

A preliminary analysis of the high field ^{13}C -NMR and ^1H -NMR spectra of poly(2-thienyl vinyl ketone)

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Summary

Poly(2-thienyl vinyl ketone) was synthesized via free radical initiation and its 300 MHz ^1H -NMR and 75.5 MHz ^{13}C -NMR spectra were recorded and analyzed. The analysis showed that poly(2-thienyl vinyl ketone) is an atactic polymer.

Introduction

We have maintained an active research program in the area of vinyl heterocycle polymerization and copolymerization for some time (1-6). We have noted that the ring heteroatom and type of ring substitution can have a significant effect on the polymer's NMR spectra. In this connection, the NMR spectra of polymers derived from vinyl ketones bearing heterocyclic substituents are of interest. 2-Furyl vinyl ketone has been polymerized previously (7) and we have recently reported on the copolymerization behavior of 2-thienyl vinyl ketone (2TVK) (8). Since little information is available concerning 2-thienyl vinyl ketone polymers we thought it would be interesting and useful to analyze the ^1H -NMR and ^{13}C -NMR spectra of a poly(2-thienyl vinyl ketone) synthesized free radically.

Experimental

All chemicals used were reagent grade and were used without further purification. ^1H -NMR spectra were obtained at 300 MHz on a Varian Gemini 300 operating in the FT mode. The ^{13}C -NMR spectrum was obtained at 75.5 MHz with a Varian Gemini 300. Both the ^1H -NMR and ^{13}C -NMR spectra were obtained at ambient temperature using CDCl_3 as the solvent with TMS added as an internal standard. Individual resonance areas were measured by tracing peaks on high quality paper, cutting out and then weighing the tracings on a five place analytical balance. Each peak area given is the average of four such cuttings and weighings. Molecular weights were measured with a Waters High Resolution 6000A chromatograph equipped with 10^6 , 10^5 , 10^4 , 10^3 , 10^2 and 500A columns. Tetrahydrofuran was used as eluent and numerical values were obtained by comparison to a polystyrene calibration curve.

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Monomer Synthesis

The monomer was synthesized as previously described (7,8) and were purified by distillation, bp = 74-76°C/6 mm of Hg.

Polymer Synthesis

The polymer was synthesized by charging a clean, dry screw cap vial with 4.0g (2.9×10^{-2} mol) of 2-thienyl vinyl ketone followed by 0.03g (0.75 wt %) of AIBN. The monomer-initiator solution was sparged with dry nitrogen and the vial was tightly capped with a polyethylene-lined cap. The vial was placed in a water bath at 65°C for 5h. The vial was removed from the bath, cooled to ambient temperature and 10 ml of cold methanol was added to precipitate the polymer. The polymer was purified by dissolving it in CHCl_3 and reprecipitating in a 7-8 fold excess of CH_3OH . The polymer was reprecipitated twice. % Conv. = 17.9; M_n = 11,000; M_w = 22,500; PD = 2.04.

Results and Discussion

Figure 1 shows the 75.5 MHz ^{13}C -NMR spectrum of poly(2-thienyl vinyl ketone). The peaks are assigned as shown in the Figure (9). Figure 2 shows horizontal expansions of all the carbon resonances. It seems that all the carbons are sensitive in some fashion to polymer stereochemistry.

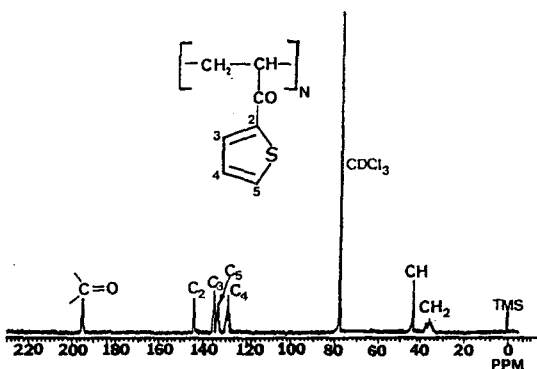


Figure 1

75.5 MHz ^{13}C -NMR Spectrum of Poly(2-Thienyl Vinyl Ketone)

The resonance patterns observed for the carbonyl, aromatic and methine carbons should, in principle, be interpretable in terms of triad, pentad or perhaps heptad stereosequence distributions but it is not possible to do this for the carbonyl, C_2 or C_3 carbon resonance (Figures 2A, 2B and 2C). Although several signals are evident in some of these resonance patterns, their approximate relative inten-

sities do not provide any clues concerning how the patterns might be interpreted. Perhaps spectra recorded at higher field strength or under different conditions will be more amenable to interpretation.

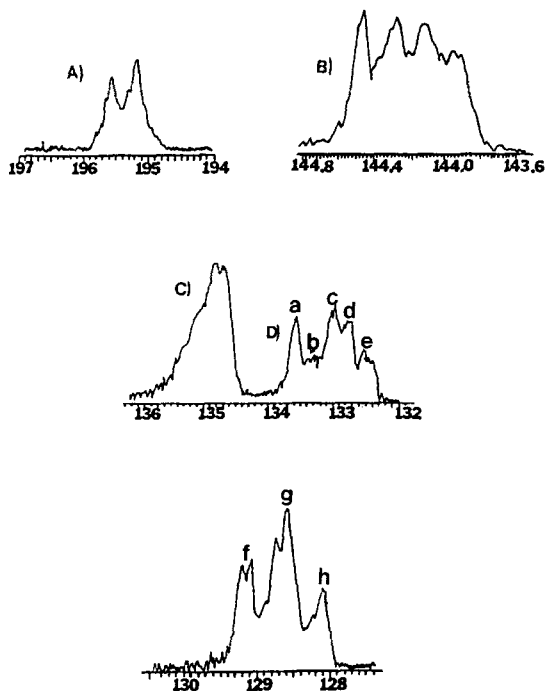


Figure 2

Linear Expansions of: A) Carbonyl Carbon Resonance;
 B) C_2 Resonance; C) C_3 Resonance; D) C_5 Resonance; E) C_4 Resonance

In contrast, the resonance patterns observed for the C_4 and C_5 aromatic carbon (Figures 2D and E), consist of peaks having relative intensities that are approximately equal to multiples of $1/4$ (0.25) or $1/8$ (0.125). This suggests that they can be analyzed in terms of triads (C_4 pattern) and pentads (C_5 pattern). The chemical shifts of these signals and their relative intensities are listed in Tables 1 and 2. The C_5 carbon resonances have fractional intensities that

are multiples of 0.125, approximately, suggesting that pentad stereosequence resonances are responsible for the pattern observed. Unfortunately without the availability of stereoregular forms of poly (2TVK), model compounds, or other means to assign several of the resonance regions, it is not reasonable to make assignments at this time.

TABLE 1

Chemical Shifts, Fractional and Relative Intensities
for the Peaks in the C₅ Carbon Resonance

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
A	133.69	0.23 ± .03	2
B	133.41	0.13 ± .02	1
C	133.14	0.26 ± .03	2
D	132.90	0.24 ± .03	2
E	132.58	0.14 ± .02	1

TABLE 2

Chemical Shifts, Fractional and Relative Intensities
of the Peaks in the C₄ Carbon Resonance

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
F	129.15	0.26 ± .03	1
G	128.60	0.51 ± .06	2
H	128.11	0.23 ± .03	1

The resonance of the C₄ carbon occurs in three areas that have relative intensities of approximately 1:2:1. This indicates that the areas reflect triad sequence distributions and that the polymer is probably atactic. Peak G probably is due to C₄ carbons in mr + rm stereosequences, but assignments for peaks F and H cannot be made with certainty. Since peak F is slightly larger than peak H, and since racemic enchainment can be expected to be favored over meso enchainment, if a preference exists, we tentatively assign peak F to rr triads and peak H to mm triads.

The aliphatic carbons also show some sensitivity to polymer stereochemistry. The methine carbon resonance (Figure 3) occurs as

two peaks that have a relative intensity ratio of 4:1 (I:J). This ratio indicates a possible sensitivity to higher order stereosequences but the resolution at present is insufficient for any reasonable interpretation to be made. The methylene carbon resonance also occurs as two broad areas that may be the result of overlapping of several signals. Previous work has shown that tetrads and hexads are responsible for the methylene resonance pattern in polystyrenes (9) and poly (2-vinyl pyridine) (3), but again resolution is not sufficient to permit any assignments to be made in the present case.

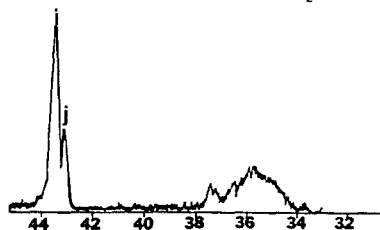


Figure 3

Linear Expansion of the Aliphatic Carbon Resonance

¹H-NMR

Figure 4 shows the 300 MHz FT ¹H-NMR spectrum of poly(2-thienyl vinyl ketone). The resonances are assigned as shown in the Figure (11). All the aromatic proton resonances appear sensitive to polymer stereochemistry, but the resonances of individual aromatic protons are overlapped with those of other aromatic protons and it is difficult to interpret the individual resonance patterns. Perhaps the use of higher field spectrometers and/or other measurement conditions might yield more readily interpretable results.

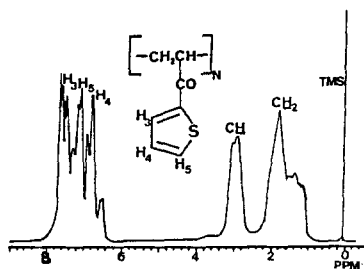


Figure 4

300 MHz ¹H-NMR Spectrum of Poly (2TVK)

Conclusion

Poly(2-thienyl vinyl ketone) has been synthesized by free radical initiation and its ^{13}C -NMR spectrum was recorded and analyzed in terms of polymer stereochemistry. The analyses showed that poly(2-thienyl vinyl ketone) is an atactic polymer. Tentative assignments were made for peaks in the resonances that had sufficient resolution. The assignments are tentative because to date no stereoregular poly(2-thienyl vinyl ketone) has been synthesized. The assignments are believed reasonable but more work is necessary before any certain assignments can be made.

References

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