Computerized Model Fitting Approach for the NMR Analysis of Polymers†

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A computer program (called FITCO) was developed for the general analysis of the NMR spectra of polymers through the (analytical) model-fitting approach. The method attempts to optimize the amount of information available from each spectrum and is especially useful for spectra with overlapping resonances and for studies of polymerization mechanisms. Examples are shown of the use of the program for the analysis of copolymer composition in ethyl acrylate-methyl methacrylate copolymers and for the studies of tacticity in polypropylene.

INTRODUCTION

NMR spectroscopy has been widely used for studies of polymer microstructure. Information available includes homopolymer tacticity, copolymer sequence determination, and polymer chain branching. Over the years numerous papers and texts[1-5] have appeared on this subject.

The analysis of polymer NMR spectra usually follows familiar patterns. A schematic is given in Figure 1 showing the logical steps needed. In general, NMR analysis of the polymer spectrum can be carried out at several levels. At the simplest level, one can treat the polymer spectrum as a fingerprint pattern and use it, for example, for the identification of unknown samples. If more information is needed about the polymer, then the spectrum must be interpreted. This process may be aided by model components or analogous polymers. Recently many advanced techniques[6-9] (e.g., polarization transfer, spectral editing, and two-dimensional NMR) have been developed and increasingly used in polymer NMR.[9] Assuming that all the significant resonances can be properly assigned, one must then devise computational schemes to obtain polymer compositions and sequence distributions. This general method of analysis can be referred to as the "analytical approach". (An alternative method, called the "synthetic approach", has also been developed[10,11] recently).

A more refined analytical approach is to approximate the copolymerization reaction with a statistical model (Figure 1).[12] One can then associate every spectral intensity with a theoretical expression involving reaction probability parameters. The observed and the theoretical intensities for all the spectral lines are then compared, and optimization is carried out to obtain the best-fit values of the reaction probability parameters. Depending on the goodness of fit, these probability parameters then fully describe the structure of the polymer system in question. This model-fitting approach has been successfully applied to a number of specific polymer systems.[12-17,29]

In this work a general computer program has been developed that is capable of rapidly and conveniently applying this model-fitting approach to a variety of polymer systems. Two examples are shown that illustrate this approach: compositional analysis of ethyl acrylate-methyl methacrylate copolymers and determination of polypropylene tacticity by ^{13}C NMR. This is the first time that the ^{13}C NMR spectra of ethyl acrylate-methyl methacrylate copolymers have been assigned and analyzed.

PROGRAM FITCO

The program is organized into eight sections. The relationships among the various sections are summarized in Figure 2. These sections are described as follows:

(1) The first section involves input of observed spectral intensities. It also produces a header in the output.

(2) In the second section, the user may wish to devise computational schemes to calculate polymer composition and sequence distribution.

(3) The format of the input data (in section 1) is specified in this section. One method is to use DATA-READ statements; corrections on the input can be easily made (e.g., lines 200-420, Figure 3).

(4) The expressions for reaction probability parameters are coded in this section. The common statistical models are (a) Bernoullian, (b) first-order Markov, (c) second-order Markov, (d) Coleman-Fox, and (e) enantiomorphic models. Other models have also been proposed. For the common statistical models the theoretical expressions for many stereosequences have been given in the literature.[18-20] Expressions that are not available may be derived if needed.

(5) The simplex algorithm is contained here. The purpose is to compare the observed vs. the calculated intensities and to provide a fast and logical means to obtain the optimal values of the reaction probability parameters.

(6) This section provides the output, viz., final reaction probabilities, optimal values for polymer composition and sequence distribution, and reactivity ratios product.

(7) This section provides additional opportunities for computations.

(8) Termination occurs last with provision for looping back to carry out other computations.

It is clear that sections 2, 3, 4, and 7 must be inserted by the user. The other sections need no user input.

EXAMPLES

Program FITCO in its present form is very versatile. It can be used for the compositional analysis and sequence distribution of copolymers and also for the tacticity of homopolymers. Examples are given here to illustrate these cases.

1. Compositional Analysis. The ^{13}C NMR spectrum of a copolymer of ethyl acrylate (EA) and methyl methacrylate (MMA) is shown in Figure 4. The complex pattern indicates the combined effects of copolymer sequence placements and tacticity on the ^{13}C shifts. In polymers of such complexity, complete interpretation of all resolvable resonances is very difficult and has been accomplished in very few cases. For EA-MMA copolymers, the interpretation of ^{13}C NMR spectra has not been previously reported. A close scrutiny of Figure 4, however, indicates that the backbone carbons (α and β) all resonate in the 33-55 ppm region. Except for this region, all other resonances can be assigned with some effort. The assignments were aided by comparing copolymer samples with different compositions. The results are shown in Table I and Figure 4. Of particular interest are the assignments of the methyl region (15-23 ppm) and the carbonyl region (173-180 ppm), where the effects of comonomer sequence placements

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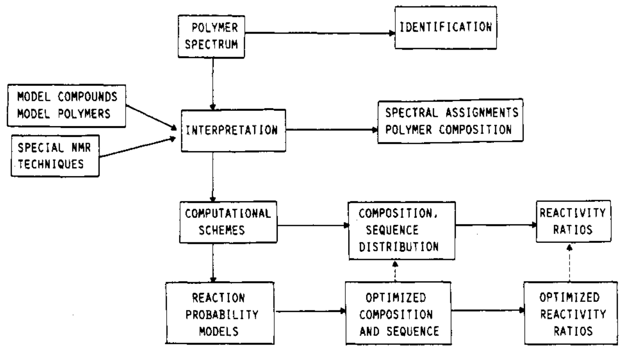

Figure 1. Logical steps in the analytical approach for the analysis of NMR spectra of polymers.

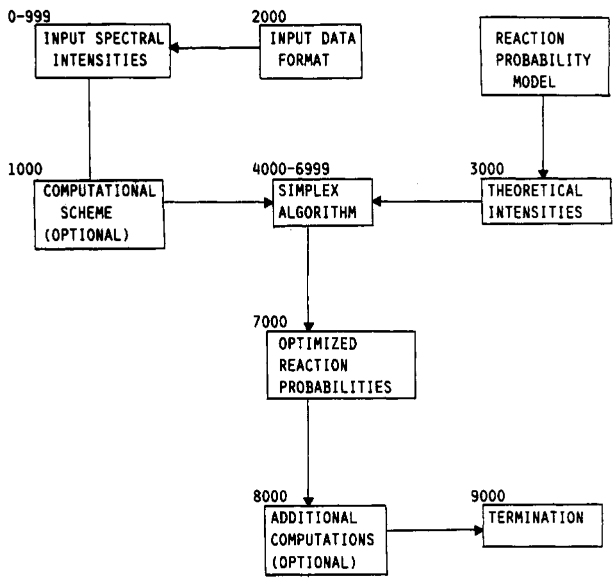

Figure 2. Schematic diagram of the FITCO program.

Table I. Assignments of the ^{13}C NMR Spectra of Ethyl Acrylate–Methyl Methacrylate Copolymers

designation[a]	shifts, ppm	assignments[b]
a_1	60.2	Z (OCH_2CH_3)
a_2	51.6	Y (OCH_3)
a_3	13.8	Z (OCH_2CH_3)
b_1	19.3–23.0	YYY (*mm*), YYZ (*m*), ZYZ
b_2	17.3–19.3	YYY (*mr*), YYZ (*r*)
b_3	15.6–17.3	YYY (*rr*)
c_1	179.0–177.4	YYY (*rr*)
c_2	177.4–176.0	YYY (*mr*), YYZ (*r*), --, YZY
c_3	176.0–175.0	YYY (*mm*), YYZ (*m*), --, ZZY
c_4	175.0–174.4	ZYZ, --
c_5	174.4–173.5	--, ZZZ

[a] *b* corresponds to the methyl resonances, and *c* to the carboxylate resonances. [b] Y = methyl methacrylate; Z = ethyl acrylate.

and tacticity have been unscrambled.

Information on copolymer composition is easy to obtain. One can simply take the ratio of peaks $b_1 + b_2 + b_3$ and a_3, for example. However, if one needs more information from this partially overlapped spectrum, then the computerized reaction probability model (FITCO) may be used. In this case one may use the Bernoullian statistical model. Let Y = MMA and Z = EA. The Bernoullian probabilities are y_m, y_r, and z, where y_m and y_r are the probabilities of the addition of meso MMA and racemic MMA to a propagating polymer radical, and z is the probability of the addition of EA. The ^{13}C NMR spectra of peaks a_1 and a_3 are not sensitive enough to the tacticity of EA to permit separate determination of z_m and z_r.

The theoretical expressions for the Bernoullian probabilities are given in Table II. These theoretical expressions are coded

Table II. Theoretical Bernoullian Expressions and Observed Intensities for Three Samples of EA–MMA Copolymers

designation	theoretical expression[a]	obsd intensities[b] 1	2	3
a_1	z	20.0	50.5	81.6
a_2	$y_m + y_r$	80.0	49.5	18.4
a_3	z	20.2	50.1	78.0
b_1	$k_1(y_m + z)^2$	19.8	24.1	17.9
b_2	$2k_1y_r(y_m + z)$	40.6	24.9	6.4
b_3	$k_1y_r^2$	27.6	8.4	2.1
c_1	$k_2y_r^2$	25.0	7.4	0.8
c_2	$2k_2y_my_r + 2k_2y_rz + k_2^2z$	51.6	33.3	6.5
c_3	$k_2y_m^2 + 2k_2y_mz + 2k_2z^2$	18.4	35.5	28.1
c_4	k_2z^2	3.0	11.0	13.7
c_5	z^3	1.0	12.7	50.8

[a] $k_1 = (y_m + y_r)/(y_m + y_r + z)^2$; $k_2 = (y_m + y_r)$; a constant multiplicative factor of 100 is used for all the expressions. [b] The intensities of the carboxy carbons (c_i) have been separately normalized to 100.

into the program FITCO (lines 3000–3999, Figure 2). The suitable input format statements are incorporated (lines 2000–2999, Figure 2). The program is ready now to accept input. A full listing of this program, written for the EA–MMA copolymer system is shown in Figure 3.

The observed intensities for three samples of EA–MMA copolymers are given in Table II. These values are directly entered into the program FITCO. Initial guess values are provided to start the simplex optimization. The program then takes over and gives the following results:

sample	y_m	y_r	z
1	0.232	0.176	0.053
2	0.578	0.322	0.164
3	0.201	0.502	0.782

Thus in all cases meso/racemic = 0.30/0.70 for the MMA tacticity. This information would be difficult and tedious to obtain by hand calculation. The use of a computerized reaction probability model thus simplifies the analysis and (by using all the observable spectral intensities) decreases the experimental error.

2. Homopolymer Tacticity. The tacticity of polypropylene is a much studied problem. The NMR assignments are well-known at present,[9b,21-23] and attempts have been made to fit the observed tacticities to different statistical models of stereospecific polymerization. At various times, Bernoullian,[22,25] Markovian,[11,22,25] and enantiomorphic site[25,26] models have been used. The latest results seem to indicate that the bicatalytic site model[24,25] is appropriate.

Program FITCO can readily handle this problem and carry out the model fitting. In this case the meso (*m*) and the racemic (*r*) additions of the propylene units can be treated like copolymerization. For the first-order Markovian process, two probabilities determine the polymer structure: P_{mr} and P_{rm}. For the second order, four parameters are needed (α, β, γ, δ), and for the bicatalytic site model,[25] three parameters (β, σ, ω). The expressions for Markovian and bicatalytic site probabilities are given in Table III.

The methyl region of the ^{13}C NMR spectrum has been generally used for tacticity measurements of polypropylene. A spectrum at 90 MHz is given in Figure 5. From the observed methyl pentad intensities, the FITCO program again can readily provide the desired reaction probabilities. The data for several samples taken from the literature are given in Table IV. Sample A resulted from the epimerization studies of Suter and Neuenschwander.[27] The data fitted the Markovian model reasonably well; the second order gave a slightly better fit than the first. As expected, P_{mr} and P_{rm} are both close to 0.5, corresponding to the totally random case. R is the response factor in the simplex algorithm. It is taken to be the mean derivation between the calculated and the observed pentad

```
1   REM  PROGRAM FITCO/EAMMA
2   REM  DESIGNED FOR THE C-13 NMR ANALYSIS OF
3   REM  ETHYL ACRYLATE/METHYL METHACRYLATE COPOLYMERS
4   REM  WRITTEN BY H. N. CHENG, HERCULES RESEARCH CENTER,
5   REM                 WILMINGTON, DELAWARE 19894, USA
6   REM
10  REM  (FOR 11-AREA FIT)
20  DIM R(9),S(10,8),O(9),Y(8),X(8)
30  DIM U(8),M(8),L(8),G(40),H(40)
100  LET V9 = 11
120  LET T = 0
130  PRINT "DATE = ";
140  INPUT A$
150  PRINT "SAMPLE DESIGNATION = ";
160  INPUT B$
170  PRINT
200  LET I = 0
210  READ V1$,V2$,C
215  LET I = I + 1
220  IF I ( T THEN 210
230  PRINT I;"-"; TAB( 6);V1$;V2$;" AREA (";C;" PPM) = ";
240  INPUT H(I)
250  IF H(I) ( 0 THEN 400
260  IF H(I) ) 1000 THEN 480
270  IF I = V9 THEN 500
290  GOTO 210
400  LET T = I + H(I)
410  IF T ( 0 THEN 480
420  RESTORE
430  GOTO 200 .
480  PRINT "WRONG ENTRY. PLEASE CHECK."
490  GOTO 230
500  REM  NORMALIZE THE INTENSITIES
510  LET H9 = H(4) + H(5)
550  IF H9 = 100 THEN 590
560  FOR I = 1 TO 6
570  LET H(I) = H(I) ● 100 / H9
590  NEXT I
610  LET H9 = 0
620  FOR I = 7 TO 11
630  LET H9 = H9 + H(I)
640  NEXT I
650  FOR I = 7 TO 11
660  LET H(I) = H(I) ● 100 / H9
670  NEXT I
900  REM  INITIATE HEADING AND PRINTOUT
905  PRINT
906  PRINT
907  PRINT
910  PRINT  TAB( 18);"C-13 NMR ANALYSIS OF"
920  PRINT  TAB( 18);"MMA-EtA COPOLYMERS"
930  PRINT
940  PRINT  TAB( 22);"SAMPLE : ";B$
950  PRINT  TAB( 22):"SAMPLE : ";A$
960  PRINT
970  PRINT "Y = MMA; Z = EA"
1000  REM  ANY COMPUTATIONS NEEDED CAN BE DONE HERE..
1001  REM  ***
1999  GOTO 5000
2000  - 3000
2010  DATA  "OBS", " B1 ",20.5
2020  DATA  "OBS", " B2 ",18.2
2030  DATA  "OBS", " B3 ",16.5
2040  DATA  "OBS", " A1 ",60.2
2050  DATA  "OBS", " A2 ",51.6
2060  DATA  "OBS", " A3 ",13.8
2070  DATA  "OBS ","C1 ",178.0
2080  DATA  "OBS ","C2 ",176.7
2090  DATA  "OBS ","C3 ",175.5
2100  DATA  "OBS ","C4 ",174.7
2110  DATA  "OBS ","C5 ",174.0
3000  REM  THIS SUBROUTINE EVALUATES THE RESPONSE R9
3004  FOR K = 1 TO N8
3005  IF X(K) ) 1.0 THEN 4700
3006  IF X(K) (  - 0.002 THEN 4700
3007  NEXT K
3010  LET G7 = X(1) + X(2)
3015  LET G9 = X(1) + X(2) + X(3)
3020  LET G8 = X(1) + X(3)
3025  LET G(1) = 100 ● G7 ● G8 ● G8 / G9 / G9
3030  LET G(2) = 200 ● G7 * X(2) ● G8 / G9 / G9
3040  LET G(3) = 100 * G7 * X(2) ● X(2) / G9 / G9
3050  LET G(4) = 100 ● X(3)
3060  LET G(5) = 100 * (X(1) + X(2))
3070  LET G(6) = 100 ● X(3)
3071  LET G6 = 100 ● G7
3080  LET G(7) = G6 ● X(2) * X(2)
3081  LET G(8) = 2 ● G6 ● X(1) ● X(2) + 2 * G6 ● X(2) ● X(3) + G6 ● G7 ●
    X(3)
3082  LET G(9) = G6 ● X(1) ● X(1) + 2 ● G6 * X(1) * X(3) + 2 ● G6 * X(3)
    ● X(3)
3083  LET G(10) = G6 ● X(3) ● X(3)
3084  LET G(11) = 100 * X(3) * X(3) ● X(3)
3090  LET G1 = 0
3100  FOR K = 1 TO V9
3110  LET G1 = G1 +  ABS (H(K) - G(K))
3120  NEXT K
3130  LET R(I) = G1 / 110
3300  RETURN
4000  REM  OPTIMIZATION OF MARKOVIAN PROBABILITIES (LL. 4000-6350)
4700  REM  FOR Y EXCEEDING LIMITS, RESET THE RESPONSE
4710  LET R(I) = 10
4720  RETURN
4750  REM  VECTOR ADDITION SUBROUTINE Y=P+C*(P-X)
4760  FOR J = 1 TO N8
4770  LET X(J) = O(J) + C1 * (O(J) - S(J9,J))
4780  NEXT J
4790  RETURN
4800  REM  THIS SUBROUTINE SORTS THE RESPONSE R9
4805  FOR I = 1 TO N9
4810  LET M(I) = L(I)
4820  LET U(I) = R(I)
4825  NEXT I
4830  FOR J = 1 TO N9 - 1
4835  FOR I = J + 1 TO N9
4840  IF U(J) (  = U(I) THEN 4875
4845  LET D9 = U(I)
4850  LET U(I) = U(J)
4855  LET U(J) = D9
4860  LET D9 = M(I)
4865  LET M(I) = M(J)
4870  LET M(J) = D9
4875  NEXT I
4880  NEXT J
4890  RETURN
4900  REM  THIS SUBROUTINE CALCULATES THE CENTROID P9
4905 . FOR J = 1 TO N8
4910  LET O(J) = 0
4915  FOR I = 1 TO N8
4916  FOR K = 1 TO N9
4917  IF M(I) = L(K) THEN 4920
4918  NEXT K
4920  LET O(J) = S(K,J) + O(J)
4925  NEXT I
4930  LET O(J) = O(J) / N8
4935  NEXT J
4940  RETURN
4950  REM  SUBROUTINE TO PRINT OUT DATA
4955  LET N7 = N7 + 1
4960  PRINT N7; TAB( 4);N6; TAB( 9);
4965  FOR I = 1 TO N8
4970  PRINT M(I);" ";
4975  NEXT I
4980  PRINT  TAB( 25);10 ● R(9); TAB( 37);
4985  FOR J = 1 TO N8
4990  LET S9 = 0.00001 ●  INT (100000 * S(J9,J))
4991  PRINT S9;" ";
4995  NEXT J
4996  PRINT  TAB( 75);"(";Z$;")"
4998  GOSUB 6200
4999  RETURN
5000  REM  SIMPLEX SUBROUTINE
5010  PRINT
5035  PRINT
5039  REM  INITIATE THE M N9 VERTICES
5040  LET N6 = 1
5050  LET N7 = 0
5060  LET N8 = 3
5070  PRINT "NUMBER OF PARAMETERS =";N8
5071  PRINT
5080  LET N9 = N8 + 1
5090  FOR I = 1 TO N9
5100  LET N7 = N7 + 1
5110  PRINT "VERTEX: ";I
5120  FOR J = 1 TO N8
5125  PRINT  TAB( 3);"PARAMETER # ";J;
5130  INPUT S(I,J)
5140  LET X(J) = S(I,J)
5150  NEXT J
5160  GOSUB 3000
5165  LET L(I) = I
5170  NEXT I
5171  PRINT
5172  PRINT
5180  PRINT "VX"; TAB( 5);"SX"; TAB( 10);"VTS RET/D";
5181  PRINT  TAB( 26);"R VALUE"; TAB( 38);"PARAMETERS"
5182  PRINT
5190  FOR I = 1 TO N9
5200  PRINT I; TAB( 4);N6; TAB( 25);10 * R(I); TAB( 37);
5220  FOR J = 1 TO N8
5230  PRINT S(I,J);" ";
5240  NEXT J
5245  PRINT
5250  NEXT I
5260  REM  BEGIN SIMPLEX LOOP HERE
5270  LET N6 = N6 + 1
5280  GOSUB 4800
5290  GOSUB 4900
5300  REM  CALCULATE Y
5310  GOSUB 6300
5320  FOR J = 1 TO N8
5330  LET Y(J) = 2 ● O(J) - S(J9,J)
5340  LET X(J) = Y(J)
5350  LET S(10,J) = Y(J)
5370  NEXT J
5380  LET I = 9
5390  GOSUB 3000
5395  LET J9 = 10
5399  LET Z$ = " "
5400  GOSUB 4950
5404  GOSUB 6300
5410  REM  TEST FOR RESPONSE OF Y HERE
5420  LET R1 = R(9)
5430  IF R1 ( U(1) THEN 5500
5440  IF R1 ) U(N9 - 1) THEN 5630
5450  FOR J = 1 TO N8
5460  LET S(J9,J) = Y(J)
5470  NEXT J
5475  LET R(J9) = R1
5480  LET L(J9) = N7
5490  GOTO 5260
5500  REM  CASE WHERE INTERVAL EXPANSION MAY BE NEEDED
5505  LET M8 = 1
5510  LET C1 = 2
5520  GOSUB 4750
5530  LET I = 9
5540  GOSUB 3000
5550  LET R2 = R(9)
5560  IF R2 )  = U(1) THEN 5450
5570  FOR J = 1 TO N8
5580  LET S(J9,J) = X(J)
5585  NEXT J
5586  ON M8 GOTO 5587,5590,5592
5587  LET Z$ = "E"
5588  GOTO 5595
5590  LET Z$ = "M1"
5591  GOTO 5595
5592  LET Z$ = "M2"
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5595  GOSUB 4950
5600  LET R(J9) = R2
5610  LET L(J9) = N7
5620  GOTO 5260
5630  REM  CASE WHERE INTERVAL CONTRACTION MAY BE NEEDED
5640  IF R1 ( U(N9) THEN 5770
5650  LET C1 =  - 0.5
5660  GOSUB 4750
5670  LET I = 9
5680  GOSUB 3000
5690  LET R3 = R(9)
5691  IF R3 ) U(N9) THEN 6000
5710  FOR J = 1 TO N8
5720  LET S(J9,J) = X(J)
5730  NEXT J
5731  LET Z$ = "C"
5732  GOSUB 4950
5735  LET R(J9) = R(9)
5740  LET L(J9) = N7
5760  GOTO 5260
5770  LET C1 = 0.5
5780  GOSUB 4750
5790  LET I = 9
5800  GOSUB 3000
5809  IF R3 ) R1 THEN 6100
5810  LET R3 = R(9)
5830  GOTO 5710
6000  REM  MASSIVE CONTRACTION APPLIED HERE
6001  LET M8 = 2
6003  LET C1 = .05
6004  GOSUB 4750
6005  GOTO 5530
6100  LET M8 = 3
6103  LET C1 =  - 0.1
6104  GOSUB 4750
6105  GOTO 5530
6200  REM  OPTIONAL TERMINATION
6210  IF N7 = 100 THEN 7000
6220  IF N7 - 10 *  INT (N7 / 10) ) 0.1 THEN 6290
6230  PRINT "MORE ? (YES/NO/RECAL)";
6240  INPUT V$
6250  IF V$ = "RECAL" THEN 5035
6260  IF V$ = "NO" THEN 7000
6270  IF V$ = "YES" THEN 6290
6280  GOTO 6240
6290  RETURN
6300  REM  REPLACEMENT RESPONSE
6310  FOR K = 1 TO N9
6320  IF L(K) = M(N9) THEN 6340
6330  NEXT K
6340  LET J9 = K
6350  RETURN
7000  REM  PRINTOUT OF FITTED RESULTS
7110  PRINT
7120  PRINT "NO"; TAB( 11);"I(OBS)"; TAB( 31);"I(CALC)"; TAB( 52);"DEV"
7130  PRINT
7140  FOR I = 1 TO V9
7150  PRINT I; TAB( 10);H(I); TAB( 31);G(I); TAB( 52);(H(I) - G(I))
7160  NEXT I
7170  PRINT
7180  FOR K = 1 TO N8
7190  PRINT " X(";K;") = ";X(K)
7200  NEXT K
7210  PRINT
8000  REM  CALCULATED COMPOSITION AND SEQUENCE DISTRIBUTION
8010  REM  ***
8028  REM  OTHER ADDITIONAL COMPUTATIONS MAY BE DONE HERE
9000  REM  END OF THE PROGRAM
9910  PRINT
9920  PRINT "DO YOU WANT TO PLAY MORE WITH THE DATA ?";
9930  INPUT V$
9940  IF V$ = "YES" THEN 5010
9950  IF V$ = "NO" THEN 9970
9960  GOTO 9930
9970  PRINT "ANOTHER SAMPLE ?";
9971  INPUT V$
9972  IF V$ = "YES" THEN 9981
9973  IF V$ = "NO" THEN 9998
9980  GOTO 9971
9981  RESTORE
9982  PRINT
9983  PRINT
9984  GOTO 120
9998  CALL EXIT
9999  END
```

Figure 3. Listing of the program FITCO, as applied to the EA–MMA copolymer case.

Table III. ^{13}C Shifts of the Methyl Pentads of Polypropylene with Reaction Probabilities

^{13}C shift, ppm	assignment	first-order Markov	second-order Markov	bicatalytic sites
21.8	*mmmm*	$P_{rm}(1 - P_{mr})^3$	$\alpha^2\gamma\delta$	$\omega(1 - 5\beta + 5\beta^2) + (1 - \omega)\sigma^4$
21.6	*mmmr*	$2P_{mr}P_{rm}(1 - P_{mr})^2$	$2\alpha\bar{\alpha}\gamma\delta$	$\omega(2\beta - 6\beta^2) + 2(1 - \omega)\sigma^3(1 - \sigma)$
21.4	*rmmr*	$P_{rm}P_{mr}^2(1 - P_{mr})$	$\bar{\alpha}^2\gamma\delta$	$\omega\beta^2 + (1 - \omega)\sigma^2(1 - \sigma)^2$
21.0	*mmrr*	$2P_{mr}P_{rm}(1 - P_{mr})(1 - P_{rm})$	$2\overline{\alpha\beta}\gamma\delta$	$\omega(2\beta - 6\beta^2) + 2(1 - \omega)\sigma^2(1 - \sigma)^2$
20.8	*mrmm* + *rmrr*[*]	$2P_{mr}P_{rm}^2(1 - P_{mr})$ $+2P_{rm}P_{mr}^2(1 - P_{rm})$	$2\bar{\alpha}\beta\gamma\delta$ $+2\overline{\alpha\beta\gamma}\delta$	$2\omega\beta^2 + 2(1 - \omega)\sigma^3(1 - \sigma)$ $+2\omega\beta^2 + 2(1 - \omega)\sigma(1 - \sigma)^3$
20.6	*mrmr*	$2P_{mr}^2P_{rm}^2$	$2\bar{\alpha}\beta\bar{\gamma}\delta$	$2\omega\beta^2 + 2(1 - \omega)\sigma^2(1 - \sigma)^2$
20.3	*rrrr*	$P_{mr}(1 - P_{rm})^3$	$\overline{\alpha\beta}\delta^2$	$\omega\beta^2 + (1 - \omega)(1 - \sigma)^4$
20.2	*rrrm*	$2P_{mr}P_{rm}(1 - P_{rm})^2$	$2\overline{\alpha\beta}\delta\bar{\delta}$	$2\omega\beta^2 + 2(1 - \omega)\sigma(1 - \sigma)^3$
19.9	*mrrm*	$P_{mr}P_{rm}^2(1 - P_{rm})$	$\overline{\alpha\beta}\delta^2$	$\omega(\beta - 3\beta^2) + (1 - \omega)\sigma^2(1 - \sigma)^2$
	total	$P_{mr} + P_{rm}$	$\overline{\alpha\beta} + 2\bar{\alpha}\delta + \gamma\delta$	1.00

[*] Not resolved.

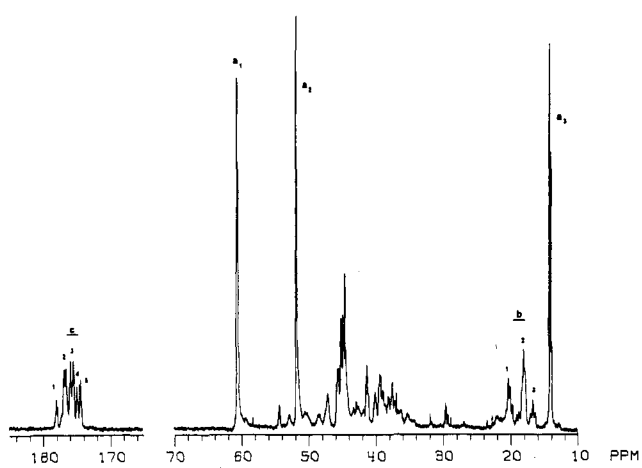


Figure 4. ^{13}C NMR spectrum at 90 MHz of ethyl acrylate–methyl methacrylate copolymer.

intensities; thus, the smaller the R, the better is the fit.

The rest of the data in Table IV were taken from the heterogeneous catalysis work of Bukatov et al.[28] Sample B is the fraction soluble in boiling heptane, whereas sample C is the insoluble fraction. The soluble fraction B can be readily fitted to either first-order or second-order Markovian or bisite models, the latter giving only slight improvement. For the insoluble fraction C, either the second-order Markovian or the

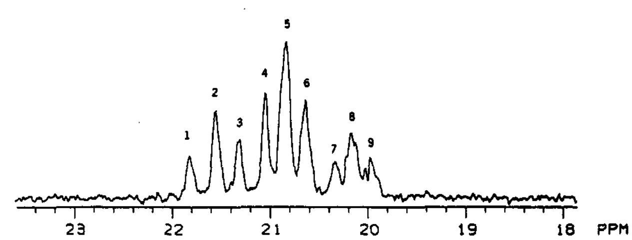
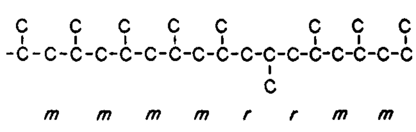


Figure 5. ^{13}C NMR spectrum at 90 MHz of the methyl region of polypropylene.

bisite model is preferred. The rather extreme values of the reaction probability parameters reflect the presence of steric propagation error, which generates only *mmmr*, *mmrr*, *mrrm* pentads.



As an example of how the FITCO program can be modified, the statements that need to be changed for polypropylene tacticity analysis are given in Figure 6. Otherwise the same program listing as in Figure 3 can be used.

3. Comonomer Sequence Determination. The use of computerized reaction probability models for sequence distributions has been previously reported for a number of copolymer

Table IV. Observed Intensities and Calculated Reaction Probabilities for the Methyl Pentads of Polypropylene

		sample A		sample B			sample C		
no.	pentad	obsd	calcd (M1)	obsd	calcd (M1)	calcd (BS)	obsd	calcd (M2)	calcd (BS)
1	*mmmm*	0.05	0.05	0.49	0.49	0.49	~0.91	0.91	0.91
2	*mmmr*	0.11	0.11	0.10	0.13	0.10	~0.05	0.04	0.04
3	*rmmr*	0.07	0.06	≤0.02	0.01	0.01	0	0.00	0.00
4	*mmrr*	0.11	0.12	0.11	0.10	0.11	~0.04	0.04	0.04
5	*rrmr* + *mmrm*	0.26	0.26	0.06	0.06	0.09	0	0.00	0.00
6	*rmrm*	0.12	0.14	≤0.01	0.00	0.03	0	0.00	0.00
7	*rrrr*	0.06	0.06	0.10	0.10	0.11	0	0.00	0.00
8	*rrrm*	0.15	0.13	0.06	0.08	0.07	0	0.00	0.00
9	*mrrm*	0.07	0.07	0.05	0.02	0.04	0	0.02	0.02
				First-Order Markov (M1)					
	P_{mr}		0.54		0.118			0.023	
	P_{rm}		0.50		0.295			0.995	
	R		0.0076		0.0122			0.0103	
				Second-Order Markov (M2)					
	P_{mmm}		0.449		0.882			0.980	
	P_{mrm}		0.462		0.302			0.010	
	P_{rmm}		0.478		0.877			0.992	
	P_{rrm}		0.513		0.295			0.991	
	R		0.0063		0.0122			0.0043	
				Bisite Model (BS)					
	β					0.058			0.018
	σ					0.249			0.428
	ω					0.669			0.998
	R					0.0096			0.0040

```
1   REM  PROGRAM FITCO/PPTAC
2   REM  DESIGNED FOR THE ANALYSIS OF METHYL PENTAD
3   REM  OF POLYPROPYLENE AS OBSERVED VIA C-13 NMR
4   REM  WRITTEN BY H. N. CHENG, HERCULES RESEARCH CENTER,
5   REM               WILMINGTON, DELAWARE 19894, USA
10  REM
90  PRINT "ANALYSIS OF METHYL PENTADS OF POLYPROPYLENE"
95  PRINT
100  LET V9 = 9
210  READ V1$
230  PRINT I;"-"; TAB( 6);V1$;" AREA = ";
500  REM  NORMALIZE THE INTENSITIES
510  LET H9 = 0
520  FOR I = 1 TO V9
530  LET H9 = H9 + H(I)
540  NEXT I
550  IF H9 = 100 THEN 900
560  FOR I = 1 TO V9
570  LET H(I) = H(I) ● 100 / H9
580  NEXT I
920  PRINT  TAB( 18);"ANALYSIS OF METHYL PENTAD OF PP"
960  PRINT
1000  REM  ***
1001  REM  ANY COMPUTATIONS NEEDED CAN BE DONE HERE
1002  REM  ***
1003  FOR K = 1 TO V9
1004  IF H(K) (  ) 0 THEN 1006
1005  LET H(K) = 0.00001
1006  NEXT K
1010  LET P1 = 2 ● H(1) / H(2)
1020  LET E1 = P1 / (1 + P1)
1030  LET P4 = 2 ● H(7) / H(8)
1040  LET E4 = 1 / (1 + 2 ● P4)
1050  LET P2 = H(4) / H(2)
1060  LET E2 = 1 - P2 * E1
1070  LET P3 = H(4) / H(8)
1080  LET E3 = P3 ● (1 - E4)
1090  PRINT "ESTIMATED 2ND ORDER MARKOV--Pmmm, Pmrm, Prmm, Prrm"
1100  PRINT  TAB( 10);E1,"(";E2;")","(";E3;")",E4
1110  PRINT
1999  GOTO 5000
2000  REM  THIS SUBROUTINE PROVIDES FORMAT FOR INPUT DATA
2010  DATA  "MMMM"
2020  DATA  "MMMR"
2030  DATA  "RMMR"
2040  DATA  "MMRR"
2050  DATA  "XMRX"
2060  DATA  "MRMR"
2070  DATA  "RRRR"
2080  DATA  "RRRM"
2090  DATA  "MRRM"
3009  ON M9 + 1 GOTO 9000,3010,3100,3200
3010  REM  FIRST ORDER MARKOV
3011  LET X(3) = X(1)
3012  LET X(4) = X(2)
3100  REM  SECOND ORDER MARKOV
3110  LET X(5) = 1 - X(1)
3111  LET X(6) = 1 - X(2)
3112  LET X(7) = 1 - X(3)
3113  LET X(8) = 1 - X(4)
3120  LET Q9 = 100 / (X(5) * X(6) + 2 * X(5) * X(4) + X(3) ● X(4))
3121  LET G(1) = Q9 * X(1) * X(1) ● X(3) ● X(4)
3122  LET G(2) = Q9 * 2 * X(1) ● X(3) * X(4) * X(5)
3123  LET G(3) = Q9 ● X(3) ● X(4) * X(5) * X(5)
3124  LET G(4) = Q9 * 2 * X(5) ● X(6) * X(3) ● X(4)
3125  LET G(5) = Q9 * 2 * (X(5) * X(2) * X(3) * X(4) + X(5) * X(6) * X(7
   ) * X(4))
3126  LET G(6) = Q9 * 2 * X(5) * X(2) * X(7) * X(4)
3127  LET G(7) = Q9 * X(5) * X(6) * X(8) * X(8)
3128  LET G(8) = Q9 * 2 * X(5) * X(6) * X(4) * X(8)
3129  LET G(9) = Q9 * X(5) * X(6) ● X(4) ● X(4)
3130  GOTO 3400
3200  REM  BI-CATALYTIC SITES MODEL
3210  LET G1 = X(1) ● X(1)
3220  LET G2 = 1 - X(2)
3230  LET G3 = 1 - X(3)
3240  LET G(1) = X(3) * (1 - 5 * X(1) + 5 ● G1) + G3 * X(2) ^ 4
3250  LET G(2) = X(3) * (2 ● X(1) + 6 ● G1) + 2 ● G3 ● G2 ● X(2) ^ 3
3260  LET G(3) = X(3) * G1 + G3 * (X(2) ● G2) ^ 2
3270  LET G(4) = X(3) ● (2 * X(1) + 6 * G1) ● 2 * G3 ● X(2) ● X(2) * G2 ●
   G2
3280  LET G(5) = 4 * X(3) ● G1 + 2 * G3 ● X(2) * G2 * (X(2) ● X(2) + G2 ●
   G2)
3290  LET G(6) = 2 * X(3) ● G1 ● 2 ● G3 * X(2) * X(2) ● G2 ● G2
3300  LET G(7) = X(3) * G1 + G3 ● G2 ^ 4
3310  LET G(8) = 2 ● X(3) * G1 + 2 ● G3 * X(2) ● G2 ^ 3
3320  LET G(9) = X(3) ● (X(1) - 3 * G1) + G3 * X(2) * X(2) ● G2 * G2
3330  FOR K = 1 TO V9
3340  LET G(K) = 100 ● G(K)
3350  NEXT K
3400  LET G4 = 0
3410  FOR K = 1 TO V9
3420  LET G4 = G4 +  ABS (H(K) - G(K))
3430  NEXT K
3440  LET R(I) = G4 / V9 / 10
3500  RETURN
5000  REM  SIMPLEX SUBROUTINE
5035  PRINT "INDICATE MODEL (1=MARKOV 1:  2=MARKOV 2:  3=BI-SITE)";
5036  INPUT M9
5037  PRINT "MARKOV 1--P(MM).P(RM): MARKOV 2--P(MMM).P(MRM),P(RMM),P(RRM
   ):"
5038  PRINT "BISITE MODEL---BETA,SIGMA,OMEGA"
5039  REM  INITIATE THE M N9 VERTICES
5040  LET N6 = 1
5050  LET N7 = 0
5055  LET N8 = M9
5056  IF N8 = 3 THEN 5070
5060  LET N8 = M9 * 2
8000  REM  CALCULATED COMPOSITION AND SEQUENCE DISTRIBUTION
8010  REM  ***
8028  REM  OTHER ADDITIONAL COMPUTATIONS MAY BE DONE HERE
8030  REM  ***
8650  ON M9 GOTO 8660,8690,8740
8660  PRINT "PMM =";X(1)
8670  PRINT "PRM =";X(2)
8680  GOTO 8770
8690  PRINT "PMMM =";X(1)
8700  PRINT "PMRM =";X(2)
8710  PRINT "PRMM =";X(3)
8720  PRINT "PRRM =";X(4)
8730  GOTO 8770
8740  PRINT "BETA =";X(1)
8750  PRINT "SIGMA =";X(2)
8760  PRINT "OMEGA =";X(3)
8770  PRINT

ALSO DELETE LINES 590-670;970;2100-2110;3020-3090;7190-7210 FROM THE
FITCO/EAMMA CASE.
```

Figure 6. Statements needed in program FITCO to carry out model fitting in homopolymer tacticity.

systems, e.g., poly(ethylene-*co*-propylene),[12,13,17] poly(propylene-*co*-butylene),[14] poly(ethylene-*co*-1-octene),[15] and poly(propylene-*co*-1-octene).[15] It has been found that the computerized analytical approaches generally provide very precise values for the comonomer sequences even for copolymer spectra that contain overlapping resonances.[15,17]

4. Chain Branching. The same approach has also been used for the determination of chain branching in low-density polyethylene.[29]

USES AND LIMITATIONS

A major advantage of this computerized approach to polymer analysis is that all the NMR spectral lines are used for the calculations. Thus, experimental errors are minimized by this procedure. In addition, because the method checks for the intensities of all the resonance lines, if a wrong (or an uncertain) assignment is present, it often shows up when the analyses are carried out for a large number of samples. Thus, the model-fitting approach can assist in spectral interpretation.

In dealing with many types of polymers, this computerized approach has been found to be most valuable for the analysis of ^{1}H or ^{13}C spectra with overlapping resonances. In these cases, although it is possible sometimes to devise computational schemes involving additions or subtractions of spectral intensities to obtain information of polymer composition or comonomer sequence distributions, in reality accurate numbers are often difficult to obtain, and if the overlap is severe, only estimates can be made. The use of the computerized reaction probability models thus can obviate these difficulties and provide precise results not otherwise available.

A final area of application is in the investigation of copolymerization mechanisms. Frequently one needs more information about a polymer system than simply the polymer composition and sequences. One may, for example, be interested in knowing the sensitivity of the reactivity ratios to changes in the initiators or the reaction conditions. One may be interested in testing the conformity of a polymerization process to a particular reaction probability model (e.g., Markovian or enantiomorphic). The tacticity of polypropylene is a good example. In these cases one can "squeeze" additional information from the NMR spectra with the present approach.

A limitation of the method is that the reaction probabilities are usually extracted from the NMR spectra of the final polymer product. As such, it only represents an average over the total polymerization process. If one is interested in the detailed description of the polymerization process as a function of conversion, one must repeat the analysis on polymer samples obtained at proper time intervals in the reaction vessel.

COMPARISON WITH SYNTHETIC APPROACH

In the synthetic approach proposed earlier,[10] one starts with a reaction probability model, obtains the expected sequence distributions, and then simulates a NMR spectrum. Comparisons can then be made visually of the experimental and the predicted spectra.

statistical model → sequence distribution →
NMR shift behavior → NMR spectrum

The analytical approach reverses the process, starting with the spectrum and ending in the reaction probability parameters. The synthetic approach has the advantage that it is purely a computer experiment, with no polymer samples or spectrometer needed. Thus, different copolymers can be readily simulated. The analytical approach is much more rigorous but more time-consuming. It requires quantitative NMR spectrum with reliable spectral integrations and produces reaction probabilities that are most consistent with the spectral data at hand. The two approaches are actually complementary, and in many cases, the joint application of both approaches is desirable. In any unknown copolymer, for example, one can first use the synthetic approach to simulate a spectrum as an aid to spectral interpretation. Once the spectral lines are assigned, the analytical approach can be used routinely for the analysis of these copolymer samples.

EXPERIMENTAL SECTION

The program FITCO was written in BASIC for the Apple IIe. A listing of the program is shown in Figure 3. Alternate versions have also been made for Nicolet 1280 and PRIME 9950 computers. Interested readers may write to the author for copies of the Nicolet and the PRIME versions.

The ethyl acrylate–methyl methacrylate copolymers were either purchased (Monomer-Polymer, Trevose, PA) or made via free radical polymerization. These were dissolved as 15% (w/w) solutions in $CDCl_3$. The spectra were taken on a Nicolet NT360WB spectrometer at 90.55 MHz and ambient temperature. The free induction decays were stored in 16K memory addresses, zero-filled upon processing with a spectral window of 20000 Hz. A pulse angle of 45° was used with 4-s delay. The T_1 values range from less than 0.2 s for the backbone carbons to approximately 0.6 s for the side chains. Combined with gated decoupling (thereby eliminating nuclear Overhauser effect), the conditions chosen should provide essentially quantitative spectra. Only carbonyl carbons give problems in quantitation. This has been taken care of in the program FITCO by separately normalizing all five carbonyl intensities to 100. (See Table II, footnote *b*.)

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