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Analysis of the ^{13}C-NMR and ^{1}H-NMR spectra of poly(2,5-dimethyl-3-vinyl thiophene)

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Summary

The title monomer was synthesized and polymerized using free radical initiation. The polymerization was facile and proceeded rapidly to high conversion. The high field ^{13}C-NMR and ^{1}H-NMR spectra of the polymer had several signals that displayed sensitivity to polymer stereochemistry. Analysis of these signals showed poly(2,5-dimethyl-3-vinyl thiophene) to be an atactic polymer.

Introduction

In previous work (1-6) we have examined the effect of ring substitution on the tacticity and nmr spectra of polyvinyl heterocycles synthesized under free radical conditions. In all cases the polymers have been shown to have an atactic stereochemistry, i.e. ring substitution has little or no effect on tacticity. However, ring substitution has a significant effect on the appearance of the nmr spectra. From previous results it has seemed that the steric bulk of the substituent group is more important than the electronic effect(s) of such a group. Our aim in the present work is to continue to evaluate this effect by introducing two ring substituents, in addition to the vinyl group. Such substitution would result in the vinyl heterocycle having only one ring proton; therefore, any multiplicity in the resonance of this proton would necessarily be the result of stereochemical sensitivity.

Experimental

General

All solvents were reagent grade and were used as received. All nmr spectra were recorded at ambient temperature on $CDCl_3$ solutions of the polymer (15% w/v) using a Varian Gemini 300 FT spectrometer (^{1}H frequency = 300 MHz). The areas of individual resonances were determined by electronic integration and by tracing the resonances on high quality paper then cutting out and weighing the tracings on a five place analytical balance. Each area peak reported is the average of 3 or 4 measurements. The molecular weight of the polymer was determined by GPC as previously described (1-4).

Monomer Synthesis

The monomer was synthesized by dehydration of the alcohol (20 g) resulting from the reduction of 3-acetyl-2,5-dimethyl thiophene (Aldrich) with sodium borohydride. The alcohol was purified by distillation (b.p. = 127°C/35 mm) and then dehydrated with fused $KHSO_4$ ($<$ 1.0 wt % based on alcohol) (7). The yield of monomer was 21%. The monomer was purified by distillation from CaH_2 (b.p. = 84-86°C/35 mm). The structure of the monomer was confirmed by ^{1}H-NMR spectroscopy.

Polymer Synthesis

The polymer was synthesized by charging 2.0g of monomer into a clean, dry screw cap vial followed by 0.8 wt % AIBN. The monomer-initiator solution was sparged with dry N_2 while cold and the vial was then sealed with a teflon lined screw cap. The vial was placed in a thermostated bath at 75°C for a period of 1.75 hr. After this time most of the sample had solidified. The polymerization was terminated by removing the vial from the bath, cooling in cold water and adding 6 ml of cold CH_3OH. The polymer was purified by reprecipitating it three times from $CHCl_3$ solution into excess CH_3OH. The polymer was dried at 35°C for 72 hr then weighed to determine conversion. Conv. = 63%; M_n = 19000, M_w = 40000.

Results and Discussion

^{1}H-NMR Spectrum

The ^{1}H-NMR spectrum of poly(2,5-dimethyl-3-vinyl thiophene), PDMT, along with an expansion of the ring proton resonance is shown in Figure 1. The ring proton resonance occurs as a 7 peak pattern in a relative intensity ratio of 3:10:10:3:1:3:2; A:B:C:D:E:F:G. The sum of this ratio if 32, which is exactly half of the number of heptads expected for an atactic polymer. Based on previous results (1-6) it is logical to multiply all the relative intensities by two, obtaining then the 'true' relative intensity ratio of 6:20:20:6:2:6:4. While the resolution is insufficient for any detailed assignments to be made, a P_m value can be calculated from the fractional intensity of peak E (0.031 ± .005), the value obtained is 0.50 ± .10, which is that expected for an atactic polymer.

^{13}C-NMR Spectrum

The ^{13}C-NMR spectrum and expansions of selected carbon resonances are shown in Figures 2 and 3. The peaks are assigned as shown in the Figure (8,9).

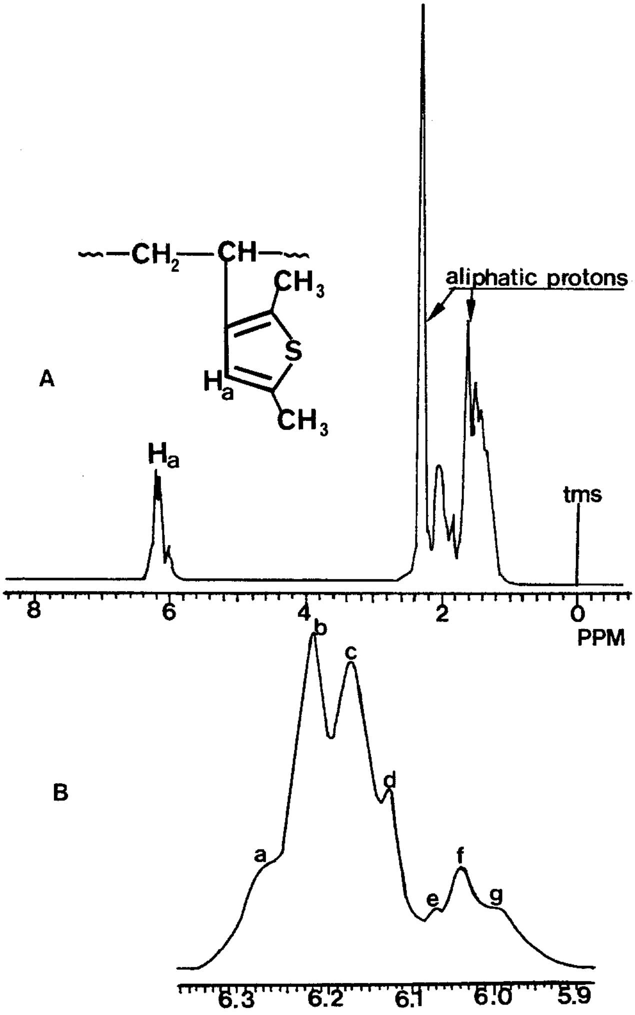

Figure 1

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

The C_5 carbon resonance (Figure 2B) occurs as an 8 peak pattern with a relative intensity ratio of 1:4:8:5:4:8:1:1; A:B:C:D:E:F:G:H. The sum of this ratio is 32, again half the value expected for the number of heptads of an atactic polymer. Again multiplying by two would be logical, yielding 2:8:16:10:8:16:2:2 as the 'true' intensity ratio. Resolution is not sufficient for detailed assignments to be made but a P_m value calculated from the fractional intensity of peak A (0.032 ± .003) is 0.50 ± .05.

The resonance pattern of the C_3 carbon (Figure 2C) occurs as a 3 peak pattern in a relative intensity ratio of 1:7:24, A:B:C. The sum of this ratio is 32, which indicates a heptad sensitivity, however, as above the resolution necessary for detailed assignments is lacking. However a P_m value can be calculated from the fractional intensity of peak A (0.032 ± .004), P_m = 0.50 ± .06.

The C_2 carbon resonance (Figure 2D) occurs as a 9 peak pattern in a relative intensity ratio of 1:3:2:19:20:11:4:2:2, A:B:C:D:E:F:G:H:I. The sum of this relative intensity ratio is 64, which is the number of heptads expected for an atactic polymer. As above, insufficient resolution produces a detailed assignment in terms of heptads but a P_m value can be calculated from the fractional intensity of peak A (0.016 ± .003 = heptad singlet), P_m = 0.50 ± .09.

The methylene carbon resonance (Figure 3A) occurs as an 8 peak pattern with a relative intensity ratio of 1:2:2:3:9:6:6:3, A:B:C:D:E:F:G:H. The sum of this ratio of 32, which is exactly the number of hexads expected for an atactic polymer. While the resolution is reasonable, the S/N ratio and the absence of a stereoregular polymer and/or previous results, prevents any detailed assignments from being made. However, peak A is due to a hexad singlet, most likely a xmmmx type (x = m or r). A P_m value calculated from the fractional intensity of peak A (0.032 ± .005) is 0.50 ± .08.

The methine carbon resonance (Figure 3B) occurs as a 3 peak pattern in a relative intensity ratio of 9:6:1, A:B:C. The sum of this ratio is 16, which indicates a pentad stereosequence sensitivity. This pattern has occurred in the spectra of other polymer heterocycles (1-6) and has been assigned in terms of pentads. Because of this previous history, we believe we can assign peaks A, B and C as containing certain pentads. While definite assignment awaits the synthesis of stereoregular polymer and possibly epimerization studies, we believe the assignments summarized in Table 1 are reasonable.

A P_m value calculated from the fractional intensity of peak C (0.063 ± .007) is 0.50 ± .06.

The resonance due to the methyl carbon attached to the C_5 ring carbon (Figure 3C) occurs as a 3 peak pattern in a relative intensity ratio of 14:1:1, A:B:C. The sum of this ratio is 16, which indicates a pentad stereochemistry sensitivity.

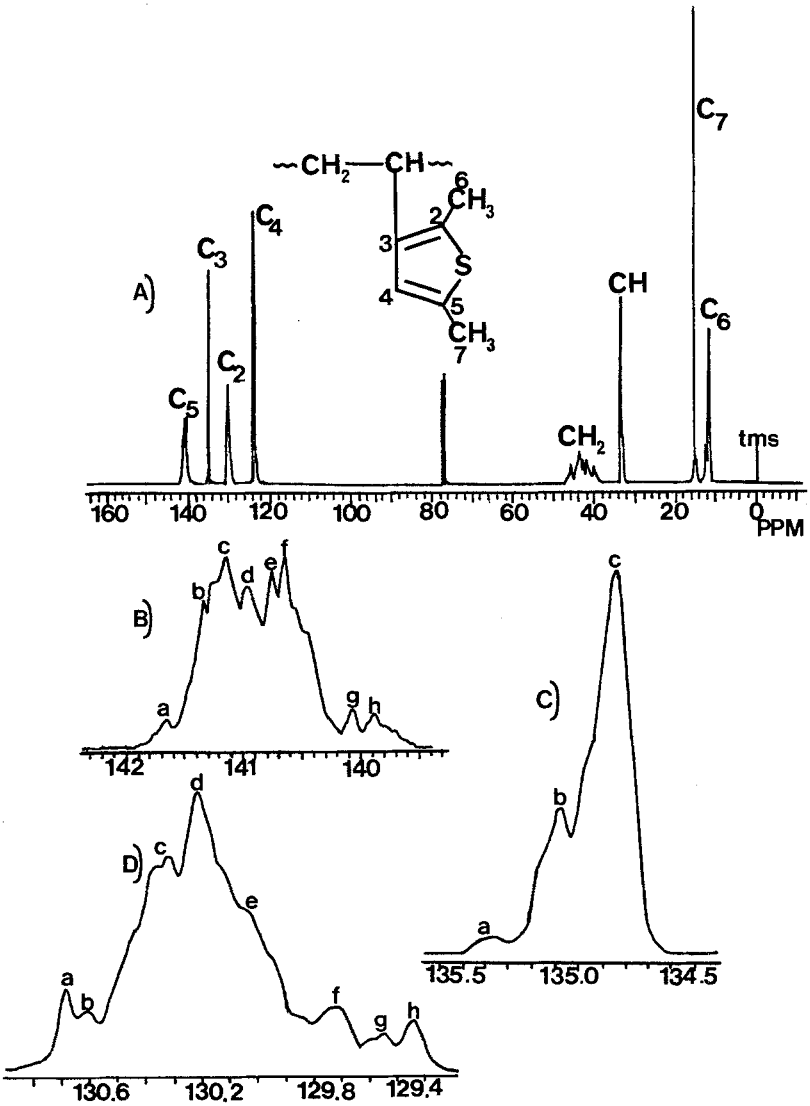

Figure 2

75.5 MHz ^{13}C-NMR of PDMT; A) Full Spectrum
B) C_5 Resonance; C) C_3 Resonance; D) C_2 Resonance

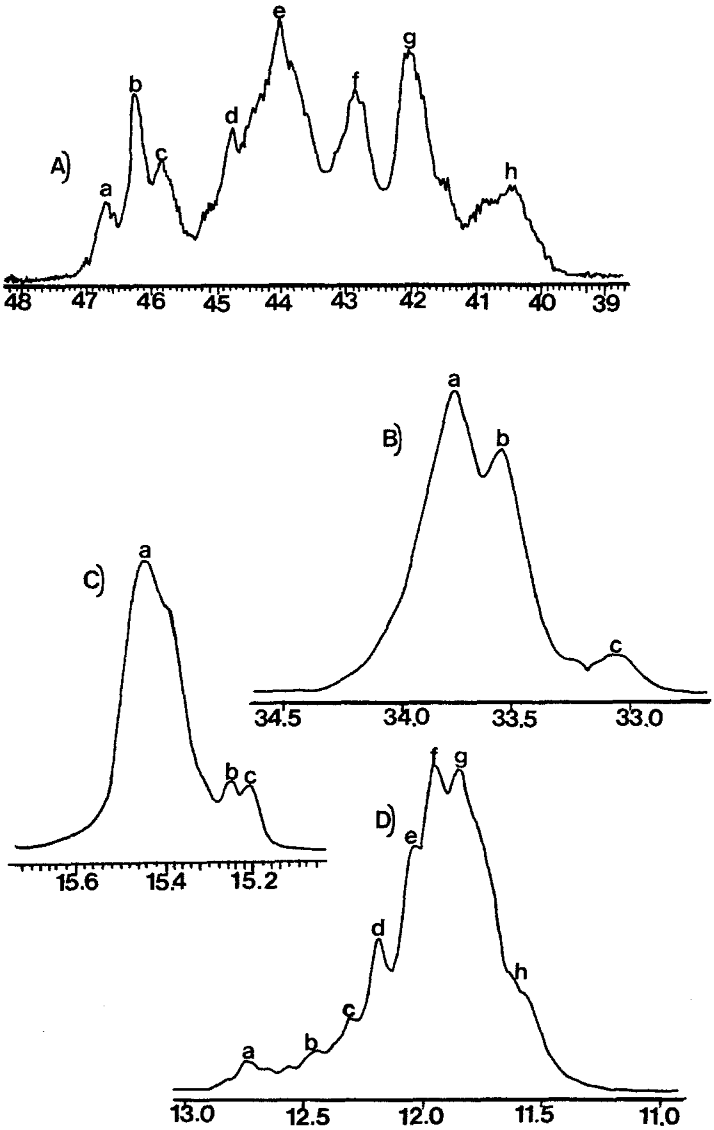

Figure 3

Linear Expansions of; A) Methylene Carbon Resonance B) Methine Carbon Resonance; C) C_5 Methyl Carbon Resonance; D) C_2 Methyl Carbon Resonance

While the resolution is not as good in the case as it is for the methine carbon resonance, peak C is most probably due to the mrrm or rrrr pentad. Although this is not certain as such an assignment would mean that the chemical shift of the rrrr pentad (or mrrm pentad) is significantly affected by which carbon atom is displaying the sensitivity i.e. methine or methyl carbon.

TABLE 1

Pentad Assignments for the Methine Carbon Resonance

Peak	Chemical Shift (ppm)	Relative Intensity	Assignment
A	33.81	9	rmmr, mmmr + rmmm, mmmm, mmrm + mrmm; rrmr + rmrr
B	33.55	6	mrmr + rmrm, mrrr + rrrm, mmrr + rrmm
C	33.08	1	mrrm

As the relative positions of these two carbons are quite different, this is could possibly be the case. More data is required to quantitatively assess this possibility. In any case, a P_m value calculated from the fractional intensity of peak C (0.062 ± .008) is 0.50 ± .06.

The resonance due to the methyl carbon attached to the C_2 ring carbon (Figure 3D) occurs as an 8 peak pattern in a relative intensity ratio of 1:1:2:3:4:7:11:3, A:B:C:D:E:F:G:H. The sum of this ratio is 32 which, as above, can be attributed to a heptad sensitivity. While the resolution is insufficient for any detailed assignments to be made, a P_m value can be calculated from the fractional intensity of peak A (0.032 ± .004) is equal to 0.50 ± .06.

Conclusions

The title monomer has been synthesized and polymerized under free radical initiation conditions. The polymerization to relatively high conversion proved rapid relative to unsubstituted 2- or 3-vinyl thiophenes. In particular, 3-vinyl thiophenes generally are somewhat sluggish even at higher temperatures with very active initiators.

Possibly, the electronic effects of the methyl groups increase the reactivity of the growing radical. More work, including MO calculations, will be necessary to define the effect with certainty. The effect of the methyl groups on the nmr was to render the stereochemical sensitivity of more individual resonances observable relative to the unsubstituted parent polymers and to show those resonances as sensitive to higher order stereosequences. While lack of resolution rendered detailed assignments impossible in most cases, P_m values could be calculated from the measured fractional intensities of select peaks. In all cases the P_m values were 0.50 which is the value expected for an atactic polymer. Because the P_m values were calculated from relatively long stereosequences and the same value was obtained from many stereosensitive resonances we can conclude that poly(2,5-dimethyl-3-vinyl thiophene) is a polymer with atactic stereochemistry.

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