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Preliminary analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(2,5-dimethyl-3-vinylfuran)

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Summary

The title monomer was synthesized by dehydration of the corresponding alcohol. The monomer was polymerized under free radical conditions and ^{1}H- and ^{13}C-NMR spectra were recorded and analyzed. The spectra displayed several resonances with sensitivity to polymer stereochemistry and analysis of these resonances showed poly(2,5-dimethyl-3-furan) to be an atactic polymer.

Introduction

For some time we have been investigating the effect of additional ring substitution on the polymerization behavior, stereochemistry and nmr spectra of various vinyl heterocycles (1-6). Previous work revealed that while 3-vinyl heterocycles with no additional substitution polymerized more sluggishly than the corresponding 2-vinyl heterocycles and had less well resolved spectra; methyl or ethyl substituents in the 2-, 5- or 2- and 5- positions of the heterocyclic ring enhanced the rate of polymerization and the resolution of the spectra of poly(3-vinyl heterocycles) vs 2-vinyl heterocycles with no additional substitution; as an extension of our investigation we synthesized and polymerized 2,5-dimethyl-3-vinylfuran (PDMF). The parent compound, 3-vinylfuran, polymerizes very slowly compared to 2-vinylfuran and has somewhat less well resolved spectra. Therefore, we wanted to investigate whether dimethyl substitution would enhance the rate of polymerization and/or spectral resolution. This paper is a preliminary account of our work.

Experimental

All solvents and other chemicals used in the work were reagent grade and were used without further purification. Spectra were recorded of $CDCl_3$ solutions of polymer (10% w/v) at ambient temperature with a Varian Gemini 300 FT NMR (^{1}H frequency = 300 MHz). Individual resonance areas were determined by electronic integration and by tracing the signals on high quality paper, cutting out and weighing the tracings on a 5-place analytical balance. Each area listed is the average of five measurements. Molecular weights were measured as previously described (1-4).

Monomer Synthesis

The monomer was synthesized by dehydration of the alcohol formed by $NaBH_4$ reduction of 3-acetyl-2,5-dimethylfuran (Aldrich). The alcohol was dehydrated by the method of Brooks (9) and the monomer was purified by distillation from CaH_2 (b.p. = 49-50°C at 35 mm). ^{1}H-NMR $CDCl_3$; δ 6.09 (d., 1H); δ 5.55 (m., 1H); δ 5.35-5.21 (AB quartet, 2H); δ 2.25 (s.s., 3H); δ 2.21 (s.s., 3H).

Polymer Synthesis

The polymer was synthesized by weighing 3.0g of monomer into a clean, dry screw cap vial followed by 0.8 wt % AIBN. This monomer-initiator solution was sparged with dry N_2 while cold and the vial was sealed with a teflon lined screw cap and placed in a thermostated water bath at 70°C. The vial was removed from the bath after 6 hours and 8.0 ml of cold CH_3OH was added to the vial 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 90 hr, then weighed to determine conversion. % Conversion = 33.8, M_n = 12,200, M_w = 21,000.

Results and Discussion

The ^{1}H-NMR spectrum along with an expansion of the ring proton resonance is given in Figure 1. The signals are assigned as shown in the Figure (10). The ring proton resonance (Figure 1B) occurs as a six peak pattern in a 1:1:9:17:3:1, A:B:C:D:E:F. The sum of this ratio is 32, which is the number of hexads expected for an atactic polymer or half the number of heptads expected for an atactic polymer. In previous cases (11) it has been established that if ring protons and/or carbons display stereochemical sensitivity, that sensitivity is to odd number n-ads (triads, pentads, etc.), therefore, it is most likely that this pattern is due to a heptad sensitivity. That being the case it is logical to multiply each relative intensity by two to obtain 2:2:18:34:6:2 as the "true" relative intensity ratio reflective of a heptad sensitivity. However, the resolution is not sufficient for any detailed assignments to be made; but a P_m value can be calculated from the fractional intensity of peak A (0.032 ± .005) as 0.50 ± .08, the value expected for an atactic polymer.

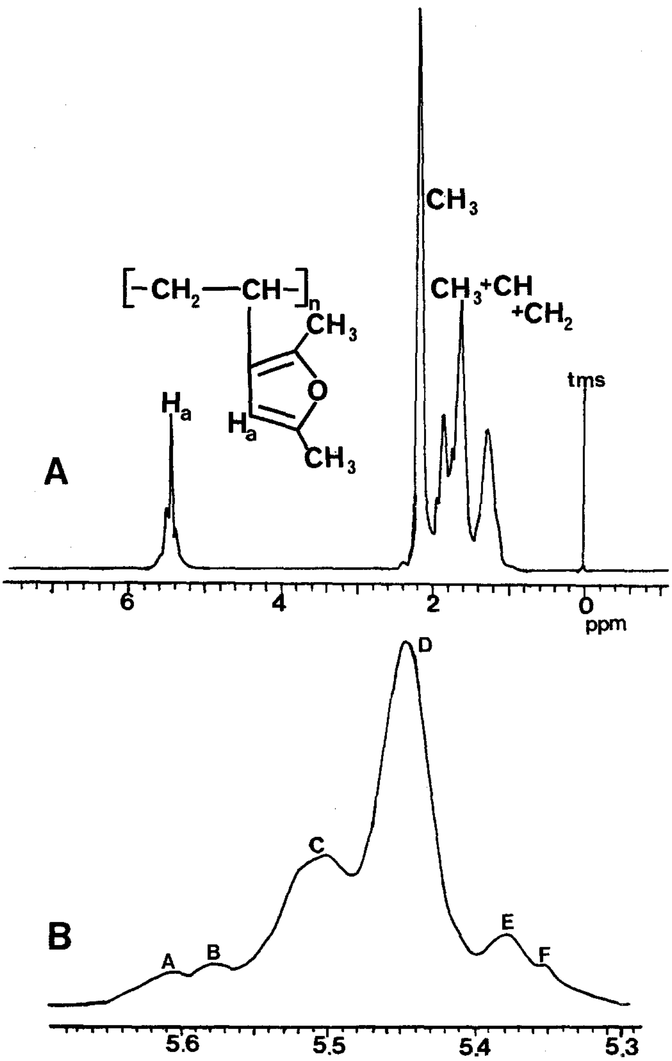

Figure 1

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

The ^{13}C-NMR spectrum and expansions of various resonances are shown in Figures 2 and 3. The resonance are assigned as shown in the Figure (12,13). The resonance assigned to the C_5 carbon (Figure

2B) occurs as an eight peak pattern with a relative intensity ratio of 1:1:1:2:4:4:7:12, A:B:C:D:E:F:G:H. The sum of this ratio is 32, which is half that expected for heptads in an atactic polymer. As in the case of the ring proton resonance it is logical to multiply these relative intensity ratios by two to obtain the "true" ratio; 2:2:2:4:8:8:14:24.

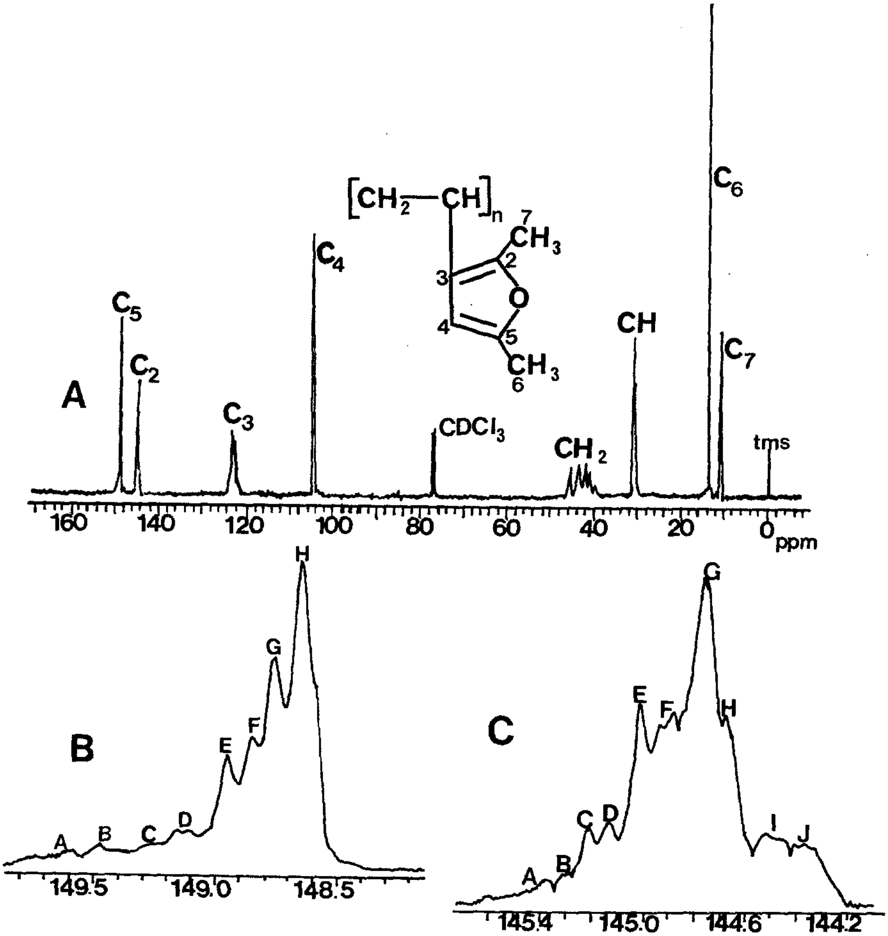

Figure 2

75.5 MHz ^{13}C-NMR Spectrum; A) Full Spectrum; B) Expansion of the C_5 Carbon Resonance; C) Expansion of the C_2 Carbon Resonance

Again, resolution is not sufficient for a detailed assignment in terms of heptads to be made but a P_m value calculated from the fractional intensity of peak A (0.031 ± .004) is 0.50 ± .07.

The C_2 carbon resonance (Figure 2C) occurs as a ten peak pattern in a relative intensity ratio of 2:1:3:3:8:8:21:8:5:5, A:B:C:D:E:F:G:-H:I:J. The sum of this ratio is 64, exactly the number of heptads expected for an atactic polymer. As before, lack of resolution precludes any detailed assignments being made, but a P_m value equal to 0.50 ± .1 can be calculated from the fractional intensity of peak B (0.016 ± .003).

The C_3 carbon resonance (Figure 3A) occurs as an eight peak pattern in a relative intensity ratio of 6:3:5:1:5:3:5:3, A:B:C:D:E:-F:G:H. The sum of this ratio is 31, which indicates that this pattern is sensitive to higher order stereosequences, possibly heptads, but because the sum is 31, not 32, the pattern may reflect a mixture of pentad and heptad sensitivities. At the current resolution no meaningful data can be extracted. Further resolution of this resonance awaits experiments at higher magnetic field strengths or possibly higher temperatures.

The methylene carbon resonance (Figure 3B) occurs as a ten peak pattern with a relative intensity ratio of 3:1:2:8:3:2:3:5:3:2, A:B:C:D:E:F:G:H:I:J. The sum of this ratio is 32, which is the number of hexads expected for an atactic polymer [typically, methylene carbon and proton resonances are assigned to even n-ads (11)]. While lack of resolution prohibits detailed assignment of such a large number of stereochemical entities, a P_m value calculated from the fractional intensity of peak B (0.032 ± .005) is 0.50 ± .08.

The methine carbon resonance (Figure 3C) occurs as a five peak pattern in a relative intensity ratio of 1:1:18:11:1, A:B:C:D:E. The sum of this ratio is 32 which, as above, indicates a sensitivity to heptad stereosequences; multiplying by two yields 2:2:36:22:2 as the "true" ratio. Once again the resolution is not sufficient for assignment of such a large number of stereosequences but a P_m value calculated from the fractional intensity of peak B (0.032 ± .006) is 0.50 ± .09.

The C_7 carbon resonance, (C_2 methyl carbon resonance, Figure 3D) occurs as a six peak pattern in a relative intensity ratio of 4:12:6:7:2:1, A:B:C:D:E:F. The sum of this ratio is 32, which means that this resonance can be assigned in terms of heptads (x 2 = 8:24:12:14:4:2 as the "true" ratio). As in previous cases the resolution is insufficient for detailed assignments to be made, but a P_m value based on the fractional intensity of peak F (0.033 ± .006) is 0.50 ± .09.

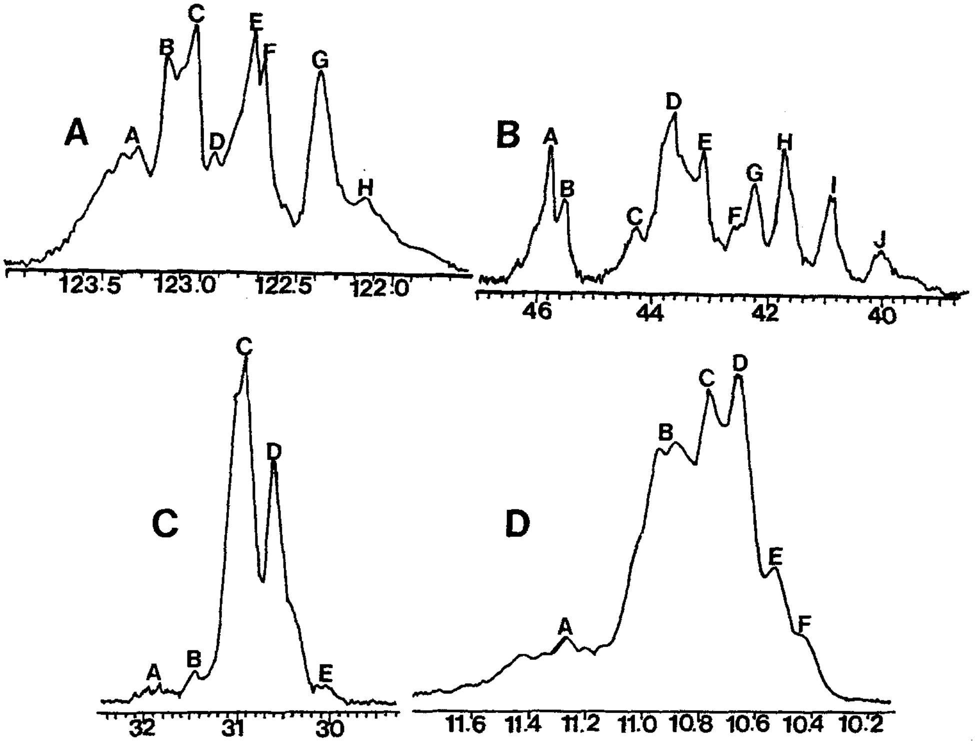

Figure 3

Expansions of: A) The C_3 Carbon Resonance; B) Methylene Carbon Resonance; C) Methine Carbon Resonance; D) C_7 Carbon Resonance

Rate of Polymerization

As concerns the rate of polymerization of 2,5-dimethyl-3-vinylfuran; a crude experiment was performed in which equal mole amounts of 3-vinylfuran, 2-vinylfuran and 2,5-dimethyl-3-vinylfuran were allowed to polymerize for the same amount of time (6 hr) at the same polymerization temperature (70°C) with the same amount of AIBN (0.7 wt %). The polymerizations were terminated and the yields of polymer compared. The 3-vinylfuran gave 6.0% conversion, the 2-vinylfuran gave 21% conversion, while the 2,5-dimethyl-3-vinylfuran gave 34% conversion. This experiment indicates that the dimethyl groups do influence the ease of polymerization of a vinylfuran monomer.

Conclusion

The rate (ease) of polymerization and resolution of the polymer nmr spectra were influenced by dimethyl substitution on the furan ring of a 3-vinyl furan. The dimethyl substitution yielded a monomer which gave higher yields of polymer in the same reaction time than the unsubstituted parent monomer. The polymer spectra were also somewhat better resolved than the spectra of the polymer from the unsubstituted parent monomer (5). While relatively improved the resolution of the spectra of PDMF was still insufficient for detailed assignments to be made. However, relatively long stereosequences could be observed and resolution was sufficient for the calculation of P_m values. The P_m values obtained all showed PDMF to be an atactic polymer ($P_m = 0.50 \pm .1$) and as these P_m values were obtained from relatively long stereosequences more confidence can be placed in them as an accurate measure of polymer tacticity (11).

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