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Magic Angle Spinning NMR of Conducting Polymers

Because of their typically intractable nature, conducting polymers as a class of materials have proved particularly difficult to characterize by the conventional techniques of polymer analysis. We present here examples of the application of a powerful new tool, cross-polarization magic angle spinning (CMPAS) ^{13}C NMR spectroscopy, to the investigation of the structure and reactions of the conducting polymers polyacetylene and polypyrrole.

Introduction

Although the emerging class of conducting organic polymers [1] represents a unique opportunity to blend traditional polymer materials properties with interesting new electronic properties, the investigation of these materials has been limited somewhat by the difficult characterization problem they present. In their conducting form all of these polymers are essentially intractable, exhibiting no melting point or glass transition temperature and no solubility. Thus, many of the more common polymer characterization techniques are inapplicable in the study of conducting polymers. Fortunately, the development of new analytical tools continues to provide new approaches to characterization. In particular, one relatively recent spectroscopic technique, cross-polarization magic angle spinning (CPMAS) ^{13}C NMR [2], has proved extremely useful in providing new insights into the structure and reactions of these materials.

Prior to 1975 [3] high-resolution NMR spectroscopy was limited essentially to samples in solution. Conventional NMR on solids yields extremely broad spectra, primarily because of the magnitude of the $^{13}C-^{1}H$ dipolar interaction, typically 10–40 kHz. ($^{13}C-^{13}C$ interactions are relatively unimportant because the natural abundance of this isotope is only 1.1%.) The $^{13}C-^{1}H$ dipolar coupling can be removed by high-power decoupling, leaving the carbon chemical shift anisotropy as the dominant broadening mechanism. In the NMR experiment the local magnetic field at a given carbon is a function of the relative molecular orientation with respect to the external magnetic field. Thus, the observed spectrum for a typical solid would represent a superposition of all possible molecular orientations, as opposed to spectra obtained in liquids, where rapid tumbling of the molecules leads to observation of an average (isotropic) chemical shift. However, careful analysis reveals that this broadening can be removed by spinning the solid sample at a rate rapid compared to the anisotropy (expressed in frequency units) about an axis inclined at an angle of 54.7° (the "magic angle") with respect to the external field. This process leads to an averaging of the anisotropy and results in a single narrowed absorption at a position characteristic of the isotropic chemical shift.

The sensitivity of ^{13}C NMR spectroscopy is normally limited by the low natural abundance of the magnetic isotope and its small magnetic moment and long relaxation time. The situation can be improved, however, by the use of cross polarization (CP). Using an appropriate pulse sequence, polarization can be transferred from the protons to the carbons, resulting in a significant enhancement in carbon magnetization over the normal value. Moreover, CP allows successive free-induction decays to be obtained on the time scale of the proton spin-lattice relaxation time rather than on the longer time scale of the carbon spin-lattice relaxation time, resulting in more rapid acquisition of the carbon

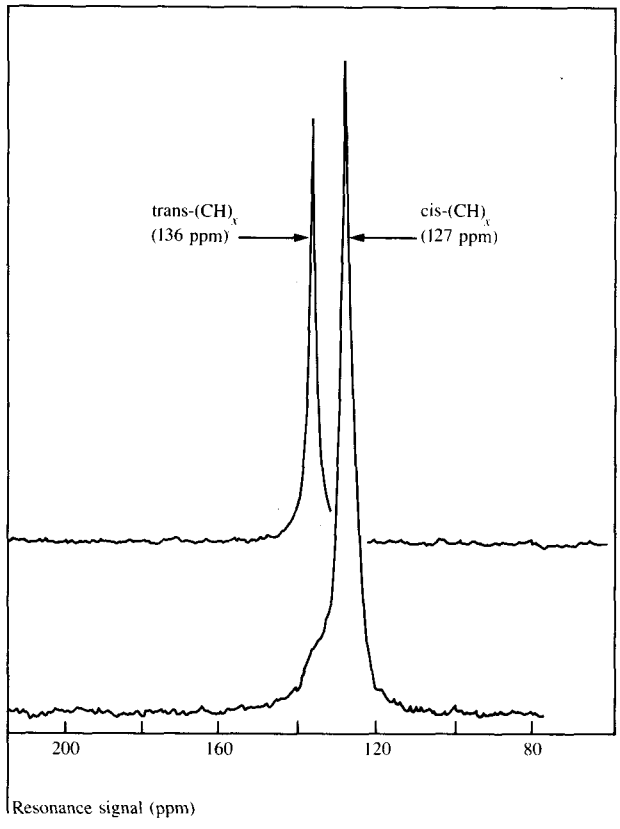


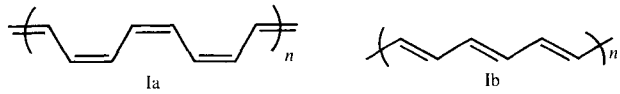
Figure 1 CPMAS ^{13}C NMR spectra of pristine cis- and trans-polyacetylene.

spectrum. Together, cross polarization and the magic angle spinning procedure allow one to obtain high-resolution spectra of solids, a technique which we have found to be invaluable in the analysis of conducting polymers.

Polyacetylene

In many respects polyacetylene, $(CH)_x$, is the simplest of the conducting polymers. First synthesized as an insoluble black powder in 1956 by the polymerization of acetylene [4], polyacetylene attracted only sporadic attention until 1971, when Shirakawa developed a technique for the growth of shiny, flexible films of this material on the surface of a Ziegler-Natta catalyst solution [5]. Coupled with this synthetic advance, the discovery in 1977 that the conductivity of polyacetylene could be raised from its normal value of 10^{-9} ohm^{-1}-cm^{-1} to greater than 10^3 ohm^{-1}-cm^{-1} by treatment with oxidizing or reducing agents provided the impetus for the current intense interest in this material and its analogs [6].

Polyacetylene is typically synthesized as the *cis-transoid* isomer (Structure Ia) but can be converted to the thermodynamically more stable *trans-transoid* (Structure Ib) form by heating. The normal solid-state ^{13}C NMR spectra of the individual isomers are essentially identical broad featureless absorptions. As first shown by Maricq et al. [7], however, application of CPMAS ^{13}C NMR (with proton decoupling) provides sharp, well-separated peaks for the cis and trans isomers at positions comparable to those observed in model compounds (Fig. 1). Subsequently, Kaplan and coworkers have used this technique in a detailed examination of the cis-trans isomerization process [8]. However, it is in the study of the doping of polyacetylene that CPMAS ^{13}C NMR has provided the most unique insights [9].



Ia Ib

The nature of the semiconductor-to-metal transition which occurs in polyacetylene at doping levels of $\approx 1\%$ has been the source of considerable controversy. On the basis of a linear increase in Pauli susceptibility with increasing dopant concentration, Tomkiewicz et al. proposed a model of inhomogeneous doping, leading to the formation of metallic islands which grow in size and/or number as doping progresses [10]. In this picture the semiconductor-to-metal transition corresponds to a percolation threshold. On the other hand, Heeger and coworkers have claimed that slower doping leads to a more homogeneous dopant distribution, which allows the proposed soliton nature of polyacetylene doping to be observed [11]. Heeger's susceptibility measurements support the model of a metallic state with spinless carriers (charged solitons) in the 1 to 7% doping regime.

In an attempt to resolve this problem Peo et al. examined the solid-state ^{13}C NMR spectrum of polyacetylene at various AsF_5 doping levels using magic angle spinning [12]. In studying only cis-polyacetylene, they reported no substantial change in the ^{13}C spectrum up to doping levels of $\approx 7\%$ AsF_5, at which point a rather abrupt change to a broad, shifted line was observed. These authors attributed the change to a Knight shift and correlated this result with the sudden increase in Pauli susceptibility in Heeger's measurements at $\approx 7\%$ doping (attributed to overlap of the soliton band with the valence and conduction bands) [11]. However, several puzzling aspects of the Peo data led us to extend their study. Particularly disturbing was their failure to observe even a chemical shift in the polyacetylene at doping levels below 7%, despite the fact that doping is believed to remove charge from the polymer π-system.

Polyacetylene for our experiments was prepared by the procedure of Ito et al. [5]. Conversion of cis-polyacetylene to the trans isomer was carried out under $\approx 0.5 \times 10^5$ Pa (≈ 0.5 atm) of helium at 200°C for one hour. The AsF_5 was purified as described earlier [13]. Doping of the polyacetylene was

performed as described in the work of Ikehata et al. [11]. Final compositions were determined by weight uptake. All manipulations of the polymer were carried out either on a vacuum line or in an inert atmosphere dry box. In particular, the NMR sample rotors were loaded in the dry box and transferred to the spectrometer under argon. Undoped samples were cut into small pieces before being packed in the rotors; doped samples were cut and dispersed by grinding with glass powder before loading. An undoped cis sample was also cut and ground to ensure that no sample degradation or cis-trans isomerization occurred on grinding. During the acquisition of data the sealed rotors were under the constant flow of helium used to spin the samples [14]. Spectra were obtained in a magnetic field of $\approx$1.1 MA/m (14 kOe) using cross polarization and magic angle spinning techniques. Shifts are expressed in ppm with respect to tetramethylsilane (TMS). In contrast to an earlier report [7], we observed no indication of sp^3 carbons in samples of either polyacetylene isomer, placing an upper limit of approximately 1% on the concentration of such species.

Figure 2 shows our results for the doping of cis-$(CH)_x$. The bottom spectrum is that of the undoped starting material. The main peak at 127 ppm corresponds to cis material; the low-field shoulder ($\approx$136 ppm) is due to the presence of a small amount of the trans isomer [7, 8, 12]. The top spectrum shows the same material after doping to a composition of $[CH(AsF_6)_{0.068}]$. As in the Peo data [12], a very broad resonance centered at $\approx$150 ppm is observed. The origin of this downfield shift in the doped polymer is discussed in detail below.

The middle spectrum in Fig. 2 shows a cis sample doped to the intermediate concentration of 3 mol %. Superficially, this spectrum resembles those presented by Peo et al. for intermediate doping levels: A sharp and apparently unchanged cis line and a slightly larger trans shoulder are readily evident. However, in contrast to the Peo results, we find that these peaks lie on top of a rather broad peak shifted downfield to a position characteristic of the doped polymer. This feature is more apparent in the expanded spectrum of the 3% sample shown in Fig. 3. This broad peak, smaller in relative intensity, is also found in a 1% doped cis sample (Fig. 4).

Figure 5 shows comparable data for AsF_5-doped trans-$(CH)_x$. (For experimental reasons only a 5% lower limit on the composition of the heavily doped sample could be determined.) The heavily doped sample exhibits a spectrum quite similar to that of 7% AsF_5-doped cis-polyacetylene. However, the spectrum of the 3.2% trans sample is quite dramatically changed from that of the undoped trans material, and appears to consist of a somewhat broadened peak at the original trans position lying on top of the broader downfield signal characteristic of the heavily doped material.

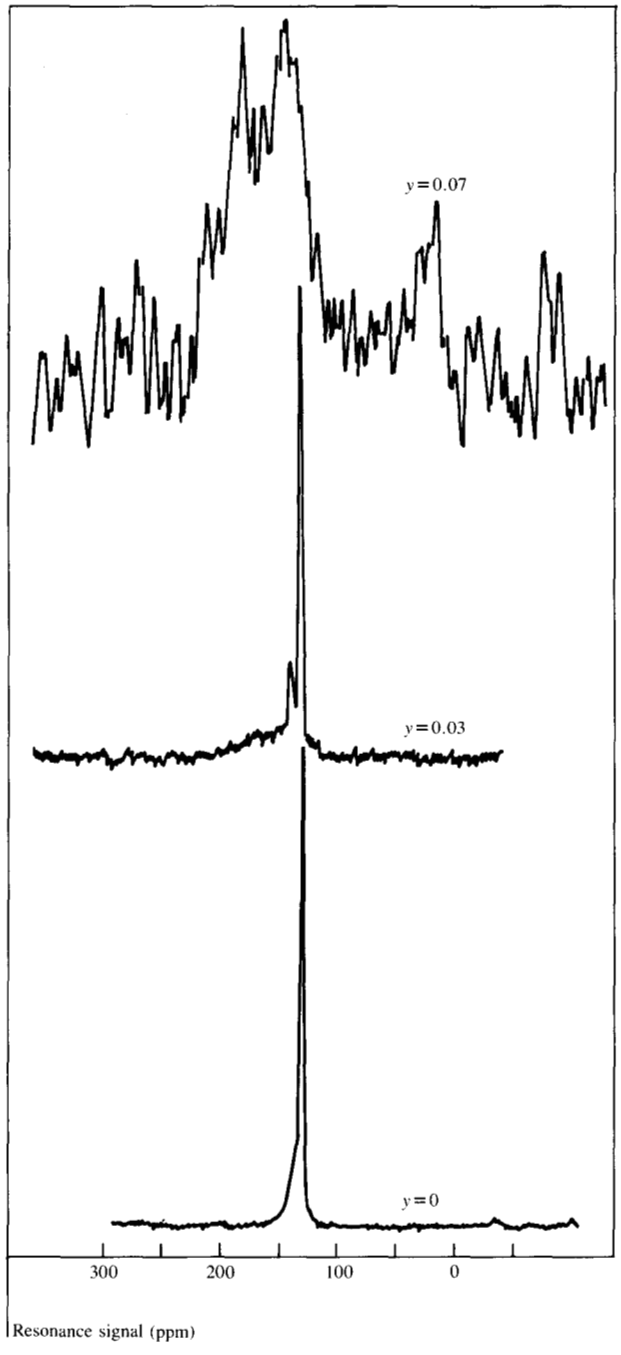


Figure 2 ^{13}C NMR spectra of cis-polyacetylene before (bottom) and after doping with AsF_5 to composition $[CH(AsF_6)_y]$.

From these data we draw several conclusions: 1) In contrast to the results of Peo et al., signals characteristic of the doped polymer can be seen in the spectrum of AsF_5-treated cis-polyacetylene at doping levels as low as 1%. Whether these signals correspond to doped material which is cis or trans in nature cannot be answered directly by these

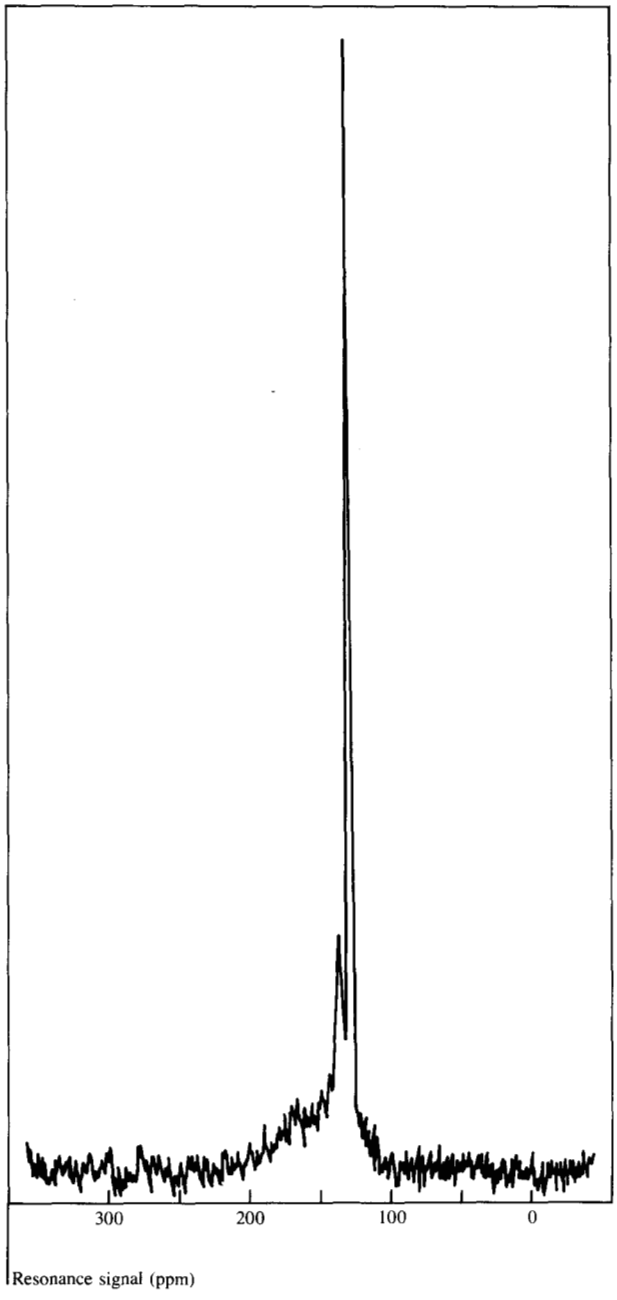


Figure 3 Expanded ^{13}C NMR spectrum of $[CH(AsF_6)_{0.03}]$.

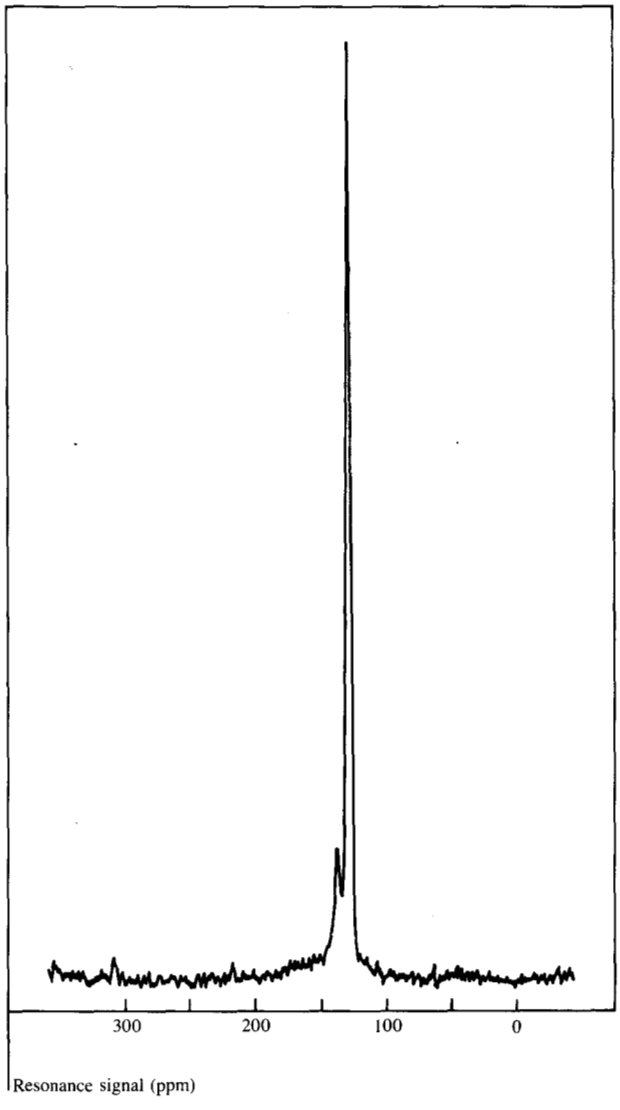


Figure 4 Expanded ^{13}C NMR spectrum of $[CH(AsF_6)_{0.01}]$.

experiments; the observation of very similar spectra for heavily doped cis and trans material is consistent with previous suggestions that the doped material is very likely trans [15]. 2) In the first ^{13}C NMR examination of AsF_5-doped trans-$(CH)_x$, we find that 3% doping causes a distinct broadening of the original trans line as well as the onset of the broad downfield signal centered at $\approx$150 ppm. In contrast, the spectrum of a 3% doped cis sample looks essentially like a superposition of the signals of undoped cis and heavily doped cis. Together these results suggest that the doping of cis-$(CH)_x$ is considerably less uniform than that of trans-$(CH)_x$. Even the trans doping, however, does not appear to be completely uniform. 3) In the unoxidized regions of the inhomogeneously doped cis isomer no extensive conversion of the cis material to trans polyacetylene is observed.

The downfield shift in the doped polyacetylene has been explained as a Knight shift [12]. However, the position of this signal is comparable to the shifts observed for the carbons of delocalized π-carbonium ions where no conduction electrons are present. For example, although the ^{13}C NMR of benzene exhibits a sharp singlet at 128.7 ppm [16], the signal of the tropylium ion, which contains one positive

charge equally distributed over seven carbon atoms, is shifted to 155.3 ppm [16]. (Determination of the charge per carbon in doped $(CH)_x$ is complicated by the obvious inhomogeneity of the doping. Motion of the already delocalized charge site would also lead to averaging on the NMR time scale.) We suggest that the primary contribution to the downfield shift on doping is the chemical shift arising from the removal of electrons from the π system, and that any Knight shift represents a smaller contribution superimposed on this chemical shift. Moreover, since the conduction electrons in this system must be π electrons, the Knight shift must involve core polarization, orbital and/or dipolar coupling; in particular, both the magnitude and direction of such a shift are uncertain [17].

The situation is further complicated by the current uncertainty over the interpretation of magnetic susceptibility studies on AsF_5-doped polyacetylene, particularly in the intermediate doping regime ($\approx$1–7%). Schumacher-Slichter measurements on the same 3.2% doped trans sample used in the above ^{13}C NMR experiments show a low Pauli susceptibility of $\approx 1.5 \times 10^{-7}$ emu/mole, while EPR studies on this sample yield a Pauli susceptibility of $\approx 1 \times 10^{-6}$ emu/mole [18]. Since any Knight shift should correlate with the Pauli spins, an independent resolution of the susceptibility problem will be required before a realistic estimate of the Knight shift contribution to the observed spectra can be made.

Polypyrrole

Oxidative polymerization of pyrrole under a variety of conditions has long been known to yield a family of conducting black powders referred to collectively as the "pyrrole blacks" [19]. The insolubility and general intractability of these materials again prohibited their straightforward characterization, although chemical degradation studies suggested a structure in which intact pyrrole rings were coupled at the α positions. More recently Díaz et al. have developed a controlled electrochemical synthesis of this polymer, more correctly named polypyrrole, leading to flexible films with conductivities as high as 40–100 ohm^{-1}-cm^{-1} [20]. Unique among the conducting polymers obtained to date, polypyrrole is remarkably stable to air in its conducting form, showing only a 10% drop in conductivity after $\approx$6 months exposure to the atmosphere.

On the basis of electrochemical and spectroscopic data [21], the polymerization of pyrrole is believed to involve coupling of the pyrrole moieties and simultaneous oxidation to yield a polymeric cation with one counter ion (derived from the supporting electrolyte) for every 3–4 pyrrole rings. Under carefully controlled conditions, this oxidized pyrrole polymer can then be electrochemically reduced to form the yellow insulating polymer in its neutral state. The characterization of polypyrrole has proved to be quite difficult; however, using CPMAS ^{13}C NMR we have now been able to provide evidence which confirms Structure II as the predom-

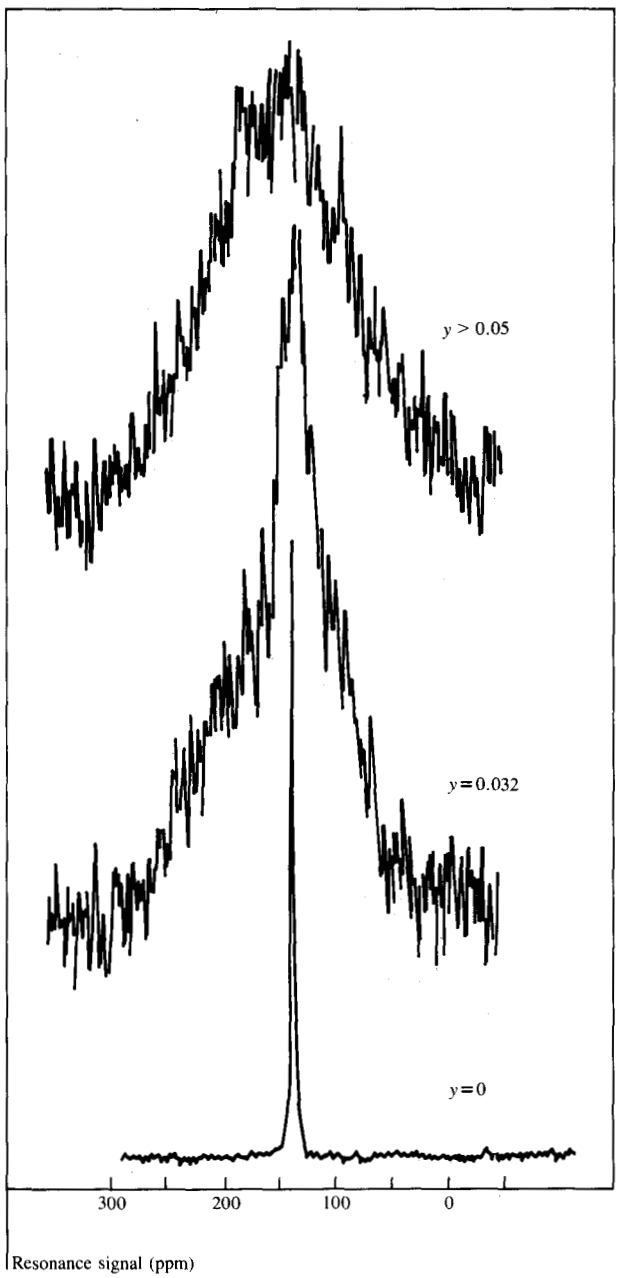
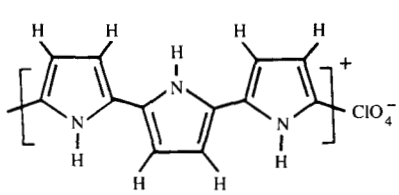


Figure 5 ^{13}C NMR spectra of trans-polyacetylene before (bottom) and after doping with AsF_5 to composition $[CH(AsF_6)_y]$.



II

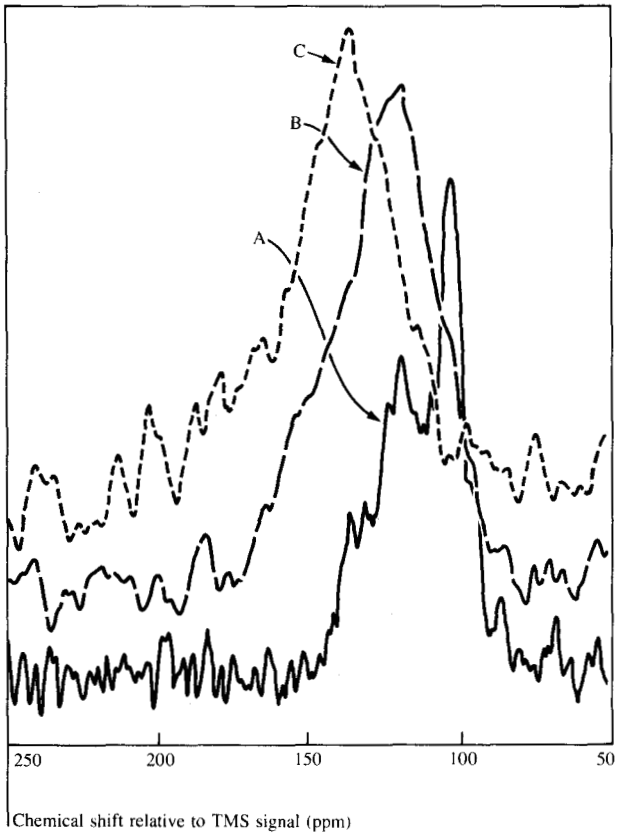


Figure 6 ^{13}C NMR spectra: Curve A, neutral polypyrrole; Curve B, polypyrrole perchlorate; and Curve C, neutral polypyrrole reacted with iodine.

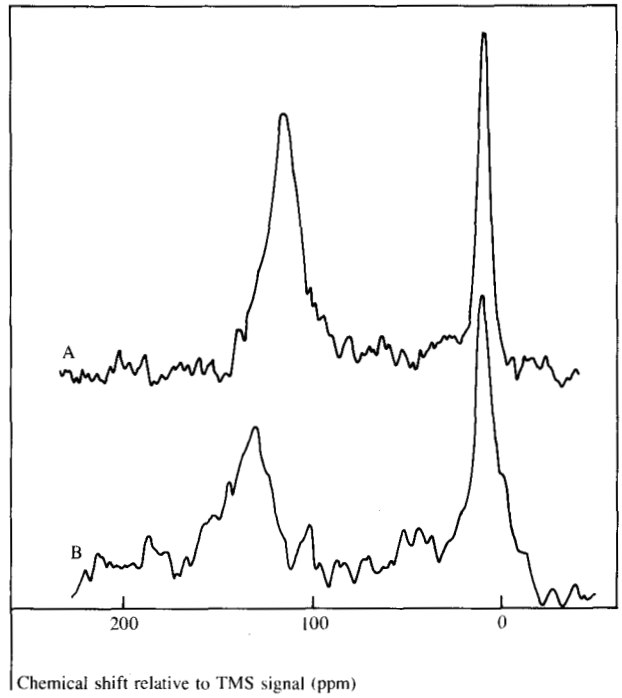


Figure 7 ^{13}C NMR spectra: Curve A, neutral poly (β,β'-dimethylpyrrole); and Curve B, poly(β,β'-dimethylpyrrole) perchlorate.

inant form of the as-prepared conducting polypyrrole. In addition, these data have provided valuable insight into possible modifications of polypyrrole which might lead to a more ordered polymer.

The relevant ^{13}C NMR data are shown in Fig. 6. Curve A shows the spectrum of a 17-mg sample of neutral polypyrrole film. (All sample preparation and handling was carried out under dry box conditions.) In this spectrum, three peaks can be distinguished. The major peaks are shifted $\approx$123 and $\approx$105 ppm downfield from TMS. These peaks correspond well with the α and β carbons of the pyrrole monomer, which occur at 117 and 108 ppm downfield relative to TMS [22]. The two peaks confirm the presence of the pyrrole moiety in the polymer, and the downfield shift of the α carbons relative to monomeric pyrrole is consistent with α-α' linkages [22]. The shoulder at $\approx$135 ppm may indicate the presence of some non-α-α' linkages, e.g., α-β linkages, although the possibility that these carbons correspond to chain end groups cannot be rigorously eliminated.

Curve B in Fig. 6 shows the spectrum of a sample of the electrochemically oxidized polypyrrole perchlorate. This conducting sample was dispersed by grinding with glass powder before being loaded into the sample rotor. The spectrum shows a very broad asymmetric peak shifted downfield relative to the neutral polypyrrole, consistent with the removal of the π electrons and the formation of a polymeric pyrrole carbonium ion. Curve C shows the spectrum of a sample of neutral polypyrrole after oxidation with iodine vapor to give a highly conducting film. The downfield shift relative to neutral polypyrrole is greater than that of the electrochemically oxidized polypyrrole perchlorate, indicating a higher degree of oxidation consistent with the higher conductivities observed for the iodine-treated samples. Although these downfield shifts for the oxidized samples are consistent with oxidation to form carbonium ions, there may also be some contribution from a Knight shift.

Poly(β,β'-dimethylpyrrole)

The suggestion of some non-α-α' bonding in the NMR spectrum of the parent polypyrrole led to the synthesis and polymerization of 3,4-dimethylpyrrole [23]. The main hope was that by eliminating the possibility for α-β pyrrole linkage, a more ordered polymer suitable for structural studies might be obtained. This has, indeed, proved to be the case [24]. Poly(β,β'-dimethylpyrrole) has been synthesized

as a conducting film by the same electrochemical techniques used for polypyrrole, and all measurement techniques imply that this polymer is, in fact, appreciably more ordered than the unsubstituted polypyrrole itself. Conductivities on the order of 10 ohm^{-1}-cm^{-1} are routinely obtained.

The CPMAS ^{13}C NMR spectrum of poly(β,β'-dimethylpyrrole) in both neutral and conducting forms is shown in Fig. 7. The most prominent difference from the spectrum of polypyrrole is, of course, the presence of the methyl carbons at $\approx$10 ppm. The presence of the methyl groups also causes the α and β carbon resonances to be less well separated than in the parent polymer. The small broad peak in the region of the methyl carbons is thought to result from some sp^3 carbons associated with the excess hydrogen found in the polymer. A similar broad peak (not shown in Fig. 6) can also be seen in the spectrum of neutral polypyrrole itself; in this case the presence of sp^3 carbons has been confirmed by infrared measurements. The oxidized conducting form of the polymer shows a downfield shift with respect to the neutral material, comparable to that observed for polypyrrole. This is consistent with the similar degree of oxidation in the two systems.

Conclusions

The above examples demonstrate the power of CPMAS ^{13}C NMR spectroscopy for the analysis of the structure and reactions of polymers which are quite difficult to characterize by more conventional techniques. It is only a matter of time before this technique becomes a routine element in the characterization of organic solids.

Acknowledgments

We thank the U. S. Office of Naval Research for partial support of this work. We are particularly grateful to C. S. Yannoni for the use of his NMR spectrometer and for his assistance and advice throughout this work.

References and notes

1. For reviews see (a) G. B. Street and T. C. Clarke, "Conducting Polymers: A Review of Recent Work," *IBM J. Res. Develop.* **25,** 51–57 (1981); (b) R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer, and L. W. Schacklette, "Structural Basis for Semiconducting and Metallic Polymer/Dopant Systems," *Chem. Rev.* **82,** 209–222 (1982).
2. (a) C. S. Yannoni, "High Resolution NMR in Solids: The CPMAS Experiment," *Accts. Chem. Res.* **15,** 201–208 (1982); (b) J. R. Lyerla, C. S. Yannoni, and C. A. Fyfe, "Chemical Applications of Variable Temperature CPMAS NMR Spectroscopy in Solids," *Accts. Chem. Res.* **15,** 208–216 (1982).
3. J. Schaefer, E. O. Stejskal, and R. Buchdahl, "High Resolution Carbon-13 Nuclear Magnetic Resonance Study of Some Solid Glassy Polymers," *Macromolecules* **8,** 291–296 (1975).
4. G. Natta, G. Mazzanti, and P. Corradini, "Stereospecific Polymerization of Acetylene," *Atti. Accad. Nazl. Lincei Rend. Classe Sci. Fis. Mat. e Nat.* **25,** 3–12 (1958); *Chem. Abstr.* **53,** 13985i (1959).
5. T. Ito, H. Shirakawa, and S. Ikeda, "Simultaneous Polymerization and Formation of Polyacetylene Film on the Surface of Concentrated Soluble Ziegler-Type Catalyst Solution," *J. Polym. Sci., Polym. Chem. Ed.* **12,** 11–20 (1974).
6. (a) T. C. Clarke and G. B. Street, "The Chemical Nature of Polyacetylene Doping," *Synthetic Metals* **1,** 119–132 (1980); (b) A. G. MacDiarmid and A. J. Heeger, "Organic Metals and Semiconductors: The Chemistry of Polyacetylene, $(CH)_x$, and Its Derivatives," *Synthetic Metals* **1,** 101–118 (1980).
7. M. M. Maricq, J. S. Waugh, A. G. MacDiarmid, H. Shirakawa, and A. J. Heeger, "Carbon-13 Nuclear Magnetic Resonance of cis- and trans-Polyacetylenes," *J. Amer. Chem. Soc.* **100,** 7729–7730 (1978).
8. H. W. Gibson, J. M. Pochan, and S. Kaplan, "^{13}C Magic Angle NMR Study of the Isomerization of cis- to trans-Polyacetylene," *J. Amer. Chem. Soc.* **103,** 4619–4620 (1981).
9. T. C. Clarke and J. C. Scott, "^{13}C NMR Study of AsF_5 Doped Polyacetylene," *Solid State Commun.* **41,** 389–391 (1982).
10. (a) Y. Tomkiewicz, T. D. Schultz, H. B. Brom, T. C. Clarke, and G. B. Street, "Evidence Against Solitons in Polyacetylene: Magnetic Measurements," *Phys. Rev. Lett.* **43,** 1532–1536 (1979). (b) Y. Tomkiewicz, T. D. Schultz, H. B. Brom, A. R. Taranko, T. C. Clarke, and G. B. Street, "Solitons or Inhomogeneous Doping in AsF_5-Doped Polyacetylene?—EPR and DC Conductivity Evidence," *Phys. Rev. B* **24,** 4348–4363 (1981).
11. S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M. A. Druy, A. Sivak, A. J. Heeger, and A. G. MacDiarmid, "Solitons in Polyacetylene: Magnetic Susceptibility," *Phys. Rev. Lett.* **45,** 1123–1126 (1980).
12. (a) M. Peo, H. Förster, K. Menke, J. Hocker, J. A. Gardner, S. Roth, and K. Dransfeld, "Absence of Knight-Shift in the Metallic State of Polyacetylene," *Solid State Commun.* **38,** 467–468 (1981). (b) M. Peo, H. Förster, K. Menke, J. Hocker, J. A. Gardner, S. Roth, and K. Dransfeld, "Absence of Knight-Shift in the Metallic State of Polyacetylene," *Mol. Cryst. Liq. Cryst.* **77,** 103–110 (1981).
13. T. C. Clarke, K. K. Kanazawa, V. Y. Lee, J. F. Rabolt, J. R. Reynolds, and G. B. Street, "Poly(*p*-Phenylene Sulfide): A Novel Conducting Polymer," *J. Polym. Sci., Polym. Phys. Ed.* **20,** 117–130 (1982).
14. C. A. Fyfe, H. Mossbruger, and C. S. Yannoni, "A Simple 'Magic Angle' Spinning Apparatus for Routine Use in NMR Spectroscopy of Solids," *J. Magnetic Resonance* **36,** 61–68 (1979).
15. (a) L. Mihaly, S. Pekker, and A. Janossy, "NMR Investigation of the Structure of Pure and Iodine-Doped Polyacetylene," *Synthetic Metals* **1,** 349–355 (1980). (b) D. Moses, A. Denenstein, A. Pron, A. J. Heeger, and A. G. MacDiarmid, "Specific Heats of Pure and Doped Polyacetylene," *Solid State Commun.* **36,** 219–224 (1980).
16. *Carbon-13 NMR Spectral Data,* W. Bremser, L. Ernst, and B. Franke, Eds., Verlag Chemie, Weinheim, Germany, 1978.
17. J. Winter, *Magnetic Resonance in Metals*, Oxford University Press, London, 1971, Ch. 8.
18. (a) Y. Tomkiewicz, J. D. Kuptsis, R. G. Schad, and A. R. Taranko of the IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598; L. R. Dalton and H. Thomann of the University of Southern California, Dept. of Chemistry; and T. C. Clarke; unpublished results; (b) J. Flood, S. Ikehata, T. Woerner, M. A. Druy, A. J. Heeger, and A. G. MacDiarmid, work performed at University of Pennsylvania (although Flood and Heeger are currently at the University of California at Santa Barbara); unpublished results.
19. For a review see G. P. Gardini, "Oxidation of Monocyclic Pyrroles," *Adv. Heterocyclic Chem.* **15,** 67–98 (1973).
20. (a) K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak, "Polypyrrole: An Electrochemically Synthesized Conducting Organic Polymer," *Synthetic Metals* **1,** 329–336 (1980); (b) A. Diaz, J. M. Vasquez Vallejo, and A. Martinez Duran, "[Pt]Polypyrrole: A New Organic Electrode Material," *IBM J. Res. Develop.* **25,** 42–50 (1981).
21. G. B. Street, T. C. Clarke, M. T. Krounbi, K. K. Kanazawa, V. Y. Lee, P. Pfluger, J. C. Scott, and G. Weiser, "Preparation and Characterization of Neutral and Oxidized Polypyrrole

Films," *Mol. Cryst. Liq. Cryst.* **83,** [1285]–[1296] 253–264 (1982).
22. R. A. Jones and G. P. Bean, *Chemistry of Pyrroles,* Academic Press, Inc., New York, 1977, Ch. 11.
23. G. B. Street and V. Y. Lee, unpublished results.
24. R. H. Geiss and G. B. Street, unpublished results.

Received December 2, 1982

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