Polymer Bulletin 12, 463–470 (1984)

Polymer Bulletin

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Two-Dimensional NMR Spectroscopy and Automated ^{1}H NMR Analysis of Ethylene-Propylene Copolymers

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Summary

The ^{13}C-^{1}H shift-correlated two-dimensional NMR spectroscopy (CSCM) is used to study ethylene-propylene copolymers. By this means, the ^{1}H NMR spectra of these copolymers can be fully interpreted. The assignments are much more complex than previously thought. Because of overlapping resonances, a direct determination of the copolymer composition cannot be made. However, the use of a first-order Markovian probability model gives not only information on composition, but also the comonomer reaction probabilities.

Introduction

Ethylene-propylene copolymers have been studied numerous times by ^{13}C NMR spectroscopy (1-8). Information available includes overall composition, comonomer sequence distribution and reactivity ratios. In contrast, ^{1}H NMR spectroscopy, although antedating ^{13}C, has not been very successful in providing equivalent information. Despite several attempts (9-13), no general scheme yet existed for the determination of copolymer composition by ^{1}H NMR. Information on comonomer sequences was even less accessible.

We have used the recently developed two-dimensional NMR (2D NMR) techniques to obtain a revised interpretation of the high-field ^{1}H NMR spectra of ethylene-propylene copolymers. 2D NMR is a family of new techniques that provide an effective means to resolve complex NMR spectra (14,15). Thus far, there are only three publications on the use of 2D NMR for synthetic polymers: ^{1}H-^{19}F shift-correlated spectroscopy of poly (p-fluorostyrene) (16); 2D NOE spectroscopy of vinylidene chloride-isobutylene copolymer (17); and ^{1}H NMR analysis of poly(vinyl alcohol) tacticity by FOCSY (18). Since ^{1}H and ^{13}C are most conveniently used to study polymers, we have concentrated on ^{13}C-^{1}H chemical shift correlated spectroscopy. As far as we know, ^{13}C-^{1}H shift correlated spectroscopy of synthetic polymers has not been previously reported.

Experimental

The copolymers used here are all experimental samples made with Ziegler-Natta stereospecific catalysts. The samples were dissolved in 1,2,4-trichlorobenzene at a concentration of 20 wt % with benzene-d_6 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 110°C. The ^{13}C-^1H shift correlated spectra were obtained using the CSCM pulse sequence included in the NMC-1280 software package. The ^{13}C spectra were obtained using a sweep width of 5 kHz and 8K data points. A total of 256 spectra were used to provide the equivalent of 1.76 kHz sweep width in the proton frequency dimension. Free induction decays in the proton frequency dimension were multiplied by sine functions before Fourier transformations and the spectra displayed in the absolute value mode. All chemical shifts were referenced to tetramethylsilane (TMS).

The computer program FIT23H (using areas of spectral regions A,B,C,D) was written in the BASIC language for the Nicolet 1280 computer. Although first-order Markov fitting of data is recommended, an option is available for second-order Markov, if needed. The program FIT23P is identical to FIT23H, except that the areas C and D are combined. Interested readers may write to the authors for a listing of either of the programs.

Results and Discussion

The ^1H NMR spectrum of an ethylene-propylene copolymer is given in Figure 1. Four regions can be noted (12-13): A, 1.82-1.40ppm; B, 1.40-1.16ppm; C, 1.16-1.00ppm; and D, 1.00-0.77ppm. Several workers have provided assignments for the spectrum (9-13). Basically, region A was assigned to methines; region B assigned to 0.5 CH_2 of propylene m-dyads plus the rest of the CH_2 groups left over; region C assigned to either CH_2 of propylene r-dyads (12), or to CH_2 located between methine and methylene groups (13); and region D assigned to 0.5 CH_2 of propylene m-dyads plus all methyl protons. From the integrated areas of the four regions, schemes have been proposed (9, 12) for the determination of composition. These schemes are, however, approximate and applicable to narrow ranges of composition.

To re-examine this problem, we have employed 2D NMR to study several samples of ethylene-propylene copolymers with different compositions: Sample 1, ethylene content 4.9 mole %; Sample 2, 21.0 mole %; and Sample 3, 50.0 mole %. The technique of heteronuclear shift-correlated spectroscopy (CSCM) permits the ^{13}C chemical shifts and the shifts of the adjoining ^1H nuclei to be correlated (14,15). A knowledge of the ^{13}C shift assignments (1,2,7) then permits the ^1H NMR spectra to be interpreted.

The ^{13}C-^1H CSCM map of Sample 3 is shown in Figure 2a. A different way of visualization is the contour plot (Figure 2b). Similar diagrams were obtained for Samples 1 and 2. Using the ^{13}C NMR assignments for these copolymers (1,2,8), we can now assign the ^1H NMR spectra. The line-to-line correlations of ^{13}C chemical shifts and ^1H regions are given in Table 1. The nomenclature used is that of Carman

Table 1. Correlation of ^{13}C and ^{1}H Chemical Shifts

Sequence	^{13}C Shift	^{1}H Region	^{1}H Shift	Second-order Markov
$S_{\alpha\alpha}$	45.0 - 46.5	B, D	0.87 - 1.27	$\gamma\delta$
$S_{\alpha\gamma}$	37.7 - 38.0	B, C	1.04 - 1.29	$2\bar{\alpha}\beta\delta$
$S_{\alpha\delta}$	37.0 - 37.6	B, C	1.04 - 1.29	$2\alpha\bar{\beta}\delta$
$T_{\gamma\gamma}$	33.1	B	1.33	$\bar{\alpha}\bar{\gamma}\delta$
$T_{\beta\gamma}$	30.7	A	1.47	$2\bar{\alpha}\gamma\delta$
$S_{\gamma\gamma}$	30.6	B	1.22	$\bar{\alpha}\bar{\beta}\delta^2$
$S_{\gamma\delta}$	30.1	B	1.22	$2\bar{\alpha}\bar{\beta}\delta\bar{\delta}$
$S_{\delta\delta}$	29.8	B	1.22	$2\bar{\alpha}\bar{\beta}\bar{\delta} - \bar{\alpha}\bar{\beta}\delta\bar{\delta}$
$T_{\beta\beta}$	28.7	A	1.57	$\alpha\gamma\delta$
$S_{\beta\delta}$	27.0 - 28.0	B	1.23 - 1.32	$2\bar{\alpha}\bar{\beta}\delta$
$S_{\beta\beta}$	24.0 - 24.9	B	1.23 - 1.32	$\bar{\alpha}\beta\delta$
$P_{\beta\beta}$	21.0 - 21.8	D	0.86	$\alpha\gamma\delta$
$P_{\beta\gamma}$	20.2 - 20.9	D	0.84	$2\bar{\alpha}\gamma\delta$
$P_{\gamma\gamma}$	19.8	D	0.82	$\bar{\alpha}\bar{\gamma}\delta$

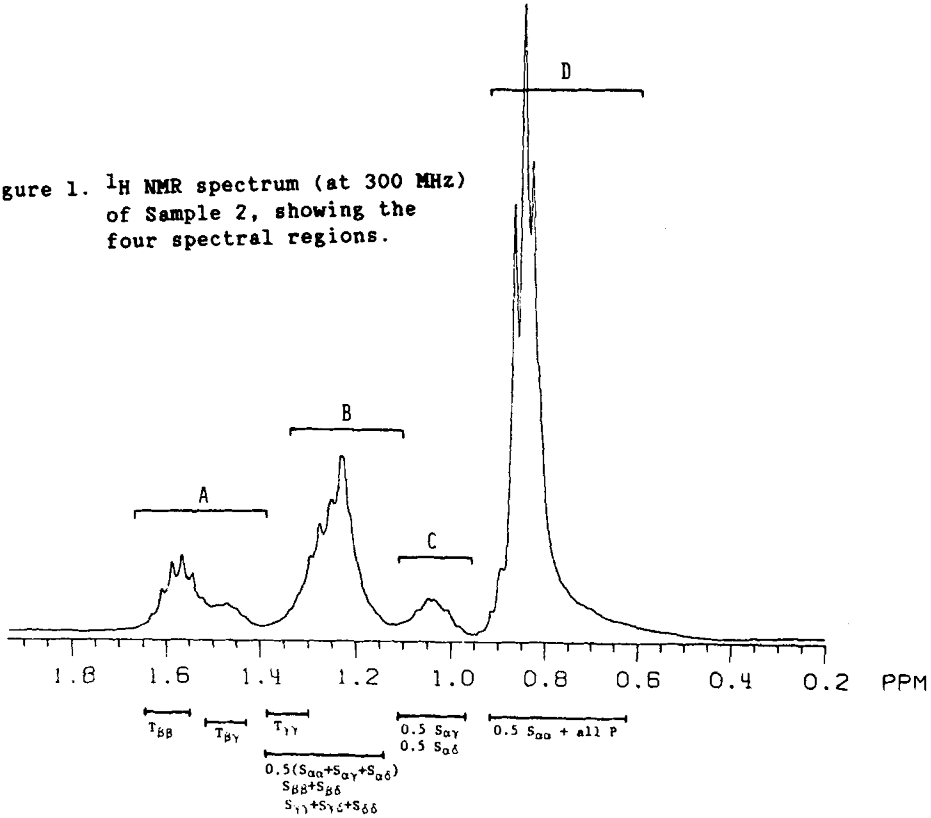

Figure 1. ^{1}H NMR spectrum (at 300 MHz) of Sample 2, showing the four spectral regions.

(1), where S, T, and P, correspond to protons attached to secondary, tertiary and primary carbons, and the Greek subscripts refer to the distances to the nearest methyl substituents. It is of interest to note that not only does $S_{\alpha\alpha}$ split in half (regions B and D), but $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ also resonate in two regions (B and C). Furthermore, the methines are spread out over a wide area (regions C and D). The assignments in Table 1 hold for stereospecific copolymers only. For non-stereospecific copolymers, racemic-$S_{\alpha\alpha}$ (CH_2) also occurs in region C and tends to complicate the spectrum even further.

The complete interpretation is summarized in Table 2. For comparison, the earlier assignments (12,13) are also given. It is apparent that the ^1H NMR spectrum is considerably more complex than what was previously thought to be. The assignments obtained in this work are also indicated in the lower half of Figure 1.

In order to obtain information concerning copolymer composition, one needs to integrate the four regions. Considering the number of protons involved in methyl, methylene, and methine groups, one can set up these equations:

$$A = T_{\beta\beta} + T_{\beta\gamma} \tag{1}$$

$$B = T_{\gamma\gamma} + S_{\alpha\alpha} + S_{\alpha\gamma} + S_{\alpha\delta} + 2\, S_{\beta\beta} + 2\, S_{\beta\delta} + 2\, S_{\gamma\gamma} + 2\, S_{\gamma\delta} + 2\, S_{\delta\delta} \tag{2}$$

$$C = S_{\alpha\gamma} + S_{\alpha\delta} \tag{3}$$

$$D = S_{\alpha\alpha} + 3(P_{\beta\beta} + P_{\beta\gamma} + P_{\gamma\gamma}) \tag{4}$$

The molar fractions of ethylene (C_2)and propylene (C_3) are related to the sums of intensities of methyls, methylenes and methines,

$$2e + p = \sum S_{ij} \tag{5}$$
$$p = \sum T_{ij} = \sum P_{ij} \tag{6}$$

and $C_2 = ke$; $C_3 = kp$, where $k = (e + p)^{-1}$.

In equations 1-6, there are more unknowns than equations. Particularly difficult is the fact that both methylenes and methines are spread out over different regions. Given the areas of the four regions by themselves, therefore, no general scheme can be devised to yield the molar compositions of the copolymers.

To bypass this problem, we have employed the Markovian reaction probability models previously used for the ^{13}C NMR spectral analysis of poly(ethylene-co-propylene) (7,19), poly(propylene-co-ethylene) (20), and 1-octene copolymers (21). The basic idea is to simulate the copolymerization of ethylene and propylene with first or second order Markov statistics. We can then associate every NMR spectral peak intensity with a theoretical expression involving reaction probabilities. These theoretical intensities are compared with the observed spectral intensities for the four regions, and adjustments made via a simplex optimization procedure until the best-fit values of the reaction probabilities are obtained. Depending on the goodness of fit, those probabilities may then provide a reasonable description of the copolymers in question.

Table 2. Assignments of the ^1H NMR Spectrum of Ethylene-Propylene Copolymers

Region	δ(ppm)	Ref. 12	Ref. 13	This Work
A	1.40 - 1.82	all T	all T	$T_{\beta\beta}$ + $T_{\beta\gamma}$
B	1.16 - 1.40	0.5 $S_{\alpha\alpha}$(m) + $S_{\alpha\gamma}$ + $S_{\alpha\delta}$ + other S_{ij}	0.5 $S_{\alpha\alpha}$ + other S_{ij}	$T_{\gamma\gamma}$ + 0.5 $S_{\alpha\alpha}$ + 0.5 $S_{\alpha\gamma}$ + 0.5 $S_{\alpha\delta}$ + remaining S_{ij}
C	1.00 - 1.16	$S_{\alpha\alpha}$(r)	$S_{\alpha\gamma}$ + $S_{\alpha\delta}$*	0.5 $S_{\alpha\gamma}$ + 0.5 $S_{\alpha\delta}$*
D	0.77 - 1.00	0.5 $S_{\alpha\alpha}$(m) + all P	0.5 $S_{\alpha\alpha}$ + all P	0.5 $S_{\alpha\alpha}$ + all P

* For atactic fraction, the $S_{\alpha\alpha}$(r) structures would occur here; see text.

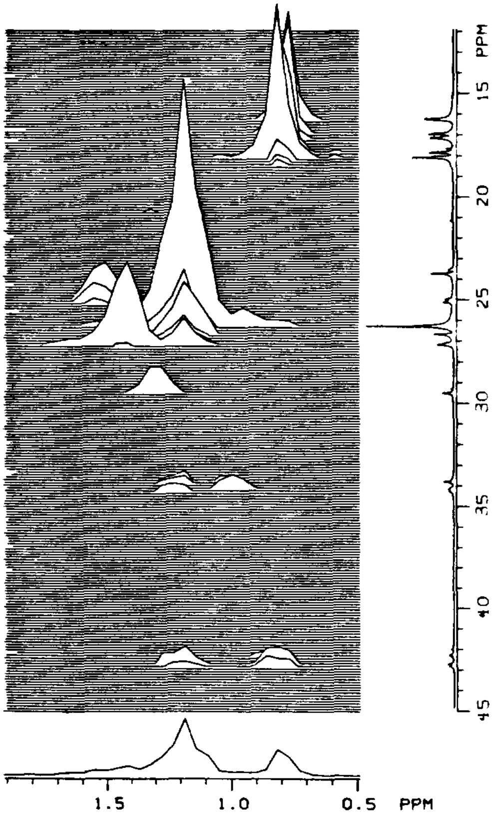

Figure 2a. ^{13}C-^1H shift-correlated map of Sample 3.

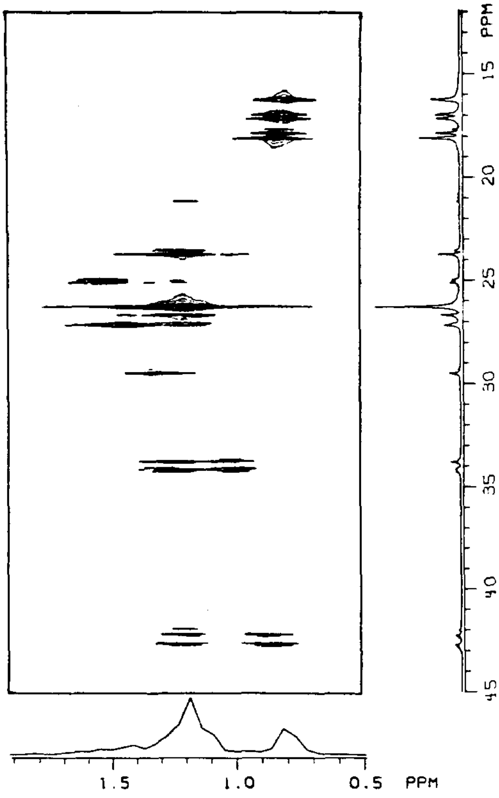

Figure 2b. ^{13}C-^1H shift-correlated contour plot of Sample 3.

The theoretical expressions for the various comonomer sequences have been previously derived (7); these are shown in the last column of Table 1. The second-order Markovian probabilities are defined as follows:

$$\begin{array}{ll} \alpha = P_{333} & \bar{\alpha} = P_{332} \\ \beta = P_{323} & \bar{\beta} = P_{322} \\ \gamma = P_{233} & \bar{\gamma} = P_{232} \\ \delta = P_{223} & \bar{\delta} = P_{222} \end{array}$$

Throughout this work, P_{ijk} is the probability of a chain terminating in units M_i and M_j, adding to monomer M_k. Also, 2 and 3 correspond to ethylene and propylene respectively.

Using equations 1-4 and substituting for the theoretical expressions, we obtained the calculated second-order Markovian intensities of the four regions of the ^1H spectrum:

Region A	$\alpha\gamma\delta + 2\bar{\alpha}\gamma\delta$
Region B	$\bar{\alpha}\bar{\gamma}\delta + \gamma\delta + 4\bar{\alpha}\delta + 4\bar{\alpha}\bar{\beta}$
Region C	$2\bar{\alpha}\delta$
Region D	$4\gamma\delta + 3\bar{\alpha}\delta$
Total Area	$10\bar{\alpha}\delta + 6\gamma\delta + 4\bar{\alpha}\bar{\beta}$

In actual practice, the second order Markovian model (involving four unknowns: $\alpha,\beta,\gamma,\delta$) is not recommended because only four known values are given (i.e. the areas of A,B,C,D). We can however, reduce the second order to the first order Markovian model by dropping the first subscript in P_{ijk}; thus $\alpha = \gamma = P_{33}$, and $\beta = \delta = P_{23}$. There are only 2 unknown parameters to solve.

The computations involved are necessarily complex. To simplify the procedure, we have written a computer program (called FIT23H) in the BASIC language that accepts as inputs the areas of regions A,B,C,D, and also the initial guess values of P_{33} and P_{23} (i.e. α and β). A simplex algorithm is then activated, that automatically gives the optimal values of the reaction probabilities. The molar composition is given by: $C_3 = k\ P_{23}$ and $C_2 = k\ (1-P_{33})$, where k is the normalization constant (such that $C_2 + C_3 = 1.0$). The results of the computerized analysis of the three copolymers are summarized in Table 3. The agreement between the ^{13}C and the ^1H NMR results is good (cf. Table 1).

For low-ethylene copolymers, special considerations should be taken because the racemic structures for methylenes also occur in region C (12,22,23). Thus, the area of region C would be too large and that of region D too small. This effect is only noticeable at low ethylene levels where the intensities of $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ are small and the effect of tacticity becomes competitive. To counter this problem, we have produced a slightly modified version of the program (called FIT23P) that accepts as input the areas of three regions, A,B and C+D. The results of this three-area fitting are also given in Table 3. With some experience, it is not difficult to decide when the three-area approach should be used, and whenever any doubt arises, both the four-area and the three-area methods should be attempted and the results compared.

Table 3. Analysis of ^{1}H NMR Data by Program FIT23H and FIT23P

	$^{13}C,C_2$	^{1}H	Input	Areas			^{1}H, C_2	Markov	Probabilities
Sample	mol %	A	B	C	D		mol %	P33	P23
1	4.9	15.7	18.4	3.2	62.6	(a)	6.4*	0.9323	0.9947
						(b)	4.3*	0.9554	0.9873
2	21.0	13.7	26.5	7.3	52.5	(a)	21.0	0.7417	0.9718
						(b)	21.0	0.7420	0.9722
3	50.0	7.3	47.3	10.9	34.4	(a)	49.8	0.4570	0.5479
						(b)	49.8	0.4798	0.5244

* (a) obtained from 4-area fit (FIT23H); (b) obtained from 3-area fit (FIT23P).

The reaction probabilities can be used to estimate dyad sequence probabilities (7): (PP) = k P_{33} P_{23}, (PE) = 2k P_{23} $(1-P_{33})$, and (EE) = k $(1-P_{33})$ $(1-P_{23})$; and comonomer reactivity ratio product.

$$r_2\, r_3 = \frac{1-P_{23}}{P_{23}} \bullet \frac{P_{33}}{1-P_{33}}$$

The results, however, should be regarded as estimates only. ^{13}C NMR analysis (6,7), which involves 24 spectral intensities, should give more accurate values for the sequence determination.

Conclusion

In this work we have used two-dimensional NMR to revise the interpretation of the ^{1}H NMR spectra of ethylene-propylene copolymers. The use of ^{13}C-^{1}H CSCM permits rapid assignments of either the ^{1}H or the ^{13}C spectrum whenever the other is known. A computerized method is also developed that simply and quickly gives the copolymer composition and Markovian reaction probabilities. Similar 2-D and computerized methods can be used for the ^{1}H NMR analysis of other copolymers.

Acknowledgment

The work reported in this paper was sponsored by the Polypropylene Resins Business Center which is now part of Himont Incorporated.

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Accepted October 1, 1984