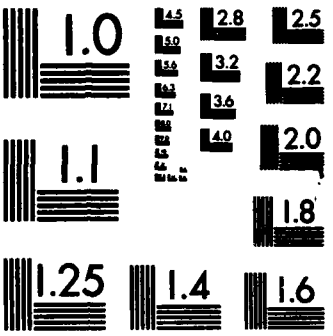
AD-A184 349 SOLID STATE C-13 NMR CHARACTERIZATION OF TEXTILES: 1/1
QUALITATIVE AND QUANTI (U) UNIVERSITY OF SOUTHERN
MISSISSIPPI HATTIESBURG DEPT OF POLYME
UNCLASSIFIED R F COLLETTI ET AL 27 AUG 87 F/G 11/5 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

(12)

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0659

Technical Report No. 3

SOLID STATE C-13 NMR CHARACTERIZATION OF TEXTILES: QUALITATIVE AND QUANTITATIVE ANALYSIS

by

Ronald F. Colletti and Lon J. Mathias

Prepared for Publication in

J. Appl. Polym. Sci., in press

Department of Polymer Science
University of Southern Mississippi
Southern Station Box 10076
Hattiesburg, MS 39406-0076

87 9 1 014

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION NONE	1b. RESTRICTIVE MARKINGS NONE
2a. SECURITY CLASSIFICATION AUTHORITY NONE	3. DISTRIBUTION/AVAILABILITY OF REPORT UNLIMITED
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE NONE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #3	5. MONITORING ORGANIZATION REPORT NUMBER(S) ONR N00014-86-K-0659
6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Avenue Arlington , VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION

11. TITLE (Include Security Classification)
Solid State C-13 NMR Characterization of Textiles: Qualitative and Quantitative Analys

12. PERSONAL AUTHOR(S)
Ronald F. Colletti and Lon J. Mathias

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 8-86 TO 8-87	87-8-27	

16. SUPPLEMENTARY NOTATION
J. Appl. Polym. Sci.

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Cross-polarization magic angle spinning (CP/MAS) carbon 13 NMR was used to qualitatively characterize textiles of various compositions. Rapid and accurate determination of cotton/polyester blends was accomplished with minimal sample preparation. Qualitative identification was demonstrated for various fiber blends including mislabeled samples. This technique demonstrates ability to characterize as-obtained fibers and fabrics and should extend to composite reinforcing materials and prepregs.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION
22a. NAME OF RESPONSIBLE INDIVIDUAL Lon J. Mathias	22b. TELEPHONE (Include Area Code) (601)266-4868 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PA

SOLID STATE C-13 NMR CHARACTERIZATION OF TEXTILES: QUALITATIVE AND QUANTITATIVE ANALYSIS

RONALD F. COLLETTI and LON J. MATHIAS*

Department of Polymer Science

University of Southern Mississippi

Hattiesburg, MS 39406-0076

Synopsis

Cross-polarization magic angle spinning (CP/MAS) carbon 13 NMR was used to qualitatively and quantitatively characterize textiles of various compositions. Rapid and accurate determination of cotton/polyester blends was accomplished with minimal sample preparation. Qualitative identification was demonstrated for various fiber blends.

INTRODUCTION

Only within the past decade has the textile industry replaced wet chemical analysis for composition of fabrics and fibers with modern instrumental techniques. The advantages of

these new techniques are that they are quick, generally non-destructive, less operator intensive, do not require difficult sample handling procedures, and are almost always more precise and more accurate. Previous instrumental analysis in the textile industry has included X-ray diffraction, infrared spectroscopy (IR), and electron spectroscopy for chemical analysis (ESCA)[1]. Nuclear magnetic resonance spectroscopy (NMR) has also been utilized to study textiles[2], and the advent of powerful solid state NMR spectrometer systems allows characterization with little or no preparation.

Specific NMR applications have included both qualitative and quantitative analyses. Proton broad line NMR was used to examine segment mobility in synthetic fibers[3] and the adsorption of water in oriented fibers[4]. Cellulose and regenerated cellulose were also studied with wide line proton NMR[5] as well as with solid state carbon-13 NMR[6,7]. Cotton/polyester blends have been examined quantitatively by IR[1], X-ray diffraction[8], density measurements[9] and ESCA[10].

The technique presented here allows rapid, accurate, and non-destructive compositional determination of cotton/polyester blends and general qualitative identification of textile fibers.

EXPERIMENTAL

Textile samples were obtained from clothing and cut into approximately 5cm by 2cm pieces. The actual composition of the fabric was taken to be that on the garment label. Each sample was rolled and placed in a rotor and tamped for best packing and spinning. If a sample did not spin well, a small amount of fine silica gel was put into the spinner to help balance it.

The carbon-13 NMR spectra were recorded at 50.32 MHz on a Bruker MSL-200 Spectrometer equipped with a magic angle spinning probe and cross polarization circuitry to satisfy the Hartmann-Hahn condition. Spectra were acquired with a contact time of 5 ms, an acquisition time of 50 ms and a recycle time of 3 s. The 90 degree pulse was set at 5 us and the magic angle was set using potassium bromide. Between 1,000 and 3,000 FID's were collected for each sample. Adamantane was used to set the Hartmann-Hahn relationship and as the chemical shift reference. Fused alumina rotors with Kel-F caps were spun at 4.9 KHz. Total scanning time was between 30 - 60 m, with about 15 m necessary to pack the sample and start spinning. All measurements were taken at a temperature of 300 K.

RESULTS AND DISCUSSION

The quantitative aspects of the ^{13}C magic angle spinning NMR experiment have already been shown[11,12]. The determination of the cotton/polyester content of commercial blends was accomplished by a peak height ratio method. The peaks at 104 and 162 ppm, for cotton (C-1 of cellulose)[13,14] and for the polyester carbonyl, respectively, were chosen since they are free of overlap with other peaks. Cotton/polyester blends examined included nominal ratios of 85:15, 75:25, 63:37, 60:40, 55:45, 53:47, 50:50 and 35:65. The ratio of the nominal cotton/polyester content was then plotted against the ratio of the cotton and polyester peak heights. Analysis by linear regression produced a straight line plot with a slope of 0.71, a y-intercept of -0.13 and a correlation coefficient of 0.993 (Figure 1). Eliminating the highest point and recalculating the straight line gave a slope of 0.67, y-intercept of -0.08 and a correlation coefficient of 0.963.

A plot of the ratio of the respective peak areas was also generated. Linear regression produced a slope of 0.72, y-intercept of 0.35 and a correlation coefficient of 0.969. Peak areas apparently do not correlate as well, perhaps due to differences in noise and baseline linearity. More careful setting of the integration regions and baseline, and a greater number of acquisitions to reduce noise may give more precise integration values. In this particular system, however, use of

peak heights gives excellent results, is much easier, and is more rapid.

The spectra of 100% cotton, 100% polyester, a 35:65 and a 50:50 cotton/polyester blend are all shown in Figure 2. The peak height ratio does not exactly equal the actual blend ratio possibly due to variations in cross-polarization efficiency between cotton and polyester, and certainly due to the differences in the ratios of crystalline to amorphous content for each polymer component.

In addition to the clothing samples used to establish the relationship in Figure 1, additional samples were obtained from a fabric store. Cotton/polyester blends with nominal ratios of 86:14, 84:16, 73:27, 72:28, and 20:80 were evaluated but did not correlate at all with the earlier data. In fact, one sample labeled as containing only 20% cotton was clearly almost all cotton; the cotton content calculated from measured peak heights corresponded to a ratio of 85:15. We are suggesting that these samples are mislabeled, either deliberately or through careless handling. In any event, fabric purchasers are not receiving the fabrics they think they are getting. It is also clear, especially from the non-zero intercept obtained from the peak height data, that careful determination of known sample blends would greatly improve the accuracy of this technique.

The utility of ^{13}C CP/MAS for qualitative analysis of textile fabrics was demonstrated for a number of clothing samples. These included fabrics nominally containing 100% rayon,

100% Qiana[T.M.] nylon, 100% shetland wool, and blends of 95:5 cotton/polyurethane, 50:50 cotton/Creslan[T.M.] acrylic, 82:12:6 cotton/acrylic/viscose rayon, 44:44:12 cotton/polyester/rayon, and 80:20 Arnel[T.M.]/nylon. In all the spectra, peak assignments were made for each component of the blend by comparison with the spectra of individual fiber component and representative model compounds. Interestingly, it was found that the spectra of the garment labelled 80:20 Arnel[T.M.]/nylon did not contain peaks for nylon. Instead it showed peaks for polyester; compare Figure 3 and the polyester spectrum in Figure 2. The spectra of Qiana[T.M.] nylon and the 50:50 cotton/Creslan[T.M.] acrylic blend are shown in Figures 4 and 5, respectively.

These solid state carbon NMR examples demonstrate the value of this technique for rapid quantitative analysis of textile blends, and for quick, positive identification of fabrics and blends. This technique has great promise for routine screening of fabric samples to confirm the identity and composition of domestic and especially imported textile products.

ACKNOWLEDGEMENT

The authors wish to gratefully acknowledge a grant from the Department of Defense to purchase our Bruker MSL-200 NMR spectrometer. This work was supported in part by the Office of Naval Research.

REFERENCES

1. R. T. O'Conner, *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose*, Marcel Dekker, New York (1972).

2. B. Focher and A. Jus, *Tinctoria*, 72, 11 (1975).

3. W. O. Statton, *Am. Dyestuff. Reptr.*, 54, 314 (1965).

4. R. E. Dehl, *J. Chem. Phys.*, 48, 831 (1968).

5. R. A. Pittman and V. W. Tripp, *J. Polym. Sci., Part A-2*, 8, 969 (1970).

6. W. I. Earl and D. L. VanderHart, *Macromolecules*, 14, 570 (1981).

7. A. Hirai, F. Horii and R. Kitamaru, *Bull. Inst. Chem. Res., Kyoto Univ.*, 63, 340 (1985).

8. Te-Hsiung Wang, *Hsin Hsien Wei*, 20, 31 (1978).

9. Te-Hsiung Wang, *Hsin Hsien Wei*, 18, 18 (1976).

10. D. M. Soignet, *Charact. Met. Polym. Surf.*, 2, 73 (1977).

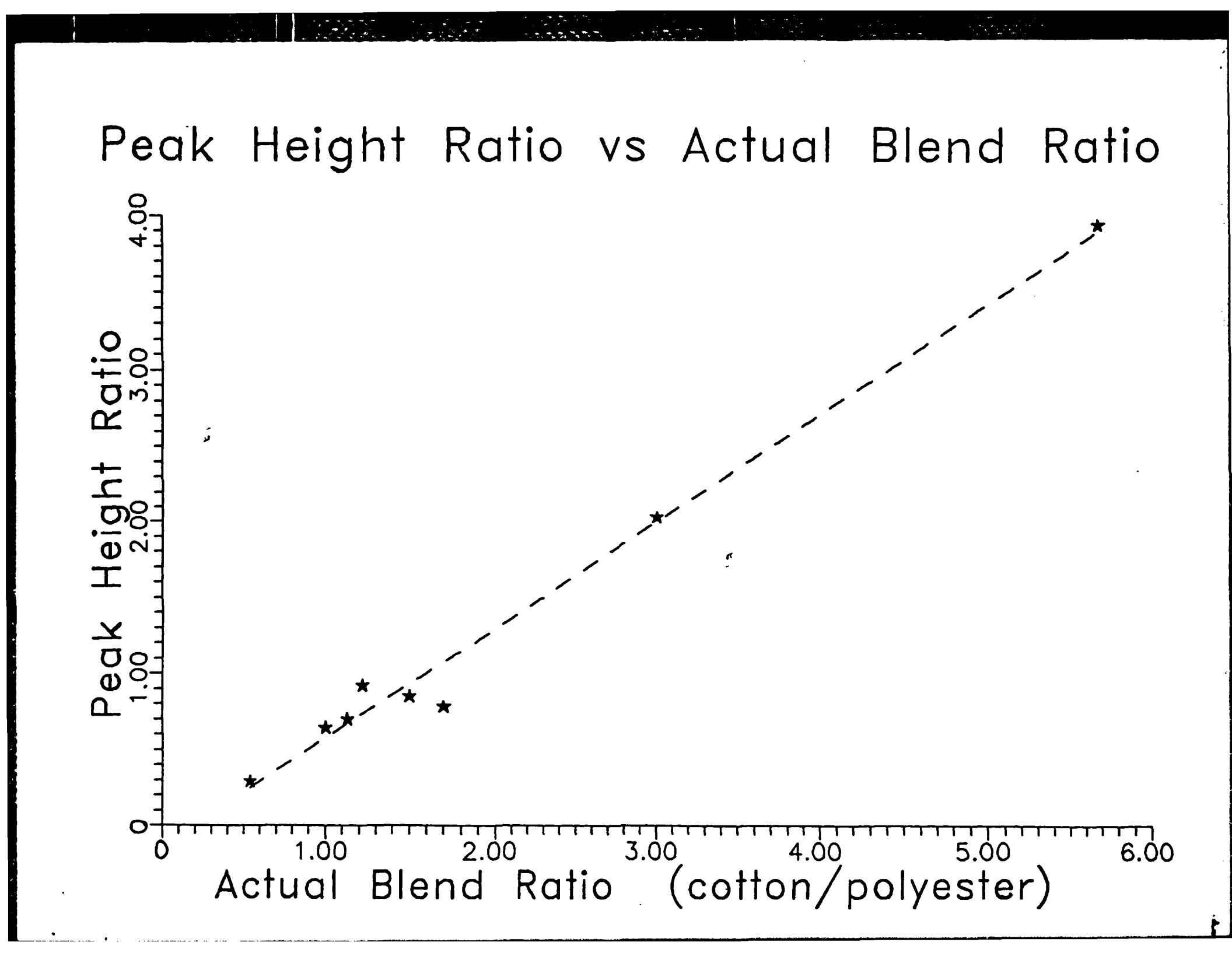
11. L. B. Alemany, D. M. Grant, R. J. Pugmire, T. D. Alger and K. W. Zilm, *J. Am. Chem. Soc.*, 105, 2133 (1983).

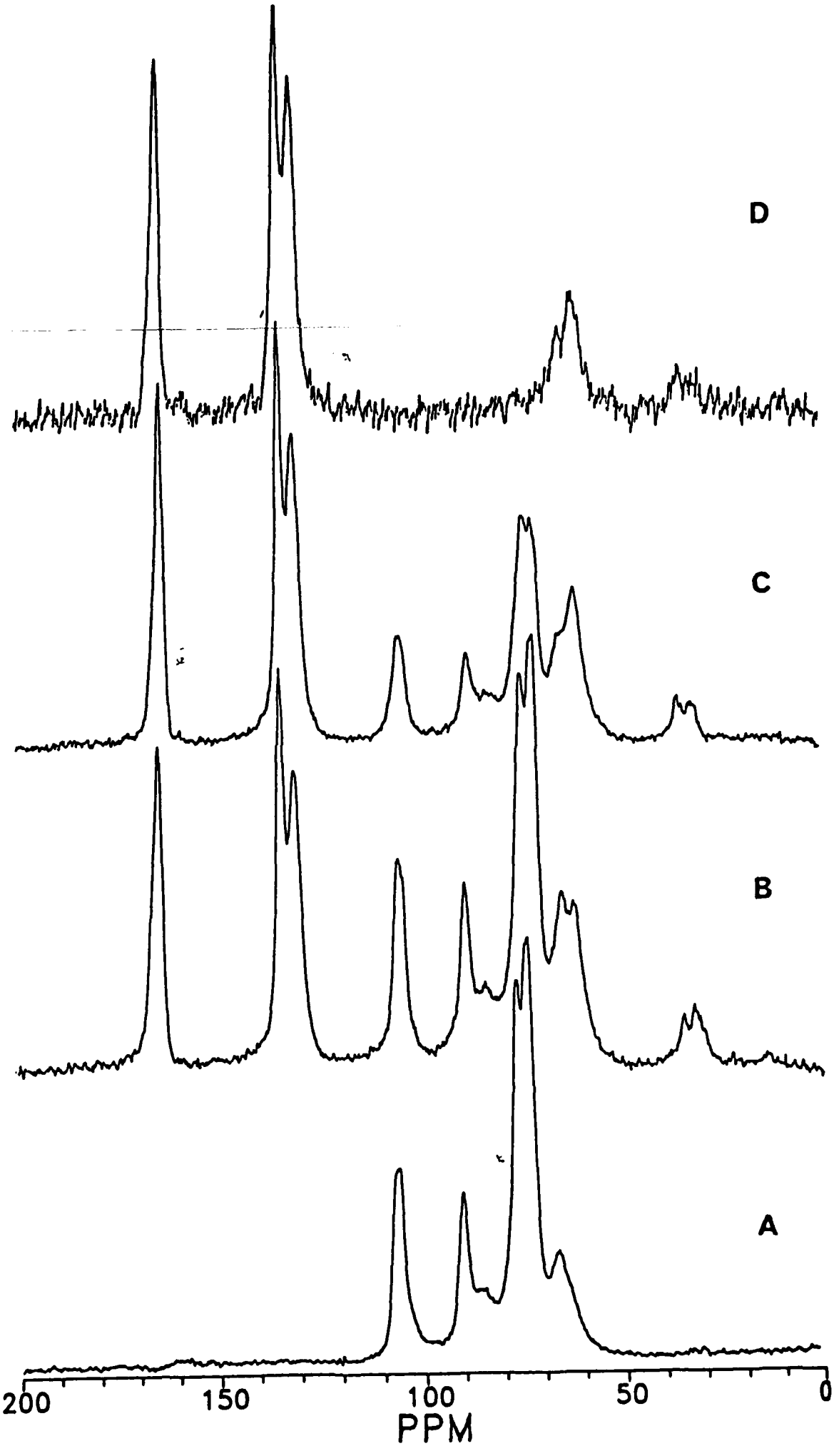
12. L. B. Alemany, D. M. Grant, R. J. Pugmire, T. D. Alger and K. W. Zilm, *J. Am. Chem. Soc.*, 105, 2142 (1983).

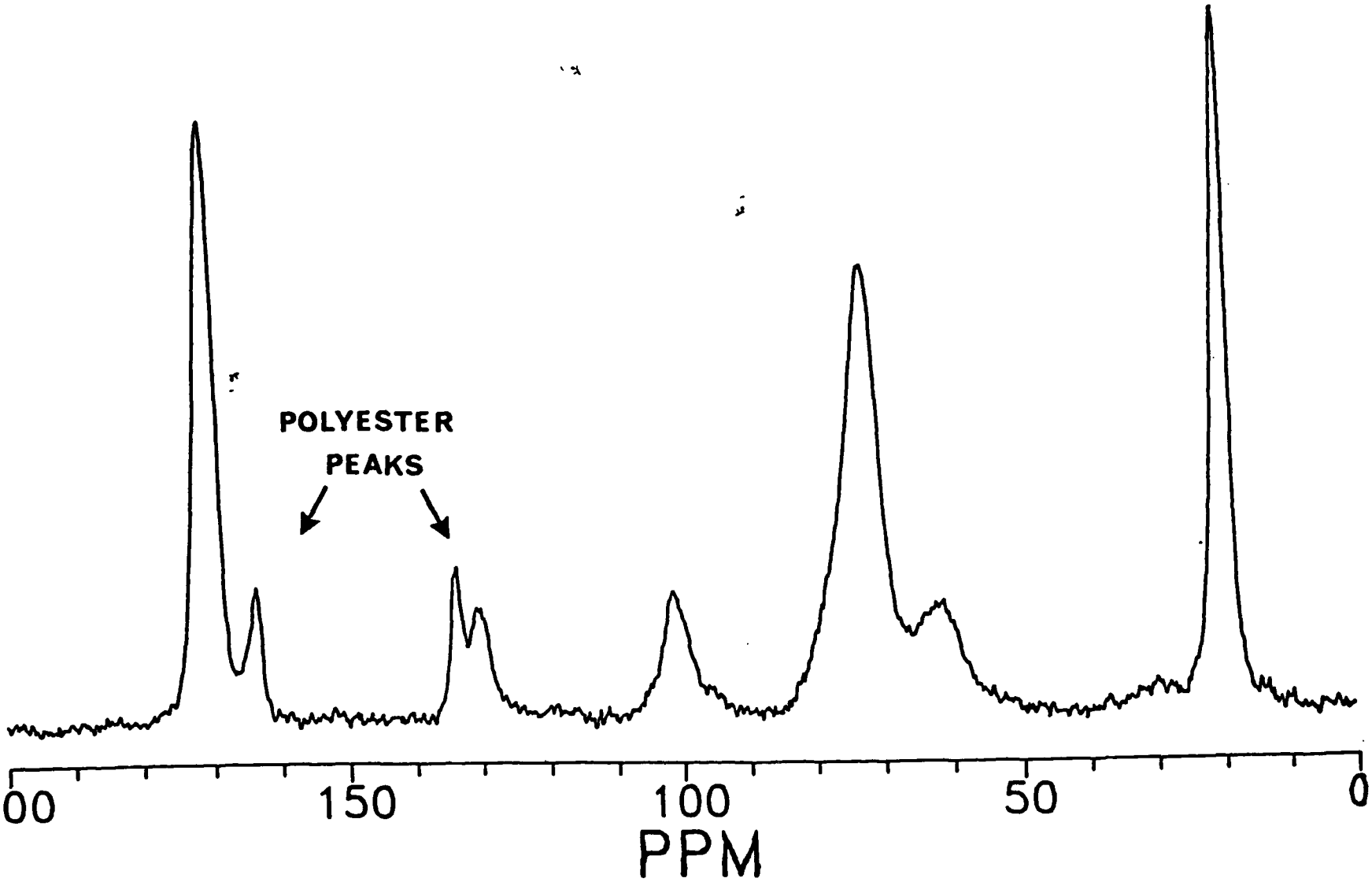
13. R. H. Atalla, J. C. Gast, D. W. Sindorf, V. T. Bartuska, G. E. Maciel, *J. Am. Chem. Soc.*, 102, 3251 (1980).

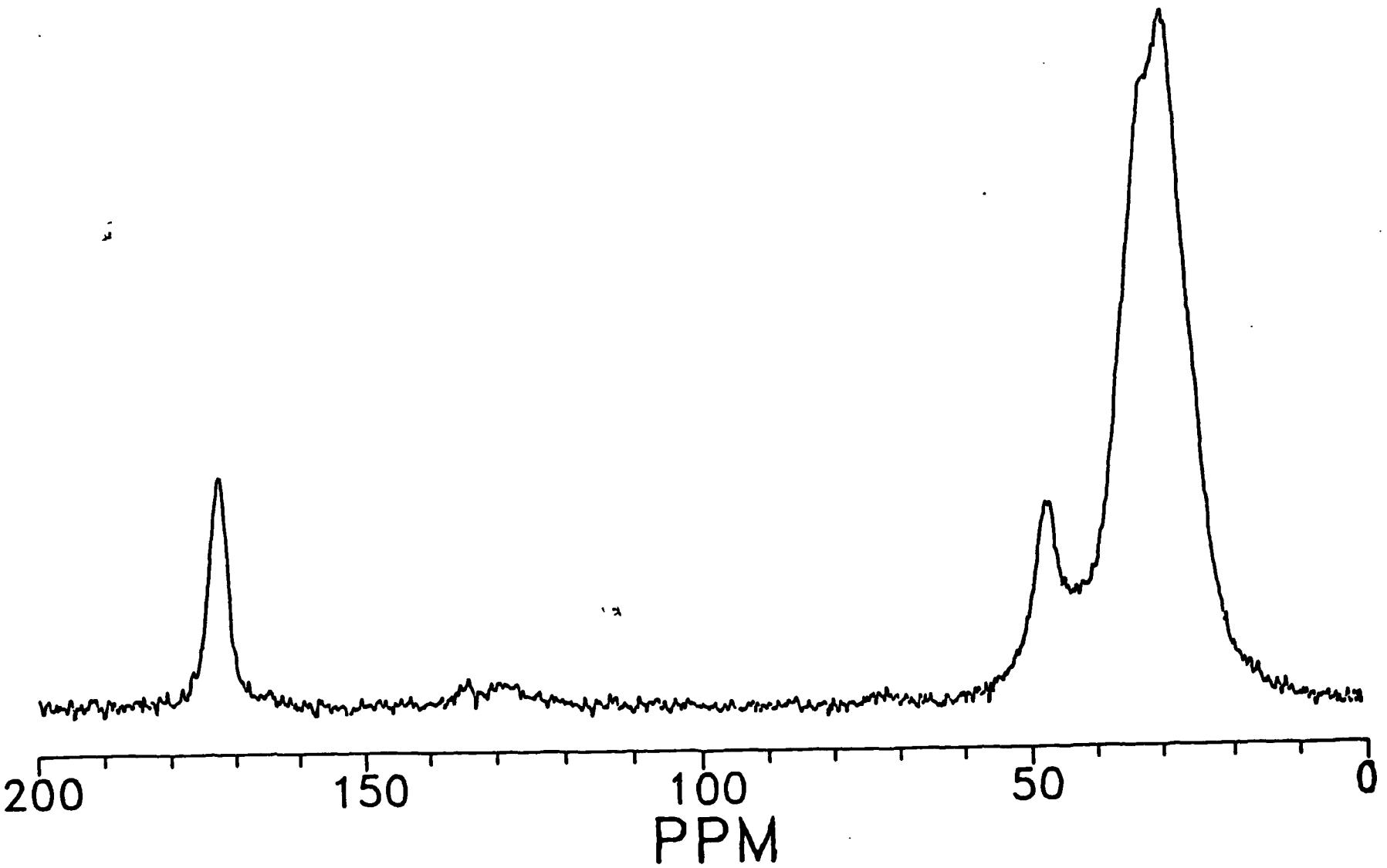
14. W. I. Earl, D. L. VanderHart, *J. Am. Chem. Soc.*, 102, 3251 (1980).

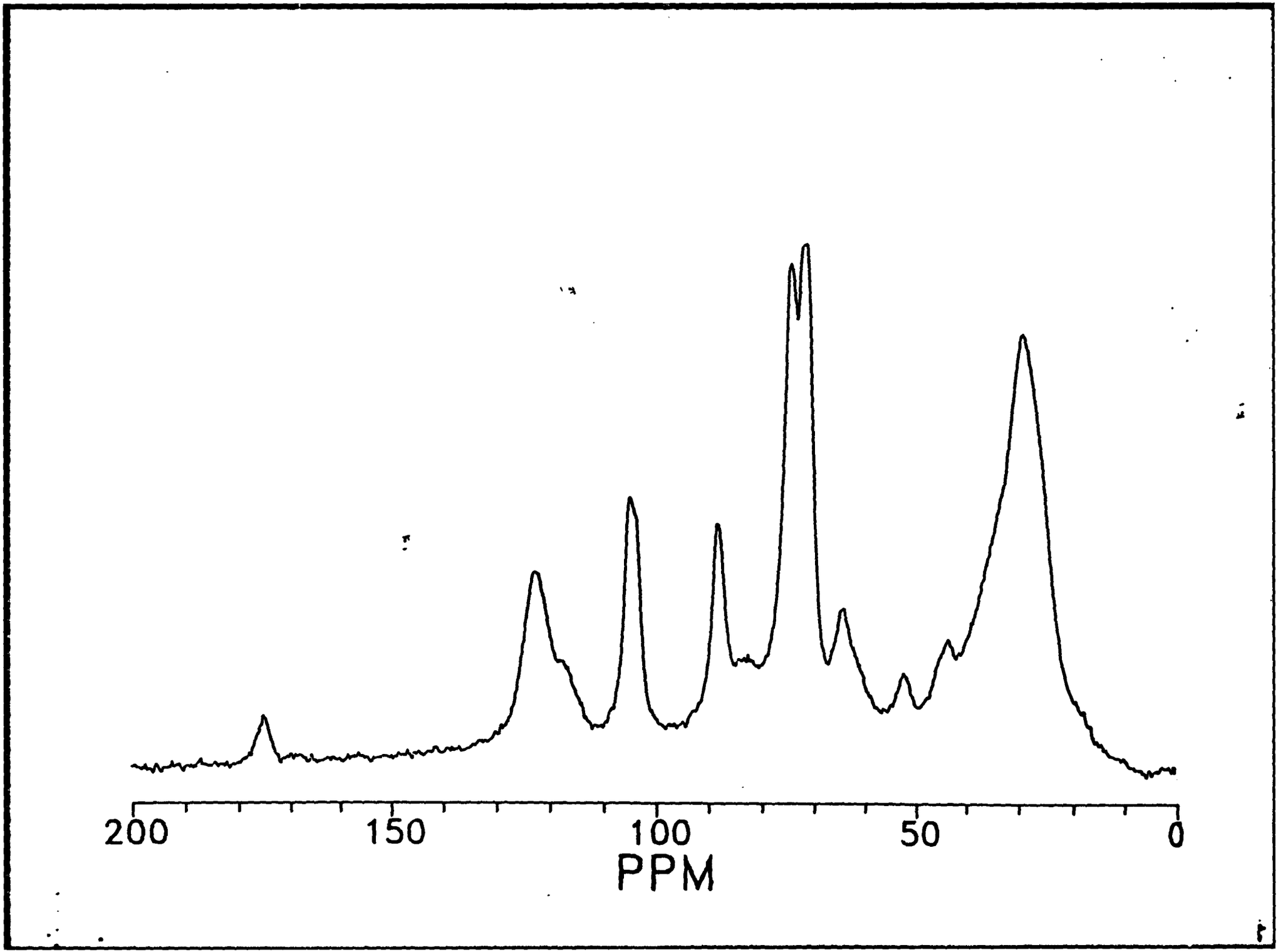
LIST OF FIGURES


Peak Height Ratio vs Actual Blend Ratio
Peak Height Ratio
0
1.00
2.00
3.00
4.00
0
1.00
2.00
3.00
4.00
5.00
6.00
Actual Blend Ratio (cotton/polyester)


D
C
B
A
200
150
100
50
0
PPM


POLYESTER
PEAKS
200
150
100
50
0
PPM


200
150
100
50
0
PPM


200
150
100
50
0
PPM

END

10-87

DTIC