these

sub-groupings reflect steric pentads and the following assignments are suggested: B1 = rrmr + mrmr; B2 = mrrm + rrrm; C1 = rrrr; C2 = rrrm + mrrr and C3 = mrrm where m represents a meso dyad and r represents a racemic dyad. The assignments of mrmr and rrrm can be interchanged (as is always the case if the statistics governing the tacticity are Bernoullian) without affecting any calculated peak areas, and therefore must be regarded as particularly tentative. Table 3 lists pentad fractions obtained from the areas of B1–C3 for the various polymer samples together with values of P_m which provide the best fits for the fractions assuming that Bernoullian statistics apply.

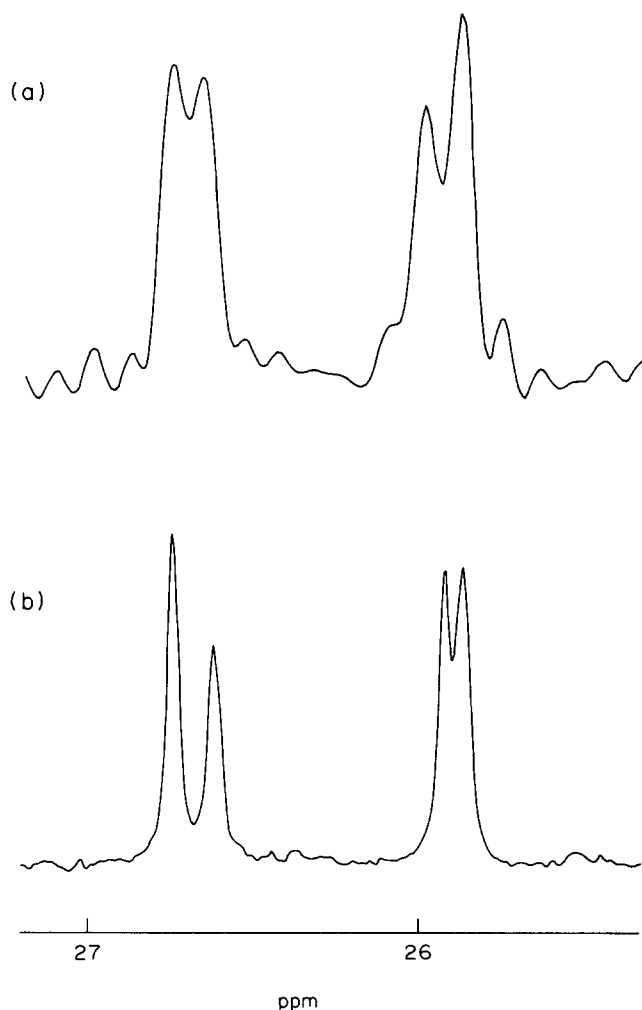


Fig. 3. Expansions of the methyl carbon end-group signals for poly(*N*-vinyl imidazole)s prepared in (a) DMF with ^{13}C -labelled AIBN at 70° and (b) in MeOH/HCl with ^{13}C -labelled AIBN at 70° .

From Table 3 (and from the spectral expansions given in Fig. 2), it is apparent that, on the basis of the pentad assignments and the measured fractions, there are some interesting trends amongst the polymers. In particular, there is a small but discernible trend

towards polymers that have an enhanced syndiotactic bias (relative to isotactic) as the temperature is raised; P_m decreases from around 0.46 at 0° to around 0.41 at 100 and 130° . Such a movement away from a random stereochemistry rather than towards it as the

Table 2. Tactic triad fractions for the poly(*N*-vinyl imidazole) samples from methine proton and carbon peak components A, B and C

| Solvent/initiator | <i>T</i> ($^\circ\text{C}$) | $^1\text{H-NMR}$ | | | $^{13}\text{C-NMR}$ | | |
|------------------------------|----------------------------------|------------------|-------------------|--------------|---------------------|-------------------|--------------|
| | | i(%) (mm) | h(%) (mr + rm) | s(%) (rr) | i(%) (mm) | h(%) (mr + rm) | s(%) (rr) |
| EtOH/AIBN | 0 | 19 | 53 | 28 | 18 | 52 | 30 |
| EtOH/AIBN | 40 | 19 | 54 | 27 | 15 | 52 | 33 |
| EtOH/AIBN | 60 | — | — | — | 18 | 50 | 32 |
| EtOH/AIBN | 70 | 20 | 51 | 29 | 22 | 48 | 30 |
| EtOH/AIBN | 80 | — | — | — | 18 | 51 | 31 |
| EtOH/BPO | 100 | 18 | 52 | 30 | 20 | 50 | 30 |
| EtOH/DTBP | 130 | 22 | 52 | 26 | 17 | 52 | 31 |
| DMF/AIBN | 70 | 21 | 51 | 28 | 19 | 53 | 28 |
| DMF/BPO | 70 | — | — | — | 21 | 51 | 28 |
| EtOH/BPO | 70 | — | — | — | 19 | 49 | 32 |
| H ₂ O/pH 8.9/ACPA | 70 | 20 | 54 | 26 | 19 | 54 | 27 |
| H ₂ O/pH 7/ACPA | 70 | 20 | 56 | 24 | 20 | 54 | 26 |
| H ₂ O/pH 1.7/ACPA | 70 | 21 | 52 | 26 | 22 | 52 | 26 |
| MeOH/AIBN | 70 | 18 | 53 | 28 | 16 | 53 | 31 |
| MeOH/HCl/AIBN | 70 | — | — | — | 28 | 50 | 22 |

All fractions $\pm 2\%$.

Table 3. Tactic pentad fractions* from methine carbon peak components B1, B2, C1, C2 and C3

| Solvent/initiator | T (°C) | B1 rrmr + mrrm | B2 mrrm + rrrm | C1 rrrr | C2 rrrm + mrrr | C3 mrrm | P_m^\dagger |
|------------------------------|--------|-------------------|-------------------|------------|-------------------|------------|---------------|
| EtOH/AIBN | 0 | 51.7 | 48.3 | 30.0 | 49.4 | 20.6 | 0.46 |
| EtOH/AIBN | 40 | 53.3 | 46.7 | 30.4 | 47.7 | 21.9 | 0.46 |
| EtOH/AIBN | 60 | 54.0 | 46.0 | 29.9 | 48.1 | 22.0 | 0.46 |
| EtOH/AIBN | 70 | 51.8 | 48.2 | 31.8 | 46.2 | 22.0 | 0.45 |
| EtOH/AIBN | 80 | 54.7 | 45.3 | 32.1 | 48.0 | 19.9 | 0.44 |
| EtOH/BPO | 100 | 55.9 | 44.1 | 35.3 | 47.6 | 17.1 | 0.41 |
| EtOH/DTBP | 130 | 56.4 | 43.6 | 34.6 | 47.4 | 18.0 | 0.41 |
| DMF/AIBN | 70 | 54.2 | 45.8 | 30.2 | 48.2 | 21.6 | 0.46 |
| DMF/BPO | 70 | 55.5 | 44.5 | 32.6 | 47.4 | 20.0 | 0.45 |
| EtOH/BPO | 70 | 50.3 | 49.7 | 30.5 | 43.8 | 25.7 | 0.48 |
| H ₂ O/pH 8.9/ACPA | 70 | 50.9 | 49.1 | 26.7 | 49.5 | 23.8 | 0.49 |
| H ₂ O/pH 7/ACPA | 70 | 50.1 | 49.9 | 25.4 | 48.7 | 25.9 | 0.50 |
| H ₂ O/pH 1.7/ACPA | 70 | 46.8 | 53.2 | 23.8 | 46.5 | 29.7 | 0.53 |
| MeOH/AIBN | 70 | 52.6 | 47.4 | 28.2 | 47.1 | 24.7 | 0.48 |
| MeOH/HCl/AIBN | 70 | 42.2 | 57.8 | 18.8 | 45.1 | 36.1 | 0.58 |

*Pentad fractions are quoted as percentages of the parent triads and not as percentages of the total pentad population. They are considered reliable to $\pm 0.5\%$.

†Best fit values assuming that Bernoullian statistics apply.

temperature is raised is very unusual regardless of whether our assignments are right (and the movement is towards increased syndiotacticity), or whether they should be reversed (and the movement is towards increased isotacticity). There are, however, two precedents at least for a movement towards increased syndiotacticity as the temperature is raised, namely poly(*N*-vinyl carbazole) [4] and poly(*N*-vinyl pyrrolidone) [3], although in the latter case the movement was in the general direction of increased randomness since the polymer was initially more isotactic than syndiotactic. It may be no coincidence that all three of these polymers are based on *N*-vinyl compounds. Also, Terrell maintains that increased syndiotacticity with increases in polymerisation temperature may be anticipated for monomers with either large positive or large negative e -values where the control of stereoregularity is probably primarily through an electronic interaction between the monomer and the growing radical in the transition state for propagation rather than through any steric effects [4]. The e -value for *N*-vinyl imidazole has most recently been reported to be around -0.7 [12, 13].

Another unusual feature of the stereochemistry is revealed in the results in Table 3 for the polymers prepared in water and/or at low pH compared with those for the other systems. In water, and especially at low pH, the polymer appears to become more isotactic than syndiotactic, in fact for MeOH/HCl medium there is an almost complete reversal of the rrrr:mrrm ratio compared with that in EtOH or even in MeOH without acid. There is also a corresponding reversal in the overall *i*:*s* ratio as can be seen from the results in Table 2. Changes in the tacticity of vinyl polymers brought about by moving from an organic to an aqueous medium have also been encountered before, for example poly(methacrylic acid)s produced in water are more syndiotactic than those produced in toluene [2] and poly(*N*-vinyl pyrrolidone)s prepared in water are more syndiotactic than those produced in bulk or in ethyl acetate [3]. However, a movement towards increased isotacticity in water and at low pH is, as far as we know, without precedent and was not expected.

Intuitively, we expected increased syndiotacticity in water because of the potential for hydrogen-bonding between the monomer and water and also for electro-

static repulsion between protonated, and therefore charged, aromatic rings in acidic media to favour racemic rather than meso addition (this expectation was the reason for undertaking the experiments in water and at low pH).

Some further information about the stereochemistry of poly(*N*-vinyl imidazole) chains appears to be available from the methyl carbon resonances of the ¹³C enriched 2-cyano-2-propyl end-groups in the polymers prepared with the ¹³C-labelled AIBN (Fig. 3). Basically there are two groups of peaks, one at around 27 ppm and the other at around 26 ppm. Overall, these two groups are of identical area and can be assigned to the two methyl carbons of the end-groups made non-equivalent through their proximity to the chiral centre of the terminal monomer unit. In this respect, the pattern of end-group resonances resembles that in poly(methyl methacrylate) prepared with the same initiator [7]. The further splitting of these peaks, especially the downfield one (components at 26.8 and 26.7 ppm), is believed to reflect the existence of both meso and racemic monomer unit dyads at the chain ends. The relative proportions of these two components are 57:43 for the polymer prepared in MeOH/HCl and 51:49 for the polymer prepared in DMF. Since low pH appears to favour meso over racemic placements for the chain as a whole, it seems reasonable to suppose that it will favour meso over racemic placements for the terminal dyads also. Thus, we assign the end-group peak component at 26.8 ppm to terminal meso dyads and that at 26.7 to terminal racemic dyads. The relative areas of these components for the two samples are consistent with a P_m value of 0.57 for the sample prepared in MeOH/HCl and 0.51 for the sample prepared in DMF. These values differ slightly from those for the chains as a whole (0.58 and 0.46) but the differences are probably not significant.

It is conceivable that some of the movement towards the formation of poly(*N*-vinyl imidazole)s of increased isotacticity in acidic media could arise from the concurrent formation of polymer by a cationic mechanism. Poly(*N*-vinyl carbazole)s prepared with cationic initiators have been shown to be more isotactic than those prepared with radical initiators [14, 15]. It is interesting to note that the poly(*N*-vinyl imidazole) prepared in EtOH with BPO as initiator is

marginally more isotactic ($P_m \sim 0.48$) than that prepared with BPO in DMF ($P_m \sim 0.45$) or that prepared with AIBN in EtOH ($P_m \sim 0.45$). There is considerable evidence that BPO can initiate both radical and cationic polymerisations of *N*-vinyl carbazole and *N*-vinyl pyrrolidone [16, 17], but work on the photopolymerisation of *N*-vinyl carbazole in various solvents suggests that a cationic polymerisation of this type of monomer is least likely to occur in a strongly basic solvent such as DMF [18]. We have some kinetic evidence (to be presented elsewhere) that polymerisations of *N*-vinyl imidazole with BPO are anomalous and that BPO may be capable of dual initiation with this monomer also [19].

However, it is unlikely that much, if any, of the movement towards increased isotacticity observed by us for the polymerisations in H₂O and MeOH/HCl can be attributed to cationic polymerisation for the following reasons: (a) no polymer is formed in MeOH/HCl without the addition of AIBN, (b) the polymer formed with ¹³C-AIBN in MeOH/HCl shows evidence of the expected 2-cyano-2-propyl end-groups and (c) it is unlikely that the poly(*N*-vinyl imidazole) cation would be capable of propagating in an aqueous medium.

CONCLUSIONS

We conclude that the tacticity of a radical poly(*N*-vinyl imidazole) depends to a slight extent upon the temperature of polymerisation and upon the nature of the medium. The probability at this stage is that low pH favours meso placements, and therefore the formation of polymers that are more isotactic than syndiotactic, whilst raising the temperature of polymerisation in organic solvents favours racemic placements. However, we acknowledge that the assignments of signals in the relevant ¹³C spectra are not certain and that our conclusions may require modification in the light of future work. Undoubtedly the effect of pH upon tacticity is connected with the marked effect of pH on polymerisation rate reported by Bamford and Schofield [1], and reflects, therefore, significant changes in the nature of propagation as the pH is lowered. There appears to be no connection, however, between tacticity and the occur-

rence of the unusual degradative chain transfer reaction, involving the 2-proton, uncovered by Bamford and Schofield [1, 6]; the tacticity of a polymer prepared from 2-deuterio-*N*-vinyl imidazole in DMF at 70° was identical to that of the polymer prepared under similar conditions from the undeuterated monomer.

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