

Preliminary analysis of the ^1H - and ^{13}C -NMR spectra of poly(3-vinyl-1-methylindole)

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Summary

The title monomer was synthesized and polymerized via free radical initiation. The high field ^1H - and ^{13}C -NMR spectra were recorded and analyzed. Many resonances displayed multiplicities indicating a sensitivity to polymer stereochemistry but, in most cases, the resolution was insufficient for any reasonable interpretations to be made. The resonances that were well enough resolved for relatively accurate measurements to be made were analyzed in terms of polymer stereochemistry. The analysis suggests that poly(3-vinyl-1-methylindole) is an atactic polymer.

Introduction

During the course of our studies on the nmr spectra of polyvinyl heterocycles, we have had the opportunity to investigate the nmr spectra of some fused ring vinyl heterocycles, e.g. vinyl benzofuran and vinyl benzothiophene (1,2). In one case the spectra were more well resolved than the spectra of the non-fused ring parent polyvinyl heterocycle (1) and in the other case the spectra were less well resolved than those of the parent non-fused ring polyvinyl heterocycle, but still yielded data on polymer stereochemistry (2). In order to extend our study of fused ring polyvinyl heterocycles to nitrogen containing materials, we decided to synthesize a vinyl indole. Previous experience (3) has shown that in nitrogen containing polyvinyl heterocycles, when the substituent on the nitrogen is hydrogen, the polymers are unstable in air. However, alkyl substitution on the ring nitrogen yields polymers that have long term stability. Accordingly, we wanted to synthesize vinyl indole with an alkyl group on the ring nitrogen. We found that 1-methylindole-3-carboxaldehyde was commercially available (Aldrich) so we decided to use it as a starting material for our monomer synthesis. This paper is a preliminary account of the data obtained on poly(3-vinyl-1-methylindole) to date.

Experimental

General

All solvents and other chemicals used in this study were used as received unless otherwise noted. The nmr spectra were recorded with a Varian Gemini 300 FT NMR on CDCl_3 solutions of polymer (15% w/v) at ambient temperature. Individual resonance areas were measured by electronic integration and by tracing them on high quality paper, cutting out and weighing the tracings on a five place analytical balance. Molecular weights were measured as previously described (1-3).

Monomer Synthesis

The monomer was synthesized via a Wittig reaction (4). After solvent removal the monomer was isolated as a viscous yellow oil. The oil was purified by column chromatography on silica gel using cyclohexane/ CH_2Cl_2 (4:1) as the eluent (yield = 63%). $^1\text{H-NMR}$, CDCl_3 ; δ 7.26-7.18 (m., 4H); δ 7.08 (s., 1H); δ 6.86-6.80 (m., 1H); δ 5.63 and 5.16 (AB quartet); δ 3.70 (s.s., 3H).

Polymer Synthesis

The polymer was synthesized by charging 4.0g of monomer into a clean, dry screw cap vial followed by 0.7 wt % AIBN (recrystallized from CH_3OH). The monomer-initiator solution was sparged with dry N_2 and the vial was sealed with a teflon lined screw cap. The vial was placed in a thermostated water bath at 70°C for 4 hours. The vial was removed from the bath and 6 ml of cold CH_3OH was added to precipitate the polymer. The polymer was purified by reprecipitating it three times from CHCl_3 solution into CH_3OH . The polymer was dried in vacuo at 30°C for 96 hours. Conv. = 43.4%, $M_n = 3700$, $M_w = 4800$.

Results and Discussion

The $^1\text{H-NMR}$ spectrum of poly(3-vinyl-1-methylindole) (VMI) is shown in Figure 1 along with an expansion of the aromatic proton resonance (Figure 1B). The signal assignments are given in the Figure (5). The aromatic resonance is in two general areas, the area from 7.70-6.32 is due to the four protons of the benzene ring and is split into two peaks, A and B, which have a relative intensity ratio of 1:63. If this pattern were due to heptads for an atactic polymer, this is the ratio expected for a singlet heptad to the remaining heptads. However, because this area is due to four protons, a singlet pentad for an atactic polymer would be expected to be 1/64 of the total area, it is more likely that this is the case i.e. the pattern is due to pentads. While the resolution is insufficient for any detailed assignments to be made a P^m value calculated from the fractional intensity of peak A (0.016 ± 0.004) is $0.50 \pm .1$, the value expected for an atactic polymer.

The resonance assigned to the proton of the pyrrole ring occurs as two peaks (C and D) in a relative intensity ratio of 5:1, C:D.

The sum of this intensity ratio indicates a sensitivity to higher order stereosequences, possibly pentads, but the resolution makes any reasonable interpretation in terms of stereochemistry impossible.

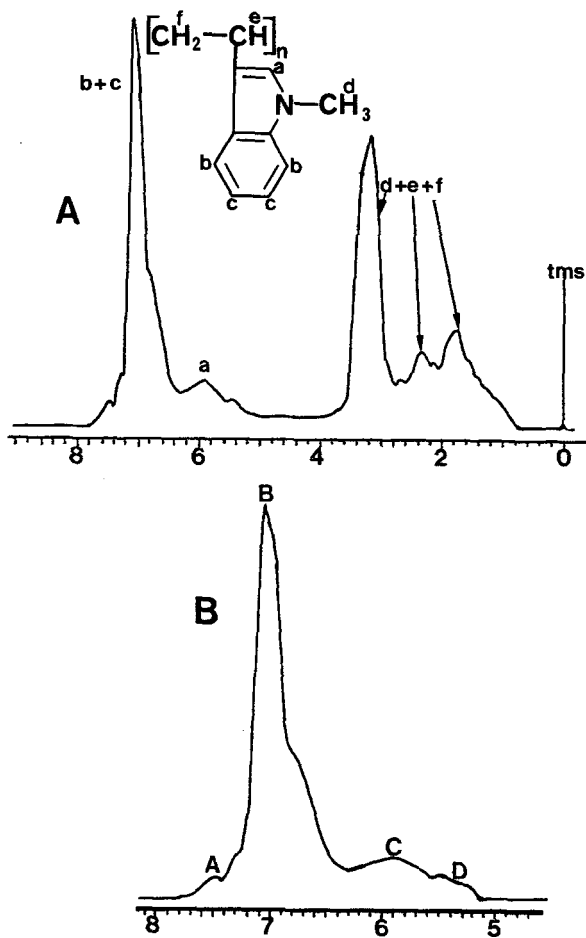


Figure 1

300 MHz $^1\text{H-NMR}$ Spectrum: A) Full Spectrum;
B) Expansion of the Ring Proton Resonance

¹³C-NMR Spectroscopy

The 75.5 MHz ¹³C-NMR spectrum of VMI is given in Figure 2A. The signals are assigned as shown in the Figure (8). The C₂ carbon resonance (Figure 2B) occurs as an eight peak pattern in a relative intensity ratio of 1:1:3:7:4:2:6:8, A:B:C:D:E:F:G:H. The sum of this ratio is 32 which is half the number of heptads expected for an atactic polymer ($\times 2 = 2:2:6:14:8:4:12:16 =$ "true" ratio). While the resolution is insufficient to allow any reasonable assignments to be made, a P value calculated from the fractional intensity of peak A ($0.035 \pm .005$) is $0.51 \pm .07$.

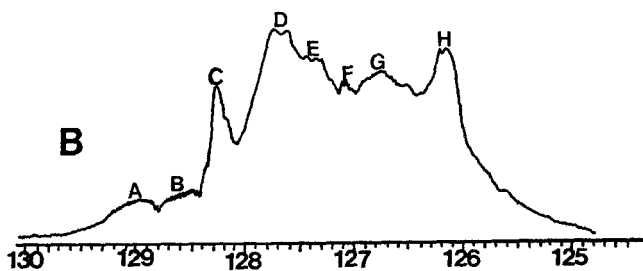
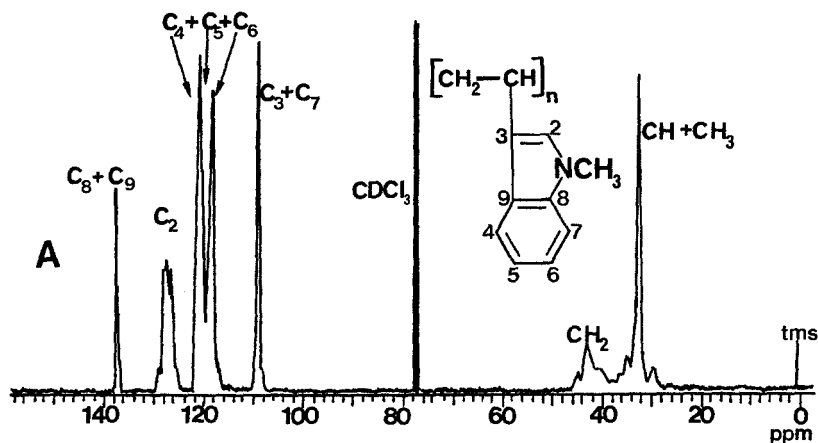


Figure 2

75.5 MHz ¹³C-NMR Spectrum: A) Full Spectrum
B) Expansion of the C₂ Carbon Resonance

The resonance area assigned to the C₄, C₅ and C₆ carbons (Figure 3) also displays a multiplicity which could indicate a sensitivity to polymer stereochemistry. As this resonance area is due to three carbons and the resolution is not good, assignment in terms of stereochemistry is not possible at present. In fact, while the remaining signals all show multiplicity which could be due to stereochemical sensitivity, either the resonances are due to more than one carbon and/or the resolution is insufficient for any assessment/assignment in terms of polymer stereochemistry to be made.

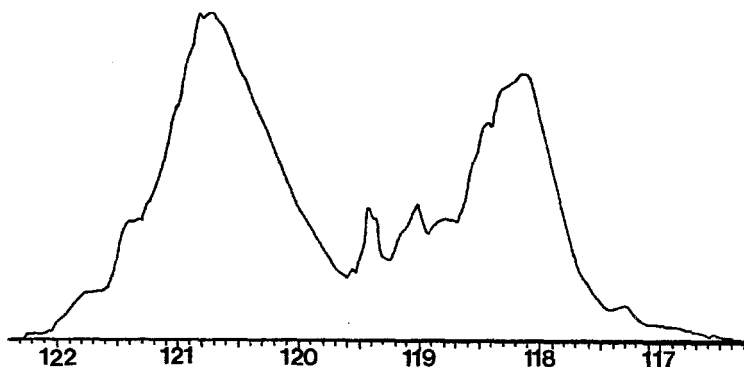


Figure 3

Expansion of the C₄, C₅ and C₆ Resonance Area

Conclusion

A vinyl indole monomer was synthesized and polymerized via free radical initiation. The high field ¹H- and ¹³C-NMR spectra display several resonances that seem to be sensitive to polymer stereochemistry. However, the resolution in most cases prohibits

any kind of reasonable assignment of the resonances in terms of polymer stereochemistry. The resonances that had sufficient resolution for a stereosequence sensitivity to be discerned indicate that VMI is an atactic polymer with a P_m value of $0.50-0.51 \pm .1$.

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