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## *Analysis*

# Two-Dimensional NMR Studies of Polypropylene Tacticity

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## Summary

The $^1$H and $^{13}$C NMR spectral assignments of polypropylene tacticity are revised using two-dimensional NMR techniques. The $^{13}$C-$^1$H hetero-nuclear shift correlation (CSCM) permits all tactic sequences to be assigned on $^1$H NMR. The $^1$H NMR J-coupling connectivities are confirmed with $^1$H shift-correlated (COSY) experiments. These techniques enable correct assignments to be made of previously uncertain tactic sequences in the $^1$H and $^{13}$C NMR spectra of stereoirregular polypropylene.

## INTRODUCTION

The newly developed two-dimensional (2-D) NMR is a family of techniques that provide effective means to resolve complex NMR spectra (1,2). Recently these techniques have been applied increasingly to polymer systems (3-9). In an earlier effort (7), we have shown how $^{13}$C-$^1$H chemical shift-correlated spectroscopy (CSCM) can be used to correlate the $^{13}$C and $^1$H resonances of stereoregular ethylene-propylene copolymers. By this means, $^1$H NMR spectral assignments for this copolymer system (previously uncertain) were obtained.

In this work we have used two-dimensional NMR techniques to study the tacticity of polypropylene. A large data base has already been accumulated over the years on this problem. Both $^1$H NMR (10-16) and $^{13}$C NMR (17-19) have been applied. Although the major features of the spectra are well known, the assignments of a few specific tactic sequences are still uncertain. We shall show how the use of 2-D NMR techniques can remove these residual uncertainties.

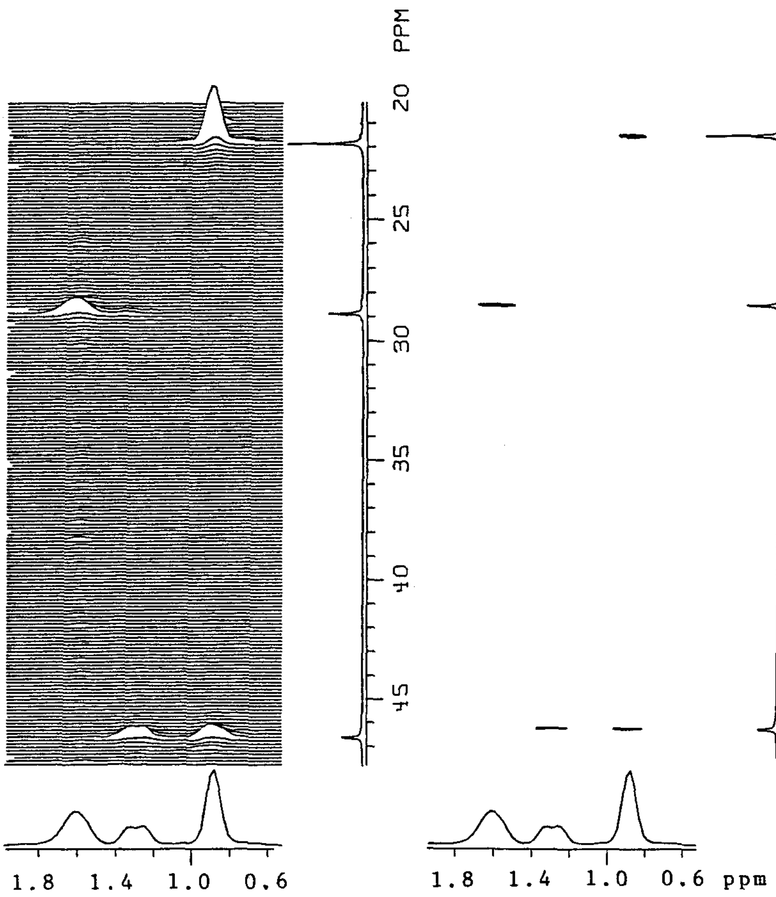
## EXPERIMENTAL SECTION

The polymers used as examples are all experimental samples. These are dissolved in 1,2,4-trichlorobenzene at a concentration of 20 wt % with $d_6$-benzene added as the lock material. The $^{13}$C spectra were obtained on a GE Nicolet NT-300 spectrometer operating at 75.46 MHz. The samples were run at 120°C. The $^{13}$C-$^1$H shift-correlated spectra and the $^1$H correlated spectra were obtained using the CSCM and COSY pulse sequences included in the NMC-1280 software package.

Table 1. NMR Spectral Assignments of Isotactic Polypropylene

| | $^{13}C$ | $^{1}H$ | |
|---|---|---|---|
| $CH_3$ | 21.8 ppm | 0.87 ppm | $J_3(CH_3\text{-}CH)$ = 6.56 Hz |
| CH | 28.7 ppm | 1.60 ppm | $J_3(CH\text{-}CH_{2,s})$ = 6.9 Hz<br>$J_3(CH\text{-}CH_{2,a})$ = 6.1 Hz |
| $CH_2$ | 46.6 ppm | 0.89 ppm (syn)<br>1.29 ppm (anti) | $J_2(CH_2$, gem) = -13.6 Hz |

Figure 1. The $^{13}C$-$^{1}H$ CSCM of Isotactic Polypropylene (a) Correlation Map, (b) Contour Plot



The $^{13}C$ CSCM spectra were obtained using a sweep width of 6 kHz and 4K data points. A total of 128 spectra were used to provide the equivalent of 1.5 kHz sweep width in the proton frequency dimension. Free induction decays in the proton frequency dimension were zero-filled before Fourier transformation and the spectra displayed in the absolute value mode. The $^{1}H$ COSY spectra were obtained using a sweep width of 1.4 kHz and 1K data points. A total of 256 spectra were used to provide the equivalent of 1.4 kHz sweep width in the second frequency dimension. Free induction decays were enhanced with sine multiplications and zero-filled in the second frequency dimension before Fourier transformation. The final COSY spectra were symmetrized and displayed in the absolute value mode. All chemical shifts were referenced to tetramethylsilane (TMS).

## RESULTS AND DISCUSSION

In the CSCM technique, the $^{13}C$ shifts are correlated to the shifts of the adjoining $^{1}H$ nuclei, thus permitting the rapid assignments of either the $^{1}H$ or the $^{13}C$ spectrum whenever the other is known. For a predominantly isotactic polypropylene sample, the $^{13}C-^{1}H$ CSCM map is shown in Figure 1a; the corresponding contour plot is given in Figure 1b. The assignments for both $^{13}C$ and $^{1}H$ spectra of isotactic polypropylene have been established (13). These are summarized in Table 1.

Figure 2. $^{13}C-^{1}H$ CSCM of Stereoirregular Polypropylene

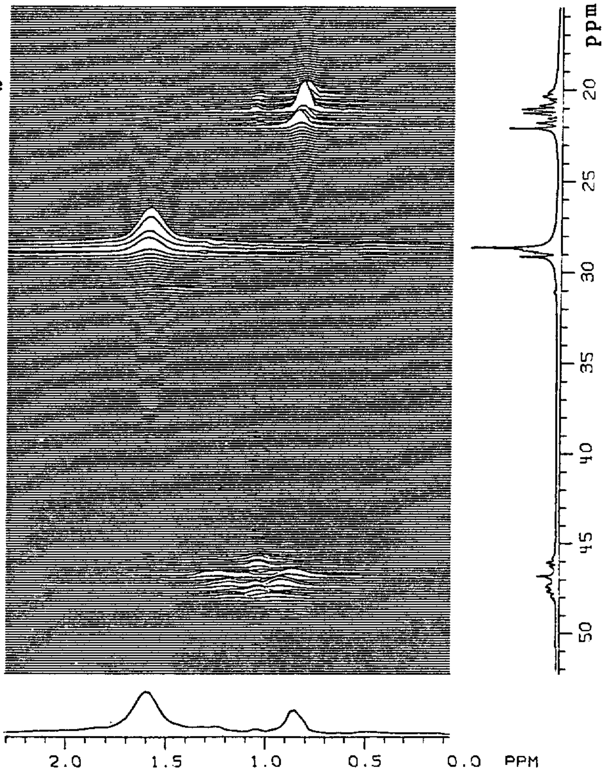


Figure 3a. CSCM Contour Plot of the Methine of Stereoirregular Polypropylene

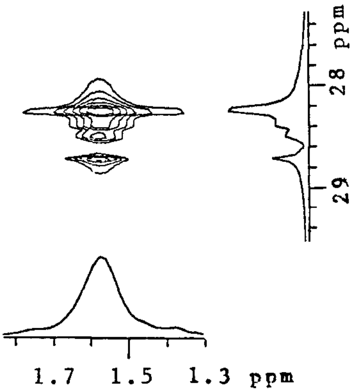


Figure 3b. CSCM Contour Plot of the Methyl of Stereoirregular Polypropylene

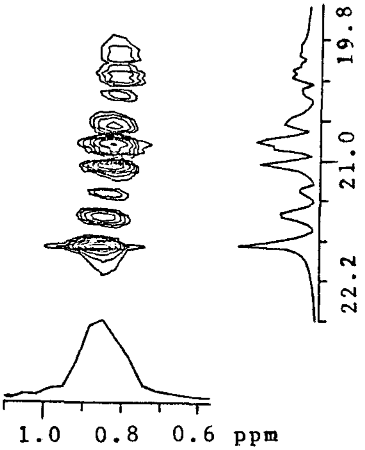


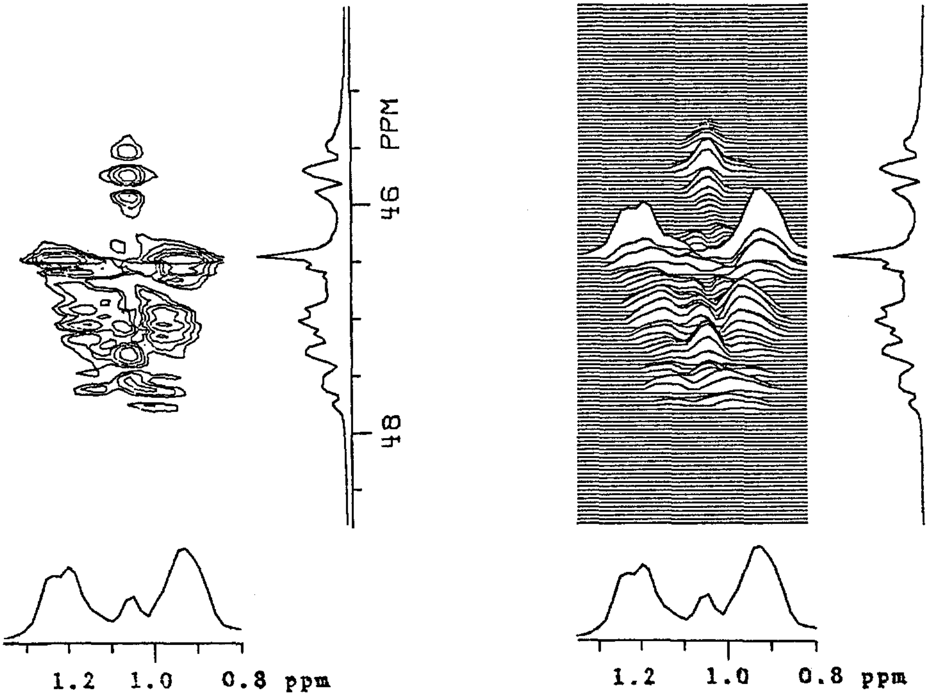
Table 2. Stereoirregular Polypropylene: Methyl Assignments

| Pentad | $^{13}C$ | $^{1}H$ Ref.13 | $^{1}H$ Ref.16 | $^{1}H$ This Work |
|---|---|---|---|---|
| mmmm | 21.8 | 0.871 | 0.871 | 0.871 |
| mmmr | 21.6 | - | - | 0.867 |
| rmmr | 21.4 | - | - | 0.859 |
| mmrr | 21.0 | - | - | 0.856 |
| mrmm | 20.8 | 0.824 | 0.849 | 0.852 |
| rmrr | 20.8 | 0.841 | - | 0.852 |
| mrmr | 20.6 | - | - | 0.846 |
| rrrr | 20.3 | 0.830 | - | 0.845 |
| rrrm | 20.2 | - | - | 0.837 |
| mrrm | 19.9 | 0.788 | 0.824 | 0.835 |

For atactic polypropylene, the spectral assignments are considerably more complex. The $^{1}H$ NMR assignments have been made by several workers (8-13), and most recently reexamined by Stehling and Knox (16). Despite the numerous publications on the subject, uncertainties still exist on the assignments of the (mrm) tetrad of methylene (11-13, 16), and the (mmrm) and (mrrm) pentads of methyl (13, 16). The $^{13}C$ NMR spectra have been assigned by Zambelli et al. (18), and Schilling and Tonelli (19). Their assignments agree with each other for the most part, although there are some disparities.

The $^{13}C$-$^{1}H$ CSCM plot of an atactic polypropylene sample produces a lot of information (Figure 2). For better visualization, separate contour plots are made for methine, methyl, and methylene (Figures 3a, b, c). Of these, the least informative is the methine region (Figure 3a). The proton lines are too squeezed together to provide separate assignments. The only distinctive feature is the isotactic (mmmm) sequence (at 28.7 ppm for $^{13}C$).

Figure 3c. CSCM Map and Contour Plot of the Methylene of the Stereoirregular Polypropylene



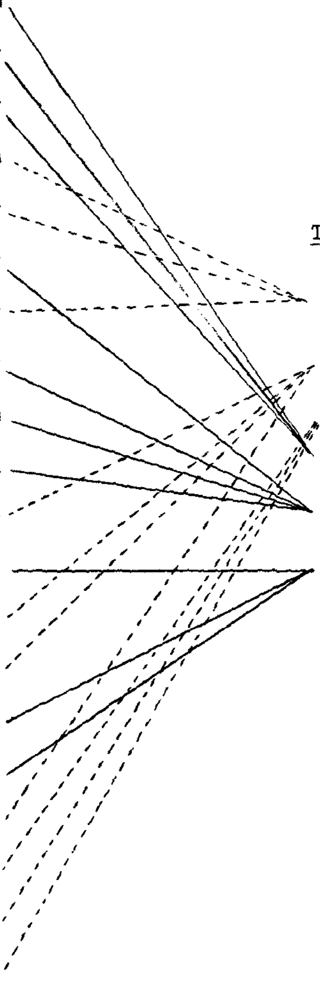
As for the 2D spectrum of the methyl carbons (Figure 3b), all the pentads in the $^{13}C$ NMR spectrum can be correlated to proton chemical shifts. The result is summarized in Table 2. It is interesting to note that the chemical shifts of the pentads occur in the same order in the $^{1}H$ spectrum as in the $^{13}C$ spectrum. Also included in Table 2 are the earlier assignments of Ferguson (13) and Stehling and Knox (16). It appears that the three pentad assignments made by Stehling and Knox (16) are correct.

A more complex case is the methylene carbons. At the tetrad level, six sequences are possible. The tetrads (mmm), (mmr), (rmr), and (rrm) have two nonequivalent methylene hydrogens, thereby producing eight distinct resonances. The methylene hydrogens for the (rrr) and (mrm) tetrads are equivalent, thus giving two resonances. The assignments for nine of these ten resonances are well established (10-16). Questions have been raised as to the exact positions of the (mrm) tetrad (11-13, 16).

The $^{13}C$-$^{1}H$ CSCM plots for the methylenes are shown in Figure 3c. The $^{13}C$ spectral assignments have been most recently carried out by Zambelli et al. (18) and Schilling and Tonelli (19). There is general agreement in the $^{13}C$ assignments of the (mrm) tetrad, viz. between 45.5 and 46.2 ppm. The CSCM plot (Figure 3c) clearly indicates that in the $^{1}H$ spectrum the (mrm) tetrad should occur at 1.05 ppm, on top of the (rrr) tetrad. Thus, this work supports the assignments of Heatley, et al. (11) and Ferguson (13). The complete $^{1}H$ assignments are summarized on the right-hand side of Table 3.

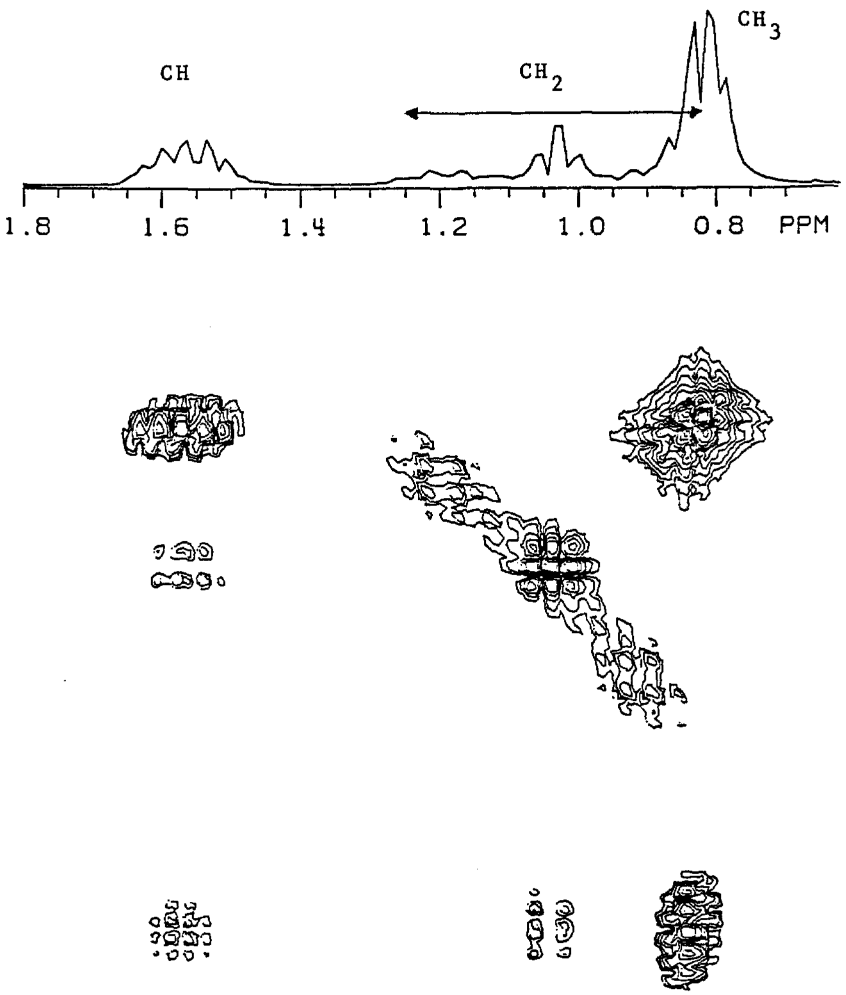
Table 3. NMR Assignments for the Methylene Regions of Stereoirregular Polypropylene

| No. | $^{13}C$ Shift | Hexad |
|---|---|---|
| 1 | 47.80 | mrmrm |
| 2 | 47.68 | mrmrr |
| 3 | 47.55 | rrmrr |
| 4 | 47.54 | mrrrm |
| 5 | 47.32 | mrrrr |
| 6 | 47.18 | mrmmr |
| 7 | 47.15 | rrrrr |
| 8 | 47.08 | rmmrr |
| 9 | 47.08 | mrmmm |
| 10 | 46.96 | rrmmm |
| 11 | 46.80 | mrrmr |
| 12 | 46.72 | rmmmr |
| 13 | 46.63 | rrrmr |
| 14 | 46.58 | mrrmm |
| 15 | 46.58 | rmmmm |
| 16 | 46.50 | mmmmm |
| 17 | 46.33 | rrrmm |
| 18 | 45.88 | rmrmr |
| 19 | 45.70 | rmrmm |
| 20 | 45.52 | mmrmm |



| Tetrad | $^{1}H$ Shift | |
|---|---|---|
| rrr | 1.075 | |
| mrr | 1.038 | 1.117 |
| mrm | 1.068 | |
| rmr | 0.974 | 1.194 |
| mmr | 0.951 | 1.242 |
| mmm | 0.888 | 1.286 |

Figure 4. ¹H COSY Plot of Atactic Polypropylene



A careful examination of the CSCM plots also helps to resolve difficulties in the $^{13}C$ assignments. For example, the methylene assignments of Refs. 18 and 19 differ in the resonance lines 11-16 (Table 3). From the CSCM plots, we are able to provide definitive assignments for these methylene hexads. The results (from CSCM) are summarized on the left side of Table 3. It is of interest to note that our assignments and the $^{13}C$ shift values appear to agree very well with the rotational isomeric state calculations of Schilling and Tonelli (19).

A $^{1}H$ shift-correlated (COSY) plot of the stereoirregular sample is shown in Figure 4. The spectrum is complex and indicate the multiple connectivities between the different spins. These connectivities are generally consistent with the CSCM results.

## CONCLUSION

In this work 2-D NMR techniques have been used to provide rather complete assignments for the tacticity of polypropylene. A particular advantage of the CSCM technique is that partial information from $^{13}C$ and $^{1}H$ spectra can be combined to provide more detailed overall spectral assignments. Similar analyses can be carried out on the $^{1}H$ and $^{13}C$ spectra of other polymer systems.

## REFERENCES

1. A. Bax, "Two-Dimensional Nuclear Magnetic Resonance in Liquids," D. Reidel Publishing Co., Boston, 1982.
2. W. E. Hull, "Two-Dimensional NMR," (Bruker Brochure), Bruker Analytische Messtechnik, Karlsruhe, W. Germany, 1982.
3. J. T. Gerig, Macromolecules, 16, 1797 (1983).
4. S. Macura and L. R. Brown, J. Magn. Resonance, 53, 529 (1983).
5. G. P. Gippert and L. R. Brown, Polymer Bull., 11, 585 (1984).
6. M. D. Bruch and F. A. Bovey, Macromolecules, 17, 978 (1984).
7. H. N. Cheng and G. H. Lee, Polymer Bull., 12, 463 (1984).
8. M. D. Bruch, F. A. Bovey, and R. E. Cais, Macromolecules, 17, 2547 (1984).
9. P. Caravatti, P. Neuenschwander, and R. R. Ernst, Macromolecules, 18, 119 (1985).
10. A. Zambelli and A. Segre, J. Polymer Sci., Part B, 6, 473 (1968).
11. F. Heatley and A. Zambelli, Macromolecules, 2, 618 (1969); F. Heatley, R. Salovey, and F. A. Bovey, ibid., 2, 619 (1969).
12. P. J. Flory and Y. Fujiwara, Macromolecules, 2, 327 (1969); P. J. Flory, ibid., 2, 613 (1970).
13. R. C. Ferguson, Macromolecules, 4, 324 (1971).
14. I. Ando and A. Nishioka, Polymer J., 2, 161 (1971).
15. A. Zambelli, L. Zetta, C. Sacchi, and C. Wolfsgruber, Macromolecules, 5, 440 (1972).
16. F. C. Stehling and J. R. Knox, Macromolecules, 8, 595 (1975).
17. A. Zambelli, P. Locatelli, G. Bajo, and F. A. Bovey, Macromolecules, 8, 687 (1975).
18. A. Zambelli, P. Locatelli, A. Provasoli, and D. R. Ferro, Macromolecules, 13, 267 (1980).
19. F. C. Schilling and A. E. Tonelli, Macromolecules, 13, 270 (1980).

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