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Analysis of the 300 MHz PMR Spectrum of Poly(2-vinyl Thiophene)

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Summary

The 300 MHz pmr spectrum of poly(2-vinyl thiophene), poly-2-VT, is presented and analyzed. The aliphatic proton resonance of this polymer is very similar to that of polystyrene, but the aromatic proton resonance is rather well defined, especially that of protons in the 3-position of the thiophene ring. The resonance of such protons occurs as a three peak pattern that has been interpreted in terms of pentad stereosequences. Based on the assignments made in this paper, poly-2-VT prepared by free radical initiated polymerization seems to be atactic.

Introduction

Although there are numerous reports of the polymerization of 2-vinyl thiophene (KUHN and DANN 1941, NAZZARO and BULLOCK 1946, FRANK et al. 1948, WALLING et al. 1948, and KOTON 1958), the nmr spectra of its polymers and their stereochemical structures have not been reported. Since the chemical and physical properties of benzene and thiophene rings are very similar, one might expect the microstructure of poly(vinyl thiophenes) to be very similar to that of polystyrene, at least when the polymers are prepared by free radical initiated polymerization. The pmr and cmr spectra of polystyrene are difficult to interpret in terms of polymer stereochemistry, and are not fully understood. It is hoped that the nmr spectra of polystyrene analogues such as poly(vinyl thiophene) will be more easily analyzed than the spectra of polystyrene itself. Hopefully, studies on such analogs will lead to an improved understanding of polystyrene spectra and structure. In the present paper, we report and analyze the 300 MHz pmr spectrum of poly(2-vinyl thiophene), poly-2-VT.

Experimental

2-Vinyl thiophene, b.p. 66-68° (50mm), was prepared according to the procedure of BROOKS (1944).

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Examination of the monomer by glc indicated a single peak. Its nmr spectrum showed the expected vinyl and thiophene ring patterns.

A mixture of 2-vinyl thiophene (7.0g., 0.064 mole) and AIBN (0.02g., 1.2×10^{-4} mole) was sealed in an evacuated glass ampoule and heated at 65° for 58 hrs. The reaction mixture was poured into methanol to precipitate the polymer, which was then reprecipitated three times from $CHCl_3$ solution into methanol and then dried in vacuo at room temperature for 48 hrs. The yield was 1.8g (26%). Analysis of the polymer by gel permeation chromatography, using a polystyrene calibration curve (THF solvent) indicated $\bar{M}n$ and $\bar{M}w$ values of 15,000 and 49,000, respectively.

2-Vinyl thiophene (5g., 0.045 mole) was added slowly at 0° to a solution prepared by mixing 10 ml of 2.1M ØMgBr (in ether) with 150 ml dry toluene under nitrogen. After 30 hrs. at 0°, the mixture was poured into methanol to obtain polymer (0.6g., 12%) that was reprecipitated twice from chloroform into methanol and then dried in vacuo for 48 hrs. at room temperature.

Pmr spectra of (10% w/v) solutions of the polymer in $CDCl_3$ (-36°, -13°, 12°, 28°, 60°), CS_2 (28°), DMSO (28°) and C_5D_5N (28°) were recorded using a Varian HR-300 NMR Spectrometer operated in CW mode. Tetramethylsilane was used as an internal standard. Individual resonance areas were determined by cutting and weighing and by using the curve fitting program of VONMEERWALL (1976).

Results and Discussion

Figure 1A shows the 300 MHz pmr spectrum of free radical polymerized poly-2-VT in $CDCl_3$ solution at room temperature. The aliphatic proton resonances of this polymer are very similar to those of polystyrene. The methylene proton resonance, occurring at $\delta=\sim1.8$ppm, is totally devoid of any fine structure. The methine proton resonance ($\delta=2.5-3.0$ppm) is very similar to that of polystyrene although less well defined. Two signals are evident, the lower field one being approximately one-third the intensity of the upper. Studies on epimerized isotactic polystyrenes (SHEPHERD, et al. 1979) have shown that the lower field methine resonance of this polymer to be due to mm-triad stereosequences. Making this same assignment, by analogy, for poly-2-VT, it seems that this polymer has an atactic structure.

The aromatic proton resonances of poly-2-VT occur in three general areas that are assigned to protons present at the 3-(H_A,$\delta=6.0-6.5$ppm), 4-(H_B,$\delta=6.6-6.9$ ppm), and 5-(H_C,$\delta=6.9-7.2$ppm) positions of the thiophene rings in the polymer. These assignments are based on assignments made previously for 2-substituted

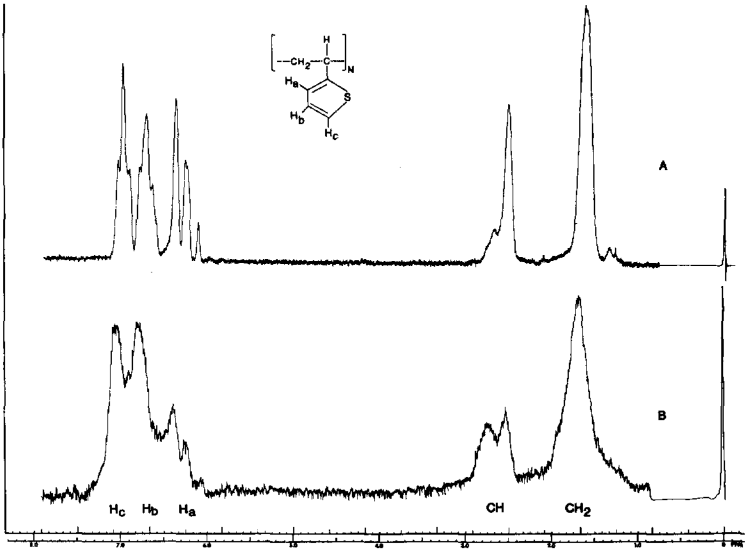

Figure 1. 300 MH_z pmr Spectrum of Poly (2-vinyl thiophene). Samples prepared by AIBN (A) and ∅ Mg Br (B) Initiated Polymerization. The samples are in $CDCl_3$ solution.

thiophenes (HOFFMAN and GRONOWITZ, 1960). An expansion of the aromatic proton resonance region of poly-2-VT is provided in Figure 2, along with possible interpretations of the resonance patterns observed for several of the protons.

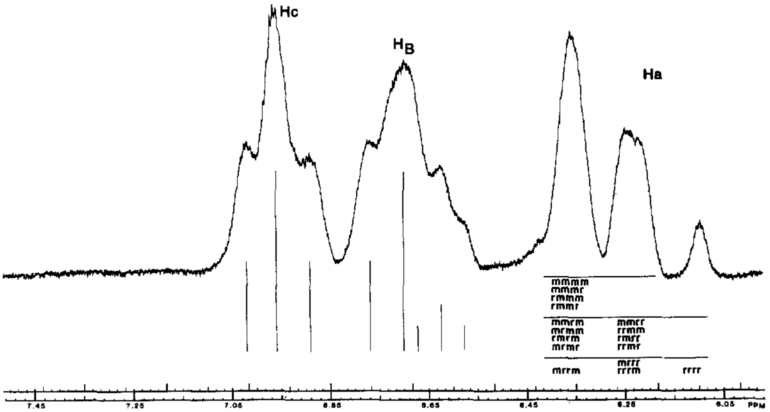

Figure 2. Expanded 300 MH_Z Aromatic Proton Resonance Spectrum of Poly (2-vinyl thiophene) and Suggested Interpretation.

The H_C-resonance pattern consists of three signals having relative intensities of 1:2:1. It seems reasonable to assign these to mm-, (mr+rm)- and rr- stereosequences. The central area can be assigned to (mr+rm)-triads, but the relative ordering of the mm- and rr- signals cannot be specified at the present time.

The H_B-resonance pattern, which consists of four peaks is difficult to interpret. It might be that resonances due to triad stereosequences are being observed, except that one of the triad resonances is split further into pentad signals. Figure 2 shows this possible interpretation which is consistent with with the polymer being atactic.

The H_A-proton resonance pattern consists of three well resolved resonances, the relative areas of which are almost exactly 9:6:1 in order of increasing field. Since there are sixteen different pentad-stereosequences, it seems reasonable to interpret these signals in terms of such stereosequences. If poly-2-VT is perfectly atactic, all pentad stereosequences will be present in equal concentration and signals present in resonance patterns that are interpretable in terms of pentad stereosequences should have relative intensities that are integral multiples of 1/16. This is the case in the present instance.

Alternatively, the 9:6:1 pattern is consistent with triad stereosequence distributions for a Bernoullian polymer with σ=0.25 or 0.75. This possibility is considered unlikely for the following reasons:

a) The resonance patterns of the other protons are more consistent with a σ value of 0.50 than with values of 0.25 or 0.75. This is also true of the ^{13}C-spectrum of the polymer, which will be covered in a subsequent publication.

b) The 300 MHz pmr spectrum of predominatly isotactic poly-2-VT, prepared by ØMgBr initiated polymerization in toluene, Figure 1B, absorbs strongly at δ=2.6-2.9ppm and at δ=6.3-6.6ppm. If resonances of mm-triads are assigned to both of these regions, difficulty is encountered in interpreting the spectrum of the free radical polymerized polymer; the methine resonance region would indicate the polymer to have a low ($\sim$25%) mm-content, whereas the resonance pattern in the δ=6.0-6.6ppm region would indicate a high ($\sim$56%) mm-content. It does not seem possible to interpret both of these resonance patterns in terms of triad stereosequences.

c) The ortho proton resonance pattern of free radical polymerized polystyrene, which has an essentially atactic structure, (SHEPHERD et al. 1979; CHEN et al. 1980) is similar to the resonance pattern observed at δ=6.0-6.6ppm in the spectrum of poly-2-VT, except that four signals having relative intensities of 1:9:5:1, in order of increasing field, are evident in the polystyrene spectrum. Since it seems necessary to utilize pentad stereosequences to interpret this region in the case of polystyrene, it also seems reasonable to do so for poly(2-vinyl thiophene).

In developing assignments for the H_A-proton resonances of poly-2-VT, it was assumed that this polymer and polystyrene are sufficiently similar that their aromatic proton resonances can be interpreted in similar ways. Studies on the o-aromatic proton resonance of partially epimerized isotactic polystyrene (HARWOOD et al. 1981) indicate that the lowest and highest field signals are due to rmmr and rrrr stereosequences, respectively. On this basis, the resonance observed at δ=6.0-6.15 in the spectrum of poly-2-VT is assigned to rrrr pentads. It should be noted that only four pentads could possibly be assigned to this region. Of the other possibilities (mmmm, rmmr, and mrrm) only mrrm is a viable alternative, based on our present understanding of the polystyrene spectrum.

The resonance observed at δ=6.15-6.30ppm is tentatively assigned to (mrrr+rrrm) (mmrr+rrmm) and (rmrr+rrmr) pentads, based on the following reasoning: The shielding responsible for the occurrence of rrrr resonance at δ=6.00-6.15 can be considered to result from interactions that occur when there is an rr configurational relationship between a vinyl thiophene unit and its next and next-nearest neighbors. This shielding could conceivably be twice as large when two rr relationships are involved (as in rrrr) as when only one is involved (as in mrrr+rrrm,mmrr+rrmm and rmrr+rrmr). Thus, a given pentad may be observed at δ=6.0-6.15, 6.15-6.30 or 6.30-6.5ppm depending on whether the central unit is the terminal unit in two, one or zero rr stereosequences, respectively. Confirmation of this interpretation will require studies on partially epimerized isotactic (or syndiotactic) poly-(2-vinyl thiophene). Unfortunately we have not been able to prepare stereoregular varieties of poly(2-vinyl thiophene) of sufficient purity to justify conducting epimerization studies.

The above discussion concerns the spectrum of poly-2-VT in $CDCl_3$ solution at room temperature. Spectra of the polymer in this solvent at several temperatures and in other solvents have also been studied but only minor differences are noted. The 9:6:1 pattern is observed in all cases, although the central signal in this pattern is split into two components of approximately equal intensity when the polymer is dissolved in deuteropyridine.

In summary, the pmr spectrum of poly(2-vinyl thiophene) indicates that it is an atactic polymer.

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References

BROOKS, L.A.: J. Am. Chem. Soc., 66, 1295 (1944).
CHEN, T. K., GERKIN, T. A. and HARWOOD, H. J.: Polymer Bulletin, 2, 34 (1980).
FRANK, R. L., ADAMS, C. E., BLEGEN, J. R., SMITH, P.V., JUVE, A. E., SCHROEDER, C. H. and GOFF, M. M.: Ind. Eng. Chem., 40, 420 (1948).
HARWOOD, H. J., CHEN, T. K. and SHEPHERD, L.: to be published.
HOFFMAN, R. A. and GRONOWITZ, S.: Arkiv für Kemi, 16, 515 (1960).
KOTON, M. M.: J. Polym. Sci., 30, 331 (1958).
KUHN, R. and DANN, O.: Ann., 547, 293 (1941),
NAZZARO, R. T. and BULLOCK, J. L.: J. Am. Chem. Soc., 68, 2121 (1946).
SHEPHERD, L., CHEN, T. K. and HARWOOD, H. J.: Polymer Bulletin, 1, 445 (1979).
VONMEERWALL, E. D.: Comp. Phys. Comm., 11, 211 (1976).
WALLING, C., BRIGGS, E. R. and WOLFSTIRN, K. B.: J. Am. Chem. Soc., 70, 1543 (1948).

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