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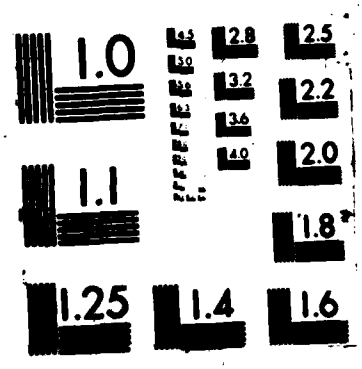
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^{13}C AND ^{15}N SOLID STATE NMR CHARACTERIZATION OF ARAMID-CONTAINING NYLON-6 POLYMERS SYNTHESIZED BY IN SITU POLYMERIZATION OF CAPROLACTAM WITH BENZOYL CAPROLACTAM DERIVATIVES

by

Douglas G. Powell, Allison M. Sikes and Lon J. Mathias

Prepared for Publication in

Polymer Preprints, in press

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Copolyamides were prepared by in situ polymerization from p-Aminobenzoylcaprolactam and caprolactam systems initiated with sodium hydride. The microstructure of the copolymers as determined by 13C solution NMR varied from alternating to blocks of aliphatic and/or aromatic units depending on the reaction conditions and the ratio of the comonomers. The solid-state CP/MAS 13C NMR were consistent with solution studies. Detailed interpretation was difficult due to large linewidth and number of resonances. Natural abundance CP/MAS 15N spectra were found to less complicated. Based on these results and 15N studies with model amides, 15N CP/MAS was shown to be a useful technique for probing copolymer composition and microstructure.

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^{13}C AND ^{15}N SOLID STATE NMR CHARACTERIZATION OF ARAMID-CONTAINING NYLON-6 BY IN SITU POLYMERIZATION WITH BENZOYL CAPROLACTAM DERIVATIVES

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INTRODUCTION

Polyamides and aramids are two important structural materials noted for their toughness, high modulus, and tensile strength.[1] They are currently used in a wide variety of applications as structural plastics and as reinforcing fibers in high performance composites.

Natural abundance ^{15}N NMR spectroscopy has been used to characterize polyamides in solution.[2,3,4,5] ^{15}N NMR spectroscopy has several advantages over ^{13}C NMR including larger spectral width and simpler spectra. Characterization of polyamides by solution ^{15}N NMR is, however, hampered by the limited solubility of many polyamides, especially homo- and copolymers containing aromatic moieties. Polyamide nitrogens are subject to large chemical shift changes in the solvents needed to dissolve them.[6,7] Moreover, solution studies cannot duplicate the crystalline structure or hydrogen bonding in solid polyamides.

Recently, polyamic acid precursors to polyimides have been characterized by solid state ^{15}N CP-MAS NMR.[8] We had previously prepared and characterized several aliphatic/aromatic copolyamides based on caprolactam and several N-benzoyl caprolactam initiators.[9] (Figure 1) We have compared these results with ^{15}N CP-MAS NMR data to evaluate the usefulness of the latter technique for polyamide microstructure characterization. In this paper we present the ^{15}N CP-MAS NMR results for several copolyamides along with model amides used for chemical shift assignments.

EXPERIMENTAL

Caprolactam homo- and copolymers were prepared as previously described.[9,10] Model amides were purchased from Aldrich Chemical Company and used as received. ^{15}N solid state CP-MAS measurements were made on a Bruker MSL-200 NMR spectrometer equipped with a Bruker MAS solids accessory. Measurements were made in a 4.7T field corresponding to ^{1}H and ^{15}N frequencies of 200.13 and 20.287 MHz, respectively. Cross-polarization was performed using a 5 μs ^{1}H pulse and a contact pulse of 1 to 5 ms to meet the Hartmann-Hahn condition. MAS rotor speeds were 3.0 to 3.2 KHz. Sample temperature was maintained at 300K. Spectral widths were 25 KHz. Between 20,000 and 50,000 scans were acquired for each sample with a delay of 3 s between scans. Chemical shifts are reported relative to $^{15}NH_4NO_3$ (NO_3 = 0 ppm; $^{15}NH_4$ = -353.5 ppm) as an external standard. Solution ^{15}N measurements were made using an inverse-gated decoupling technique with a

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pulse width of 25 μs. All solution spectra were obtained in concentrated sulfuric acid solvent. $^{15}NH_4NO_3$ dissolved in D_2O was used as the reference (NH_4^+ = 353.5 ppm) by inserting a tube containing the solution coaxially into the sample.

RESULTS AND DISCUSSION

^{15}N chemical shifts of model amides and polyamides are listed in Table I. As expected, the chemical shifts of the solid samples are approximately 30 ppm upfield of the solution resonances. Protonation of the amide carbonyl causes unpredictable shifts in ^{15}N resonances depending on the pKa of the amide and solvent acidity.[9] Typical linewidths at half height were 8-10 ppm.

The solid-state chemical shifts of di-functional initiated and star initiated nylon-6 are similar to wholly linear nylon 6 although the star polymer is insoluble in concentrated H_2SO_4. We were disappointed to find that nitrogens on the initiator species were not visible in the spectrum. The low concentration of initiator (<1%) makes this technique inadequate without ^{15}N enrichment in the initiator. With atom enrichment, determination of the number of imide sites consumed would give the efficiency of initiation as well as confirm the synthesis of a star polymer.[10]

Figure 2 shows the ^{15}N CP-MAS spectra of a previously prepared copolymer of p-aminobenzoic acid and caprolactam with alternating aliphatic and aromatic units. This copolymer consists of only two types of amide nitrogens in equal proportions. The resonances at -240.6 and -261.3 show equivalent areas consistant with the alternating copolymer structure. Comparison with the model acetanilide (-241.9) indicates the downfield resonance is due to the aromatic substituent on the nitrogen. N-methyl benzamide, however, lies well upfield of any other resonances in the Table. It is apparently a poor model for an aliphatic substituted amide in the copolymer. A possible explanation is that the methyl group of these models cannot duplicate the effects of an aliphatic chain on the nitrogen resonance. These "neighboring residue effects" have also been recognized in solution ^{15}N experiments as well.[2-6] The solution ^{15}N spectrum of the copolymer in sulfuric acid is also shown and is consistant with the solid state spectrum with the exception of large chemical shift changes.

Figure 3 shows a series of copolymers synthesized under conditions slightly different than those for the alternating copolymer. By altering conditions it was found that blocks of aromatic units could be generated <u>in situ</u> and incorporated into novel copolymers. Figure 3a shows a copolymer containing blocks of p-benzamide with few caprolactam units. The downfield shift of the ^{15}N resonance is consistent with nitrogen in a deshielding environment between an aromatic ring and carbonyl group. This shift also compared favorably with the ^{15}N spectrum of fully aromatic

-poly(p-benzamide) (-248.5 ppm). Figures 3b and 3c show copolymers containing 6% and 20% aramid units, respectively, with the remainder being caprolactam units. The upfield shift is consistant with the of nylon-6 spectrum shown in 3d. The copolymer peak, however, is 5-6 ppm downfield of the homopolymer. It is surprising that the presence of the aramid species causes such a shift even though the concentration is too low for the aramid ^{15}N resonances to be seen. Solution ^{15}N NMR of these samples gave a chemical shift identical to that of the nylon-6 homopolymer.

The presence of two crystal forms of nylon-6 is well known and both have been previously characterized by IR and x-ray.[11,12] Figures 4a and 4c show the ^{15}N NMR of α and γ crystal forms of nylon-6, respectively, while 4b shows a mixture that is predominately α. Although ^{13}C and ^{15}N chemical shifts have been reported to be conformationally dependent,[13] the ^{13}C CP-MAS chemical shifts were identical for both crystal forms. It is clear that ^{15}N solid state NMR is a better tool for differentiating the two crystal forms. Moreover, the the chemical shifts correlate well with observed nylon-6 resonances seen in the copolymers in Figure 3. The ^{15}N solid state NMR clearly shows that the nylon-6 blocks in the copolymers are mostly of the γ form.

SUMMARY AND CONCLUSION

Natural abundance ^{15}N NMR of solids has been demonstrated as a useful characterization tool for polyamides. Anisotropies and crystal forms can be examined in the solid phase which are not present in solution. ^{15}N CP MAS NMR provides a new method for determining the crystal structure of nylon-6. The greater sensitivity of nitrogen to its environment in solid state NMR compared to carbon opens up a broad area for study of crystalline polyamides. Potential also exists for characterization of peptides and other nitrogen containing crystalline materials using ^{15}N CP-MAS NMR to complement traditional X-ray analysis.

ACKNOWLEDGEMENT

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TABLE I

	CP-MAS	Solution
N-methyl benzamide	-273.3	-226.3
Acetanilide	-241.9	-221.0
poly(p-benzamide)	-248.5	-----
Alternating copolymer	-240.6, -261.3	-224.1, 229.2
Nylon-6 (*annealed*)	-261.7	228.4
3-Arm star nylon-6	-258.4	
Nylon-6 (quenched)	-256.7, -261.1	

LIST OF FIGURES

Figure 1: a) Synthesis of aliphatic/aromatic block and alternating copolymers. b) Synthesis of nylon-6 star polymers using tri functional initiators.

Figure 2: ^{15}N CP MAS spectrum (upper trace) and ^{15}N solution spectrum (lower trace) of poly(p-benzamide-alt-caproamide) alternating copolymer

Figure 3: ^{15}N CP-MAS NMR spectra of block copolymers of caprolactam and p aminobenzoic acid: a) 80-90 mole% aromatic comonomer; b) 10 mole % aromatic comonomer; c) 20 mole % aromatic comonomer; d) nylon-6 homopolymer

Figure 4: ^{15}N CP-MAS NMR OF Nylon-6 homopolymer crystal forms: a) mainly gamma nylon-6; b) predominately alpha nylon-6; c) alpha nylon-6

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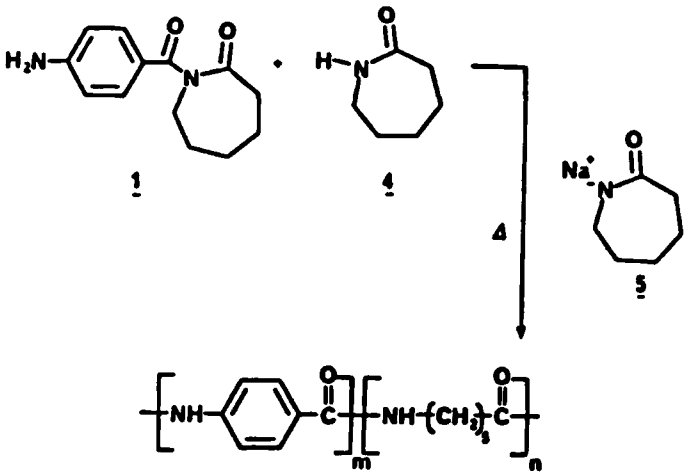

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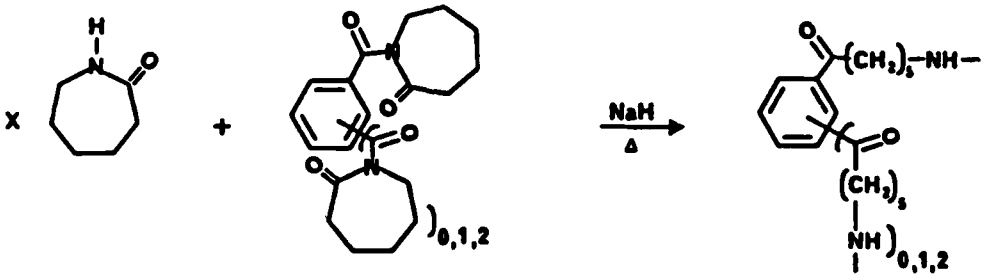

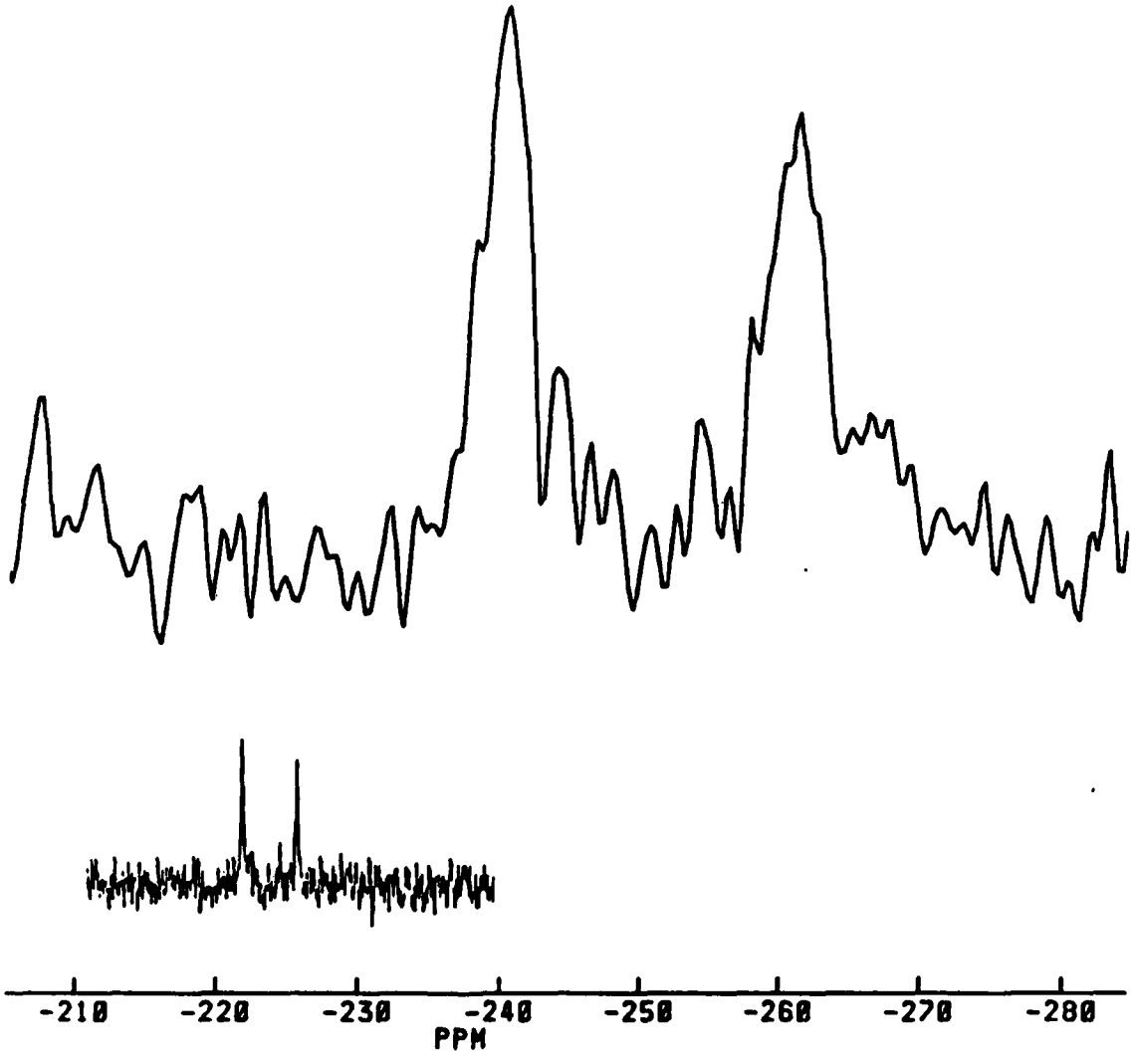
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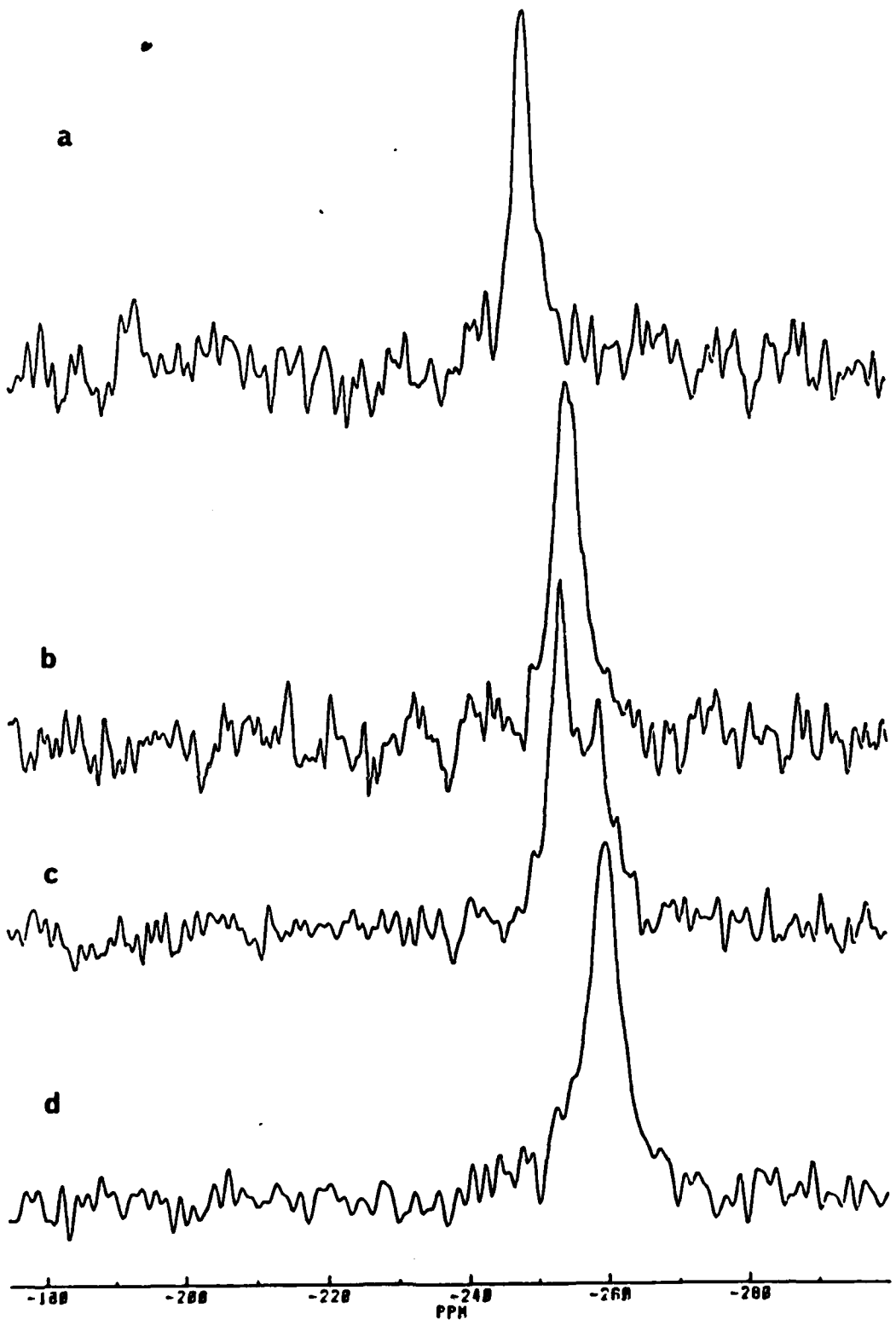
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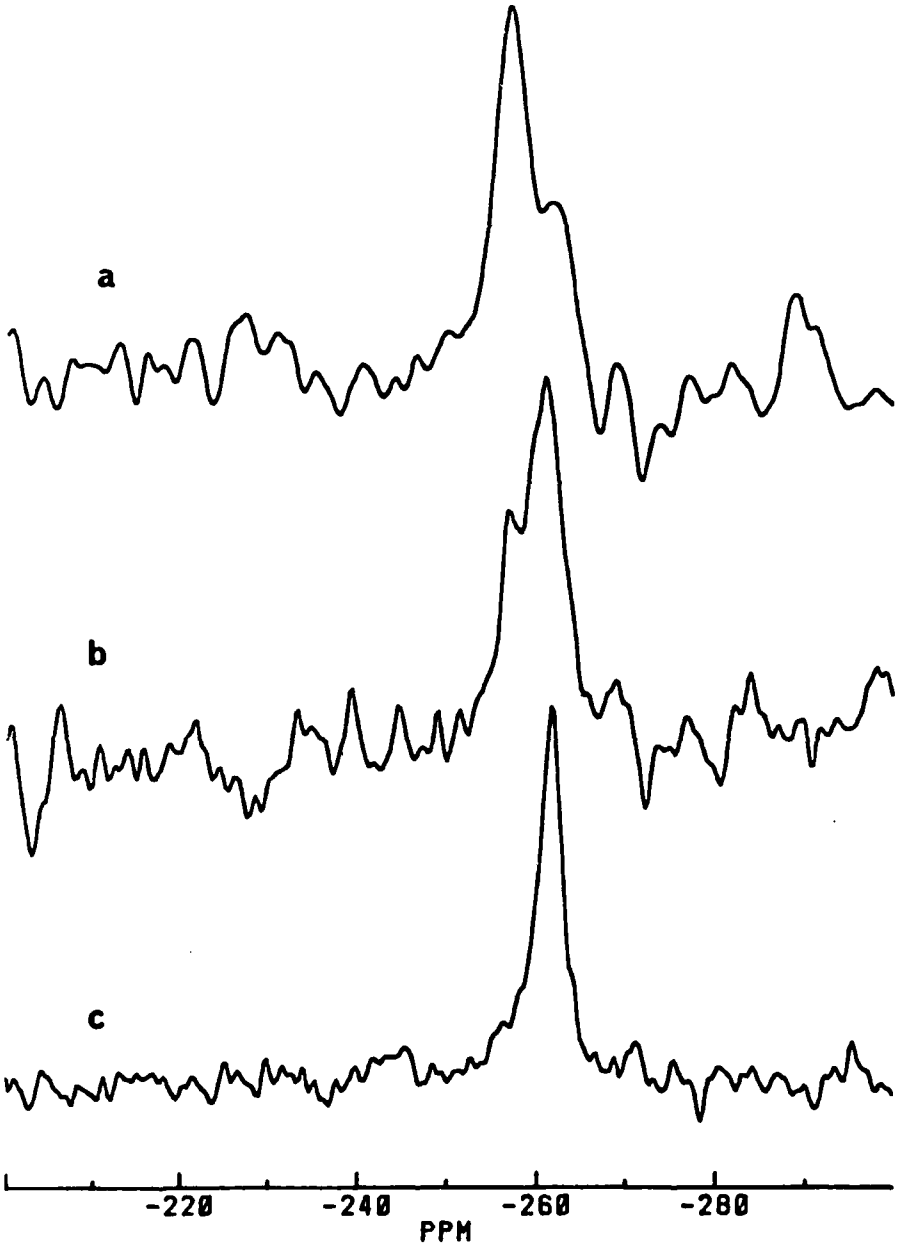
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