Polymer Bulletin 34, 455-460 (1995)

Polymer Bulletin

An analysis of the ^{1}H-NMR and ^{13}C-NMR spectra of poly(2-methyl-*N*-vinyl imidazole)

David L. Trumbo

S.C. Johnson Polymer, S.C. Johnson & Son, Inc., 1525 Howe Street, Racine, WI 53403-2236, USA

Received: 12 January 1995/Accepted: 18 January 1995

Summary

The title monomer was polymerized via free radical initiation. The polymerization proved very rapid, yielding quantitative conversion in ~ 5-10 min. Most of the polymer proved to be insoluble in any solvent tried, but good quality ^{1}H-NMR and ^{13}C-NMR spectra could be obtained from the soluble fraction. The soluble fraction of the polymer proved to have an atactic stereochemistry.

Introduction

All of our previous work on the stereochemistry of vinyl heterocycle polymers has been with monomers that had the vinyl group attached to a ring carbon atom (1-4 and references therein). To date, all of the monomers we have studied yield atactic polymers when the polymerization is initiated via free radical means. Investigation of the stereochemistry of poly(vinyl heterocycles) where the vinyl group is attached to an atom other than carbon seemed a logical extension of our work. We chose to examine N-vinyl imidazoles because the monomers are readily available, polymerization is facile and previous work has been done on unsubstituted poly (N-vinyl imidazole). In fact, previous work on poly(N-vinyl imidazole) initiated by free radical means has shown that while polymerization media and temperature have a slight effect on stereochemistry, the poly(N-vinyl imidazole(s)) produced were atactic (5,6). We thought it would be of interest, given our experience with other ring substituted vinyl heterocycles; including methyl substituted species (7,8), to investigate the effect a ring methyl group would have on the ^{1}H-NMR and ^{13}C-NMR spectra and/or tacticity of the resultant polymer.

Experimental

All solvents used in this study were reagent grade and were used as received. The AIBN and 2-methyl-N-vinyl imidazole (2MNVI) were purchased from Aldrich. The AIBN was purified by recrystallization from CH_3OH and the 2MNVI was purified by distillation from CaH_2.

The nmr spectra were obtained with a Varian Gemini 300 FT NMR. Peak areas were measured by electronic integration and by cutting and weighing tracings of the individual peaks. The polymer was dissolved in d_6-DMSO (8% w/v) and TMS was added as an internal standard. Molecular weight measurements were performed with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A microstyragel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Polymer Synthesis

The polymer was synthesized by charging 1.0g of 2MNVI into a clean, dry screw cap vial followed by 0.6 wt % of AIBN. The monomer solution was sparged with dry N_2 and the vial was sealed with a teflon lined screw cap. The vial was placed in a water bath thermostated at 75°C. After 10 min. the entire monomer sample had solidified and the vial was removed from the bath. The vial was allowed to cool to room temperature and $CHCl_3$ was added to dissolve the polymer. However, the polymer proved insoluble in $CHCl_3$. Dimethyl sulfoxide was added and ~ 40 wt % of the polymer dissolved. The soluble polymer was purified by precipitation and reprecipitation into 2-butanone (MEK) from DMSO solution. The polymer was a white powder. Conversion after reprecipitation was 26.6%. This is conversion to soluble product only, the overall conversion of monomer to polymer (soluble and insoluble) is ~90%. $M_n = 2400$, $M_w = 3700$, $M_w/M_n = 1.33$.

Results and Discussion

Figure 1 shows the 300 MHz ^{1}H-NMR spectrum of poly-2MNVI as well as a linear expansion of the ring proton resonances (Figures 1A and B). The signals are assigned as shown in the Figure (9). The peaks labeled A-D (assigned to H_5) occur in a 1:1:3:3, A:B:C:D ratio. The sum of these relative intensities = 8. Can these resonances be assigned to pentads? The fractional intensities of the peaks which are 0.12 ± .02, 0.13 ± .02, 0.35 ± .05 and 0.36 ± .05 (A,B,C,D respectively) indicate that it would be logical to multiply the relative intensities by 2 (since the fractional intensity of a pentad doublet for an atactic polymer would be expected to be 0.125). If this is done the relative intensity ratio becomes 2:2:6:6, A:B:C:D which totals 16. Because there are 16 pentads of equal concentration in an atactic polymer, it is logical to assign this pattern as due to a pentad sensitivity and suggest that poly 2-MNVI is an atactic polymer. A P_m value calculated from the fractional intensity of peak A is 0.49 ± .07.

The signals labeled E-I are assigned to the H_4 proton. The relative intensity ratio of these peaks is 1:2:4:2:1, E:F:G:H:I. The sum of these relative intensities is 10. The fractional intensity ratios and the sum of the relative intensities indicate that sensitivity to higher order stereosequences is being displayed, probably a pentad sensitivity which is being influenced by heptads. At present the resolution is insufficient for any reasonable assignments to be made. The aliphatic resonance pattern proved to be a result of overlap of signals from the methylene, methine and methyl protons and yielded no meaningful information in terms of polymer stereochemistry.

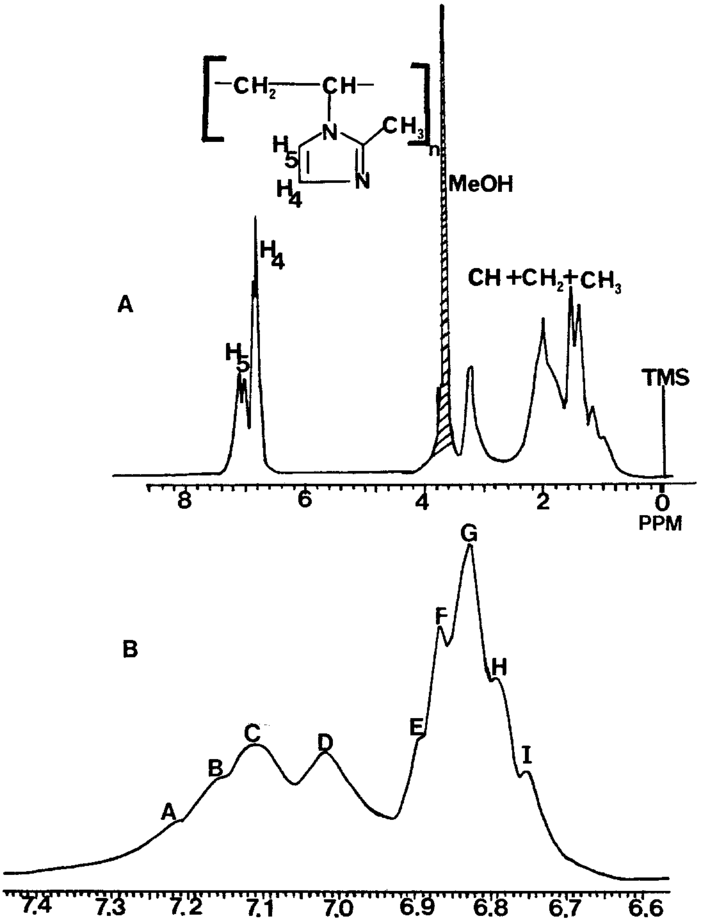

Figure 1

300 MHz ^{1}H-NMR spectrum of poly-2MNVI. A) Full scale spectrum; B) Expansion of ring proton resonances

^{13}C-NMR

Figure 2 shows the 75.5 MHz ^{13}C-NMR of poly-2MNVI as well as linear expansions of the C_2 ring carbon and the $-CH_3$ carbon resonances (Figures 2B and 2C respectively). The peaks are assigned as shown in 2A (10).

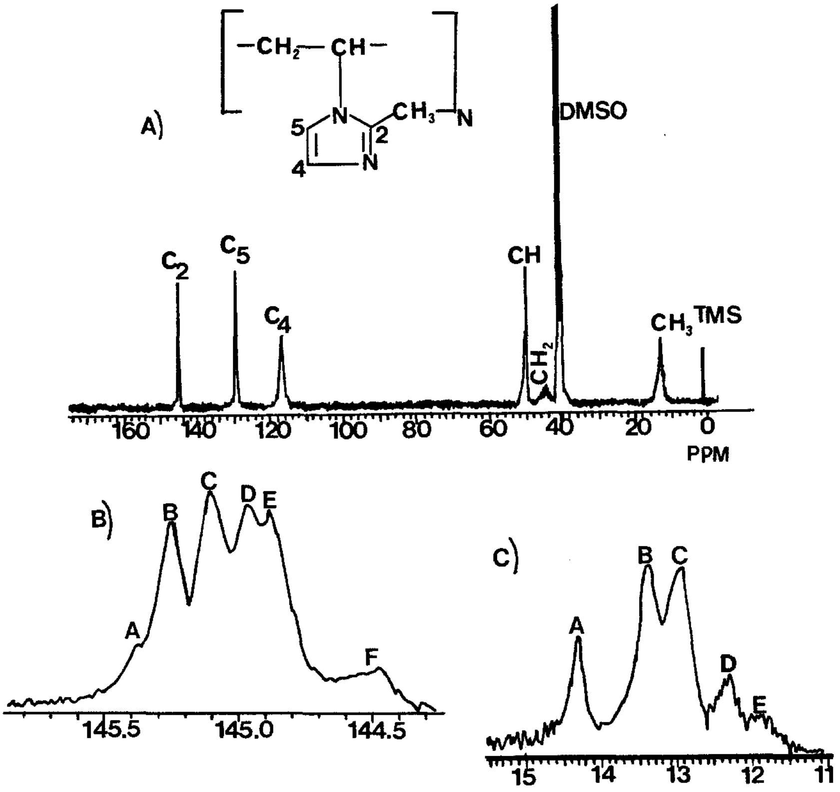

Figure 2

75.5 MHz ^{13}C-NMR spectrum of poly-2MNVI. A)Full spectrum B) Expansion of the C_2 carbon resonance; C) Expansion of the methyl carbon resonance

The signals labeled A-F for the C_2 ring carbon resonance occur in a relative intensity ratio of 1:3:4:3:4:1, A:B:C:D:E:F. The sum of the relative intensity ratios is 16. As previously stated, since there are 16 pentads of equal concentration in an atactic polymer, this pattern is most logically assigned to pentads. Again the high degree of overlap makes any reasonably detailed assignment unfeasible at this time, calculation of a P_m value from the fractional intensity of F (0.073 ± .008) yields P_m = 0.52 ± .06 which is in good agreement with the value calculated from the ^{1}H-NMR.

The $-CH_3$ resonance is somewhat better resolved than the C_2 resonance. The relative intensity ratio of peaks A-E is 3:5:5:2:1, A:B:C:D:E. Again this sums to 16, strongly indicating a pentad sensitivity. A P_m value calculated from the fractional intensity of E (0.064 ± .006) is 0.50 ± .05. A tentative assignment of this resonance in terms of pentads is given in Table 1.

TABLE 1

Pentad Resonance Assignment for the $-CH_3$ Carbon Resonance

Peak	Chemical Shift (ppm)	Proposed Pentad Assignment
A	14.30	mmrm + mmmr, rmmr
B	13.40	mmrm + mrmm, rmrr + rrmr mmmm
C	12.89	rmrm + mrmr, rrrm + mrrr rrrr
D	12.32	rrmm + mmrr
E	11.90	mrrm

The peaks are assigned as containing the pentads listed no specific ordering is possible in the absence of a stereoregular polymer, but the assignments are believed to be reasonable (6,11).

Conclusions

The 2MNVI proved a very reactive monomer with only the lower molecular weight species produced in the polymerization being soluble in common laboratory solvents. The soluble polymer proved to have an atactic stereochemistry when all the spectroscopic evidence was considered. This suggests that having the vinyl moiety bonded to nitrogen instead of carbon does not influence the stereochemistry of the polymer when it is synthesized by free radical initiation. The spectra themselves proved to have more protons and carbons displaying discernible stereochemical sensitivity than is typical for the spectra of poly (vinyl heterocycles) with the vinyl group bound directly to carbon.

References

1. D. L. Trumbo, T. Suzuki and H. J. Harwood, Polym. Bull., 4, 766 (1981).
2. D. L. Trumbo, Polym. Bull., 29, 377 (1992).
3. D. L. Trumbo, Polym. Bull., 29, 535 (1992).
4. D. L. Trumbo, Polym. Bull., 31, 191 (1993).
5. P. M. Henrichs, L. R. Whitlock, B. R. Sochor and J. S. Tam, Macromolecules, 13, 1375 (1980).
6. B. B. Dambatta, J. R. Ebdon and T. N. Huckerby, Eur. Polym. J., 20(7), 645 (1984).
7. D. L. Trumbo, Polym. Bull., 33, 75 (1994).
8. D. L. Trumbo, submitted for publication, Polym. Bull., November 1994.
9. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, NY (1969).
10. E. Breitmaier and W. Voelter, "Carbon-13 NMR Spectroscopy" 3rd Ed. VCH, Germany (1990).
11. D. L. Trumbo, F. T. Lin, F. M. Lin and H. J. Harwood, Polym. Bull., 28, 87 (1992).