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An analysis of the ^{13}C-NMR spectrum of poly(*N*-vinyl-2-oxazolidone)

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Summary

N-Vinyl-2-oxazolidone monomer was synthesized and polymerized in bulk and in solution using a free radical initiator. The ^{13}C-NMR spectra of these polymers were recorded and analyzed in terms of polymer stereochemistry. The carbonyl carbon was found to be sensitive to pentad stereosequences and the fractional and relative intensities of the signals in the carbonyl resonance pattern show that the polymers are atactic.

Introduction

N-Vinyl-2-oxazolidone was first synthesized by Arond and Trieschmann (1) in 1956, followed by a synthesis from more commonly available materials reported by Drechsel in 1957 (2,3). Drechsel also reported on the polymerization of this monomer in both bulk and solution initiated by AIBN. Polymers of very low to moderately high molecular weights could be obtained. Since these early reports several investigators have described the copolymerization behavior of N-vinyl-2-oxazolidone and the properties of the copolymers (4-9). However, the stereochemistry of N-vinyl-2-oxazolidone (NVO) homopolymer has, to the author's knowledge, never been investigated. Polymers of NVO can be classified as polyvinylheterocycles, which have been the subject of much of our research (10, and references therein), particularly in the areas of homopolymer stereochemistry and copolymerization behavior of heterocyclic monomers. To date however, our work has concentrated on vinyl heterocycles which are analogs of styrene e.g. vinylthiophenes, vinylfurans and vinylpyridines. We thought then, that it would be interesting to investigate the stereochemistry of a polyvinylheterocycle which is not a styrene analog, e.g. poly NVO. This report summarizes our results to date.

Experimental

General

All solvents and other chemicals used were reagent grade and were used without further purification. The NMR spectra were recorded on a Varian Gemini 300 FT-NMR with d_6-DMSO as a solvent and TMS added as an internal standard. Molecular weight measurements were made with a Waters 150 ALC/GPC equipped with 500, 10^3, 10^4, 10^5 and 10^6 A ultrastyragel columns. Numerical values for the molecular weights were obtained from a polystyrene calibration curve.

Monomer Synthesis

The NVO monomer was synthesized accrording to the method of Drechsel (3) and was purified by distillation. b.p. = 98-100 at 3.0 mm of Hg [lit. b.p. = 70 at 0.1 mm Hg (3)]. H-NMR, $CDCl_3$; δ 3.60 (2H, AB quartet); δ 4.35 (4H, m); δ 6.60 (1H, m).

Polymer Synthesis

Homopolymers of NVO were synthesized in bulk and in solution. The solvent used was DMF. In both cases the initiator used was Vazo 67 and it was used at the 0.8 wt % level. For the bulk polymerization 1.5g of monomer was charged into a clean, dry screwcap vial followed by 0.012g of Vazo 67. The monomer was sparged with dry N_2 and the vial was sealed with a teflon lined cap. The vial was then placed in a water bath at 65°C for 0.5h. The vial was removed from the bath, cooled with cold water and xylene was added to precipitate the polymer. The solution polymer synthesis was performed similarly except that an equal weight of DMF was added, i.e. a 50 wt % solution of NVO was prepared. In both cases the polymers were purified by dissolving them in DMSO and precipitating in CH_3OH/xylene (70/30 v/v). The polymers were reprecipitated twice. The conversions were: bulk = 86%, solution = 71%. The polymer molecular weights were: bulk, M_w = 38600, PD = 1.86; solution M_w = 31000, PD = 1.79.

Results and Discussion

The 75.5 MHz ^{13}C-NMR spectra of both the bulk and solution polymers are shown in Figure 1. Peak assignments were made as shown in the Figure (11,12). It is apparent that three of the carbons are sensitive, in some fashion, to polymer stereochemistry. Horizontal expansions of the carbonyl carbon resonance of each polymer are given in Figure 2. In both cases seven separate peaks can be ascertained. The relative and fractional intensities of these peaks are given in Table 1 and Table 2. The peak areas were determined by tracing the peaks on high quality paper, cutting out and then weighing the tracings on a five place analytical balance.

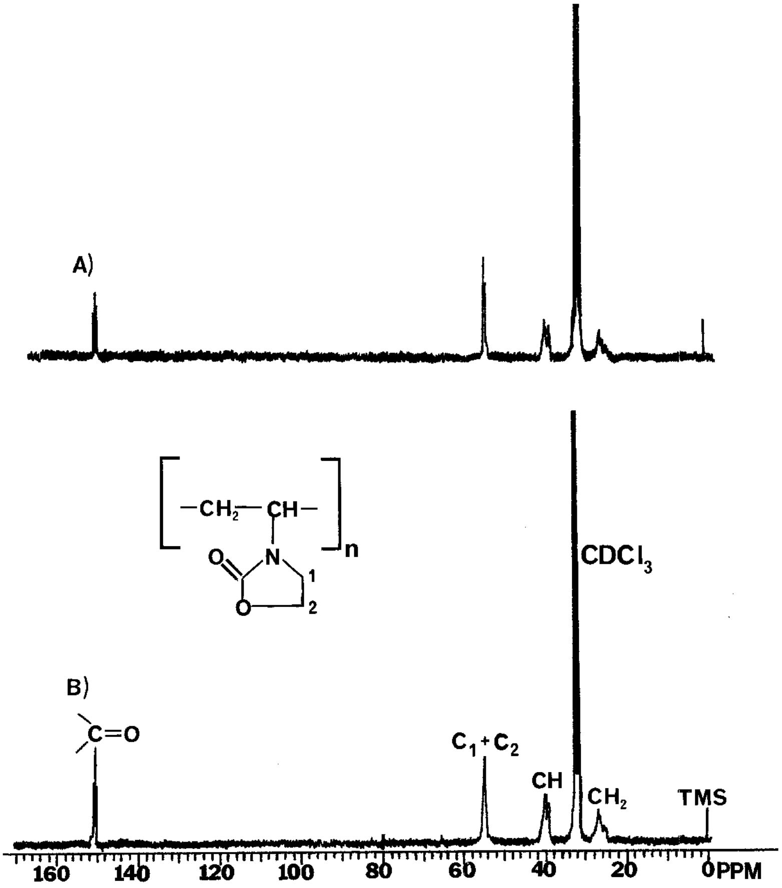

Figure 1

75.5 MHz ^{13}C-NMR spectra of A) Poly NVO synthesized in bulk; B) Poly NVO obtained from solution polymerization. Spectra were recorded at ambient temperature on 10% w/v solutions in d_6-DMSO

Each individual signal was cut out and weighed five times and the average weight was used in the calculation of the fractional and relative intensities. For both the bulk and solution polymers the sum of the relative intensities is 16 and since there are 16 pentads, each of equal intensity in an atactic polymer, it seems quite likely that the carbonyl resonance for both the bulk and solution polymers can be assigned to the pentad stereosequences of an atactic polymer.

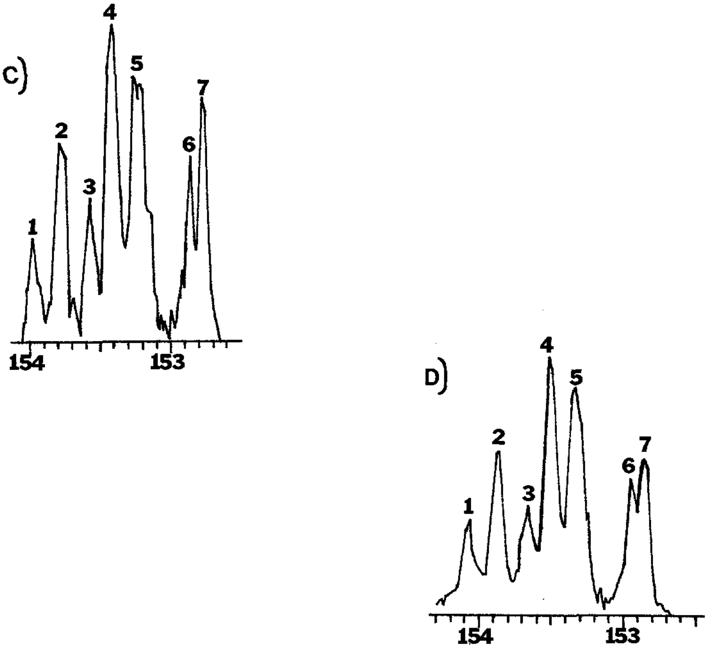

Figure 2

Horizontal expanses of the carbonyl carbon resonances of
C) Poly-NVO synthesized in bulk; and
D) Poly-NVO synthesized in solution

TABLE 1

Relative and Fractional Intensities of the Carbonyl Carbon Resonances of Bulk Poly-N-Vinyl-2-Oxazolidone

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
1	153.99	0.062 ± .006	1
2	153.80	0.14 ± .01	2
3	153.59	0.070 ± .008	1
4	153.42	0.24 ± .03	4
5	153.22	0.25 ± .03	4
6	152.88	0.11 ± .01	2
7	152.79	0.13 ± .01	2

TABLE 2

Relative and Fractional Intensities of the Carbonyl Carbon Resonances of Solution Poly-N-Vinyl-2-Oxazolidone

Peak	Chemical Shift (ppm)	Fractional Intensity	Relative Intensity
1	151.09	0.069 ± .007	1
2	150.90	0.14 ± .01	2
3	150.68	0.071 ± .009	1
4	150.50	0.25 ± .03	4
5	150.35	0.25 ± .03	4
6	149.95	0.11 ± .01	2
7	149.88	0.12 ± .01	2

A preliminary assignment of the peaks in the carbonyl resonance in terms of pentads, is given for both polymers in Table 3.

It should be noted that the peaks are assigned as containing the pentads indicated and that the assignments are certainly not unique but are believed to be reasonable, given arguments previously advanced (13). In any case P_m values calculated from the fractional intensity of the peak assigned to the mmmm pentad are 0.50 ± .06 for the bulk polymer and 0.51 ± .05 for the solution polymer. These are the P_m values expected for atactic polymers.

TABLE 3

Peak Assignments of the Carbonyl Resonance of Poly-N-Vinyl-2-Oxazolidone

Peak	Assignment
1	mmmm
2	mmmr + rmmm
3	rmmr
4	mmrm + mrmm, mrmr + rmrm
5	rrmr + rmrr, mmrr + rrmm
6	mrrr + rrrm
7	rrrr + mrrm

The methylene and methine carbons also show some sensitivity to polymer stereochemistry. The methine resonance for both the bulk and solution polymers occurs as three approximately equal peaks (Figure 3A).

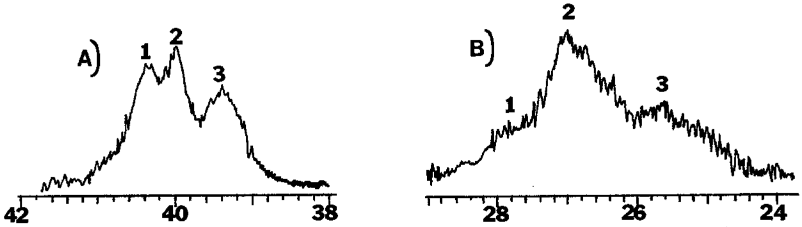

Figure 3

A) Methine carbon resonance of poly-NVO synthesized in bulk and B) Methylene carbon resonance of poly-NVO synthesized in solution. The methine and methylene resonances had the same appearance for both the bulk and soluton polymers.

The resonance pattern observed most probably reflects a sensitiviity to higher order stereosequences (pentads e.g.), however, the resolution is not sufficient for any reasonable assignments to be made. The methylene carbon resonance, Figure 3B, also occurs as a three peak pattern. The relative intensity ratio of 1:2:3 is 1:4:2 respectively. The same ratio is observed for both the bulk and solution polymers. The relative intensities indicate that the methylene resonance pattern reflects a sensitivity to at least tetrad sequences with higher order sequences also having some influence on the resonance pattern observed. However, as with the methine resonance, the resolution is insufficient for any reasonable assignments to be made at this time.

Conclusions

N-Vinyl-2-oxazolidone was synthesized and polymerized in bulk and in solution by free radical initiation. The 75.5 MHz ^{13}C-NMR spectrum of each polymer was obtained and analyzed. The carbonyl carbon proved to be sensitive to pentad stereosequences and the relative and fractional intensities of the individual peaks strongly indicated that the polymer was atactic. In fact P_m values calculated from the fractional intensities of the peak assigned to the mmmm pentad for both the bulk and solution polymer, were 0.50 ± .06 and 0.51 ± .05, these are the values expected for an atactic polymer. It should be noted that the experimental errors were assigned based on repeated peak area measurements, signal to noise ratios and peak resolution, which while not baseline, is very good for the peaks in the carbonyl region.

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