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Publisher: Taylor & Francis

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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

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Version of record first published: 14 Oct 2011.

To cite this article: T. C. Clarke, B. W. Mcquillan, J. F. Rabolt, J. C. Scott & G. B. Street (1982): The chemistry of polyacetylene doping, *Molecular Crystals and Liquid Crystals*, 83:1, 1-16

To link to this article: <http://dx.doi.org/10.1080/00268948208072151>

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Mol. Cryst. Liq. Cryst., 1982, Vol. 83, pp. 1-16
0026-8941/82/8301-0001\$06.50/0
© 1982 Gordon and Breach, Science Publishers, Inc.
Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

THE CHEMISTRY OF POLYACETYLENE DOPING

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Submitted for publication August 31, 1981

Natural abundance ^{13}C NMR experiments using cross polarization and magic angle spinning provide a unique method for monitoring the doping of polyacetylene. In contrast with previous authors we find that the doping of *cis*-polyacetylene with AsF_5 leads, even at low doping levels, to a new signal characteristic of the doped regions of the polymer. Similar measurements on *trans*-polyacetylene indicate that the doping of the *trans* isomer proceeds considerably more uniformly than that of the *cis* isomer. Comparisons with appropriate model compounds suggest that the observed shift of the ^{13}C NMR signal on doping is primarily a chemical shift rather than a Knight shift. Finally we discuss recent results on the nature of proton acid doping of polyacetylene, a process which shows remarkable similarities to oxidative doping.

^{13}C NMR OF DOPED POLYACETYLENE

The nature of the semiconductor-to-metal transition which occurs in polyacetylene at doping levels of $\sim 1\%$ 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.¹ In this picture the semiconductor-to-metal transition corresponds to a percolation threshold. On the other hand, Heeger has claimed that slower doping leads to a more homogeneous dopant distribution, which allows the proposed soliton nature of polyacetylene doping to be observed.² 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 ¹³C NMR spectrum of polyacetylene at various AsF₅ doping levels using magic angle spinning.³ In studying only *cis*-polyacetylene, they reported no substantial change in the ¹³C spectrum up to doping levels of ~7% AsF₅, 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 ~7% doping (attributed to overlap of the soliton band with the valence and conduction bands).² 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.*⁴ Conversion of *cis*-polyacetylene to the *trans* isomer was carried out under ~0.5 atm of helium at 200°C for one hour. The AsF₅ was purified as described earlier.⁵ Doping of the polyacetylene was performed as described in the work of Ikehata *et al.*² 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 ground with glass powder before loading. During the acquisition of data the sealed rotors were under a constant flow of helium. Spectra were obtained using cross polarization and magic angle spinning techniques. Shifts are expressed in ppm with respect to tetramethylsilane (TMS).

In agreement with previous authors, we find sharp signals for the undoped *cis*- and *trans*-polyacetylene at 127 and 136 ppm respectively.^{3,6-7} Figure 1 shows our results for the doping of *cis*-(CH)_x. The bottom spectrum is that of the undoped starting material; the low-field shoulder is due to the presence of a small amount of the *trans* isomer in this predominantly *cis* sample. The top spectrum shows the same material after doping to a composition of [CH(AsF₆)_{0.068}].

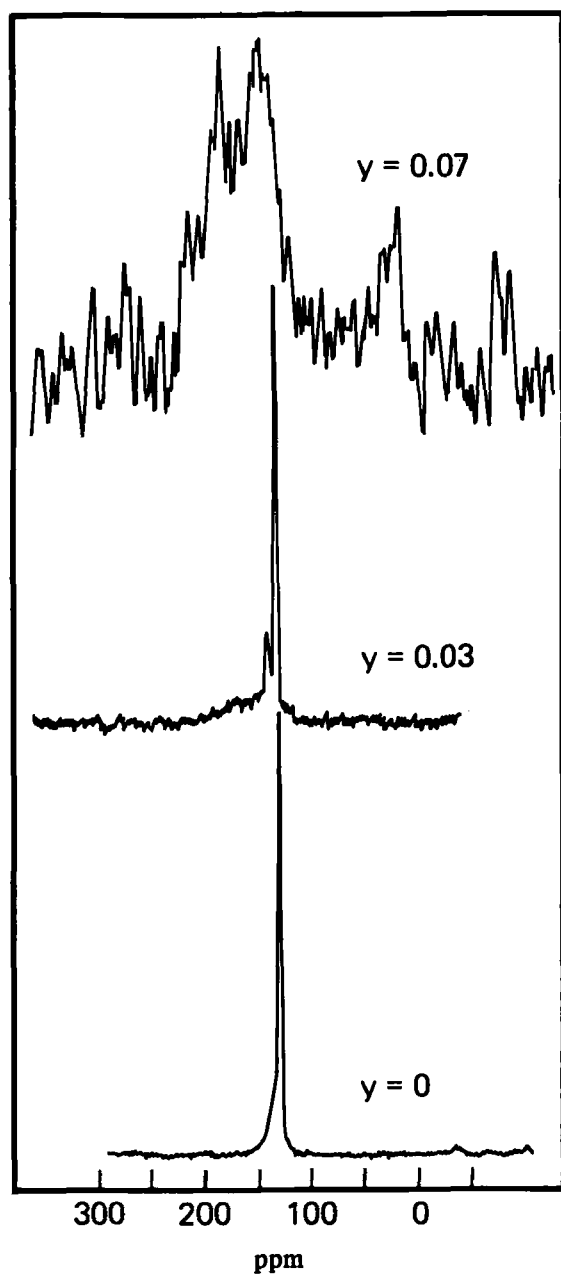


Figure 1 ^{13}C NMR spectra of *cis*-polyacetylene before (bottom) and after doping with AsF_5 to composition $[\text{CH}(\text{AsF}_6)_y]$

As in the Peo data³ a very broad resonance centered at ~ 150 ppm is observed. The origin of this downfield shift in the doped polymer will be discussed in detail below.

The middle spectrum in Figure 1 shows a *cis* sample doped to the intermediate concentration of 3 mole %. Superficially, this spectrum resembles those presented by Peo *et al.* for intermediate doping levels: a sharp and apparently unchanged *cis* line as well as 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 Figure 2. This broad peak, smaller in relative intensity, is also found in a 1% doped *cis* sample.

Figure 3 shows comparable data for AsF₅ doped *trans*-(CH)_x. (For experimental reasons the exact composition of the heavily doped sample was not determined. However, a lower limit of 5% was established.) The heavily doped sample exhibits a spectrum quite similar to that of heavily 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.

From these data we draw several conclusions: 1) Low levels of doping do not lead to extensive conversion of *cis*-polyacetylene to the unoxidized *trans* isomer. 2) In contrast to the conclusion of Peo *et al.*, however, signals characteristic of the doped polymer can be seen in the spectra of AsF₅ treated *cis*-polyacetylene at doping levels as low as 1%. Whether these signals correspond to material which is *cis* or *trans* in nature cannot be answered directly by these 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*.⁸ 3) In the first ¹³C NMR examination of AsF₅ 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 ~ 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.

The downfield shift in the doped polyacetylene has been explained as a Knight shift.³ However, the position of this signal is not unusual when compared to the shifts observed for the carbons of delocalized π -carbonium ions where no conduction electrons are present.

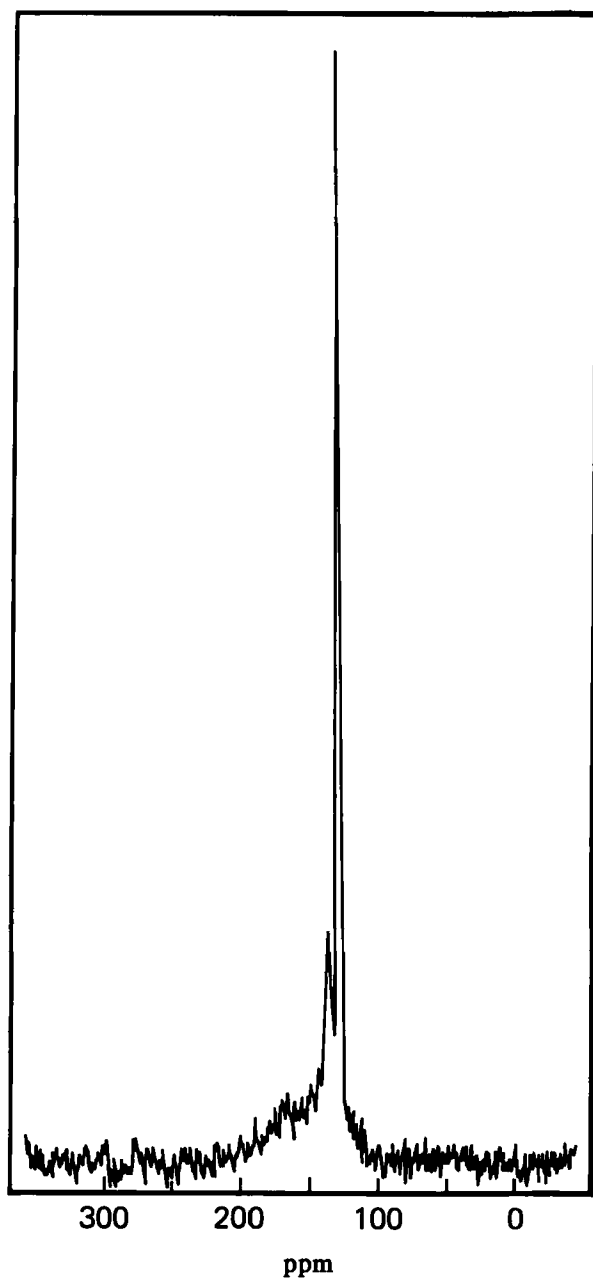


Figure 2 Expanded ^{13}C NMR spectrum for $[\text{CH}(\text{AsF}_6)_{.03}]$

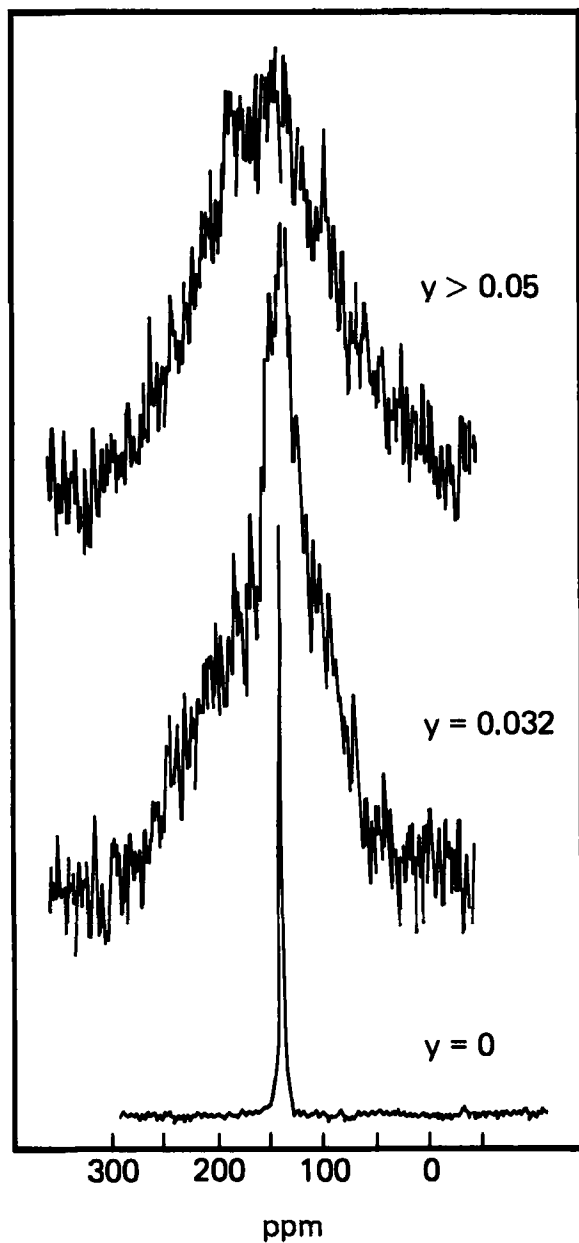


Figure 3 ^{13}C NMR spectra of *trans*-polyacetylene before (bottom) and after doping with AsF_5 to composition $[\text{CH}(\text{AsF}_6)_y]$

For example, although the ^{13}C NMR of benzene exhibits a sharp singlet at 128.7 ppm,⁹ the signal of the tropylium ion, which contains one positive charge equally distributed over seven carbon atoms, is shifted to 155.3 ppm.⁹ 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 ($\sim 1\text{--}7\%$). 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 $\sim 1.5 \times 10^{-7}$ emu/mole, while EPR studies on this sample yield a Pauli susceptibility of $\sim 1 \times 10^{-6}$ emu/mole.¹⁰ Moreover, since the conduction electrons giving rise to any Pauli susceptibility must be π -electrons, the Knight shift must involve core polarization; in particular both the magnitude and direction of such a shift are uncertain.¹¹ 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.

HF DOPING OF POLYACETYLENE

Although formal oxidizing and reducing agents were the first classes of materials demonstrated to be effective dopants of polyacetylene,¹² Gau *et al.* subsequently showed that exposure to proton acids could also raise the conductivity of polyacetylene to high levels.¹³ The actual mechanism of proton acid doping has remained ambiguous, however. For example, HClO_4 and H_2SO_4 , the most effective proton acid dopants, are known to be strongly oxidizing acids, with anhydrides which are also good oxidative dopants of $(\text{CH})_x$. On the other hand, HBr and HCl , acids without oxidizing anhydrides and with no formal oxidizing capabilities, do not raise the conductivity of polyacetylene higher than $\sim 10^{-4}$ ohm $^{-1}\text{cm}^{-1}$.^{14,15} We report here studies on the reaction of $(\text{CH})_x$ with HF , another non-oxidizing acid, which clearly indicate that proton acid doping does, indeed, proceed by a mechanism different from formal oxidation, but that the resulting delocalized carbonium ions are quite similar in both cases.

Polyacetylene and polyacetylene- d_2 were prepared by published procedures.⁴ *Cis-trans* mixtures were used in these experiments. HF (Matheson) was made anhydrous by addition to excess K_2NiF_6 (Alfa) in a Teflon FEP tube attached via Swagelock connectors to a stainless steel vacuum line. The mixture was cooled to -96°C and pumped to remove residual SiF_4 ; gas phase infrared spectra of the resulting material revealed no impurities. Since the FEP is somewhat permeable, the

HF/K₂NiF₆ mixture was frozen at -196°C and pumped before each reaction to remove any oxygen within the container. NH₃ (anhydrous, Matheson) was condensed at -196°C and degassed by means of several freeze-pump-thaw cycles. Exposure of polyacetylene to the NH₃ was accomplished by warming the ammonia to -78°C and allowing the vapor (pressure ~46 torr) to react with the (CH)_x for approximately one hour. ND₃ was prepared by reaction of D₂O (Aldrich Gold Label, 99.8%) vapor with LiN₃ (Alfa, 94%) and distilled prior to use. All sample manipulation was carried out in an inert atmosphere dry box. Conductivity measurements were made using the standard four point probe technique.

The changes in polyacetylene conductivity on exposure to HF are shown in Figure 4 as a function of HF weight uptake. If one assumes that each HF molecule acts as a (CH)_x dopant, the data would suggest that HF is somehow a less efficient doping agent than oxidants such as iodine or AsF₅.¹² However, HF is known to coordinate strongly with the fluoride anion to form initially the HF₂⁻ species; compositions as high as H₄F₅⁻ have been reported.¹⁶ Thus, the actual stoichiometry for a given weight uptake probably lies between [CH(H⁺F⁻)_y]_x and [CH(H⁺H₄F₅⁻)_y]_x. These compositions are both plotted in Figure 4 and can be considered upper and lower limits, respectively, on the actual extent of doping.

The more heavily doped samples are opaque in the infrared. No change in conductivity was observed when sufficient current was passed through a sample to cause complete polarization of any ionic conducting species. Thus, we conclude that the conductivity is electronic and not ionic in nature. Exposure of these samples to air leads to a gradual decay of the conductivity over 24 hours, yielding finally an insulating material.

Transmission infrared spectra for lightly doped (CH)_x and (CD)_x are shown in Figure 5. In both samples the tail of a strong absorption in the near IR can be seen in the region above 2000 cm⁻¹. Strong absorptions are observed at ~1420 cm⁻¹ and ~1200 cm⁻¹ respectively for the (CH)_x and (CD)_x samples. Broader absorptions are centered at roughly 900 cm⁻¹ for (CH)_x and 750 cm⁻¹ for (CD)_x. A relatively sharp peak at 1295 cm⁻¹ can be seen in the [CH(HF)_{0.016}] sample. Although C-F bond stretching modes might be expected in this region, the absence of this feature in the (CD)_x sample and the independent observation of this band in [CH(I₃)_x] samples^{17,18} rule out this interpretation.

In fact, the spectra of lightly HF doped polyacetylene are remarkably similar to those obtained for (CH)_x samples lightly doped with iodine or AsF₅.¹⁷⁻¹⁹ Here, however, HF has no formal oxidizing power and appears to function by protonating the polymer chain (see below).

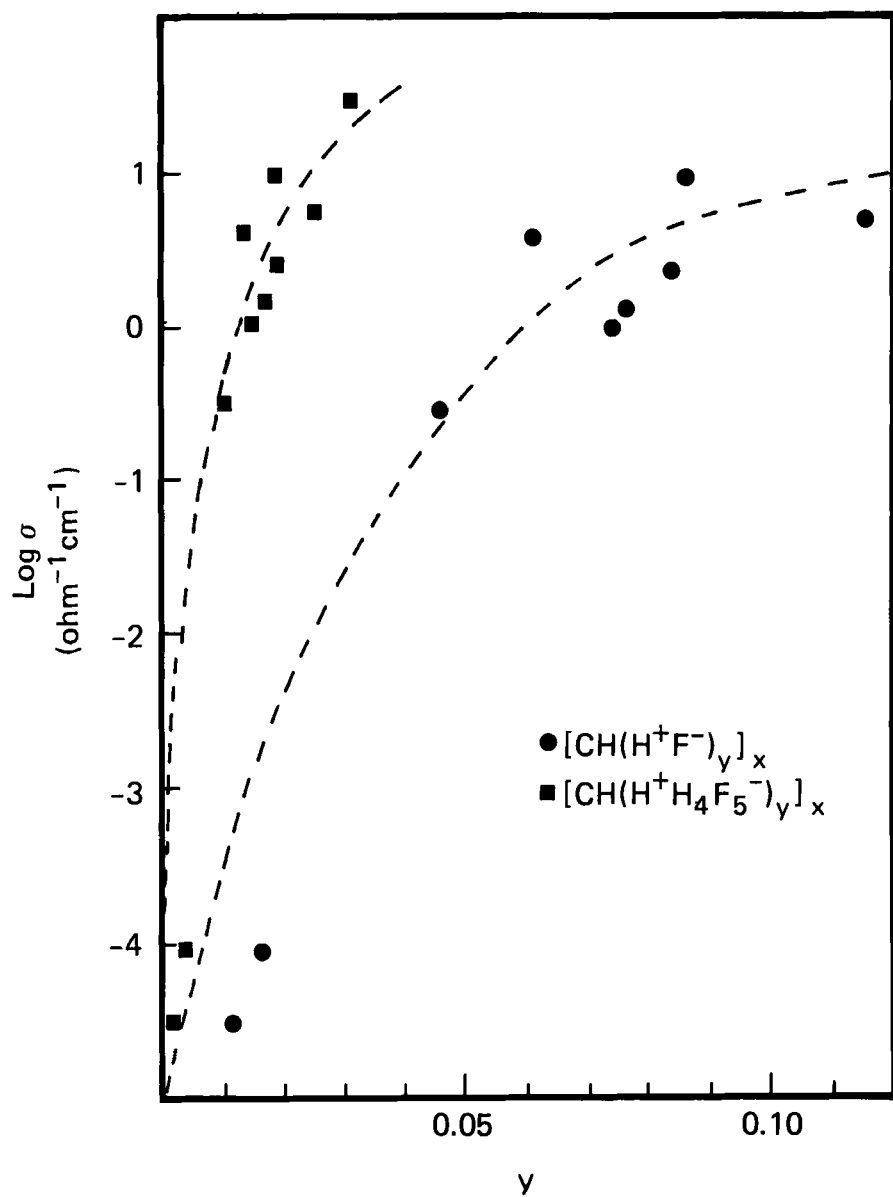


Figure 4 Polyacetylene conductivity as a function of reaction with HF

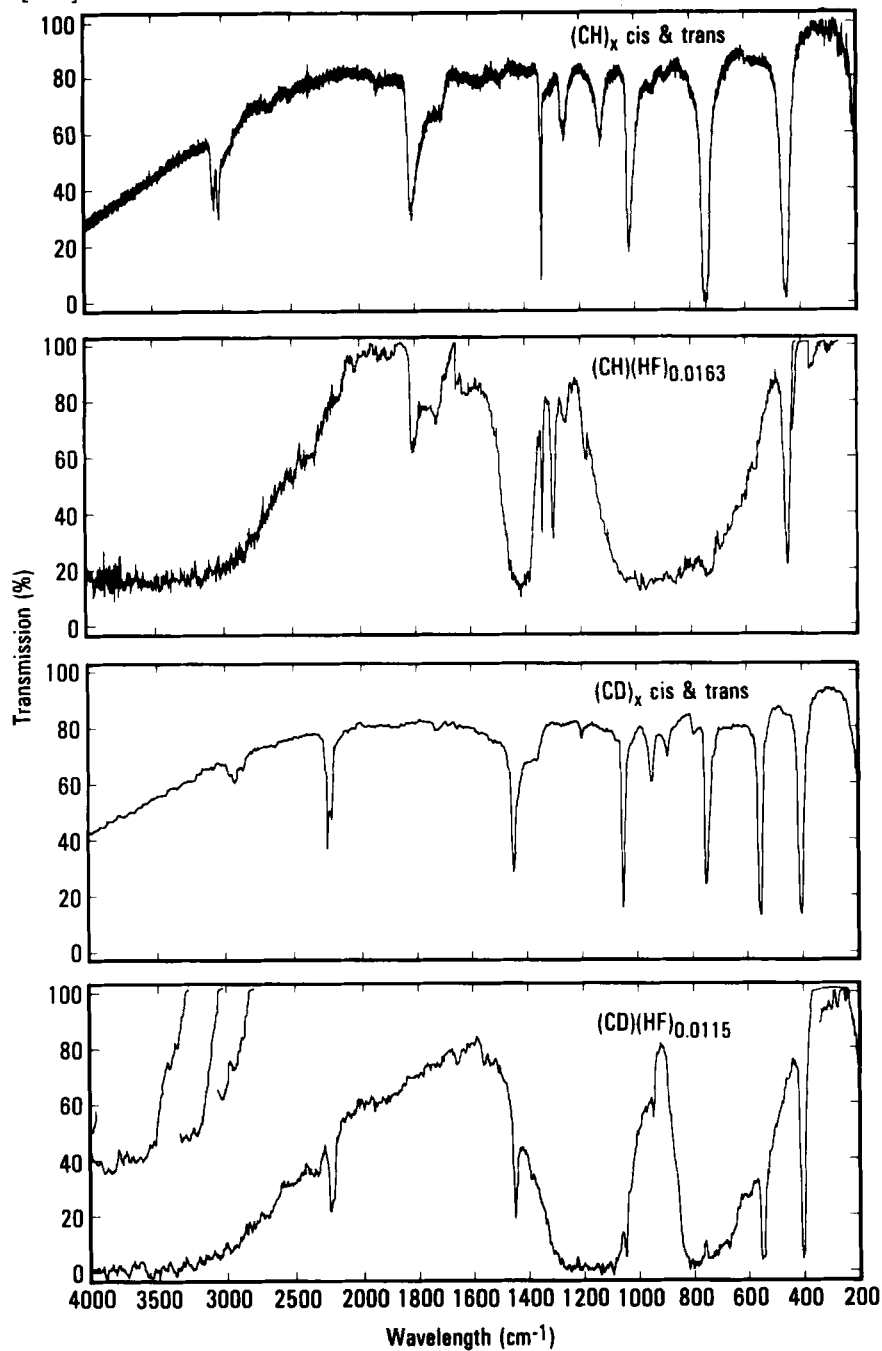
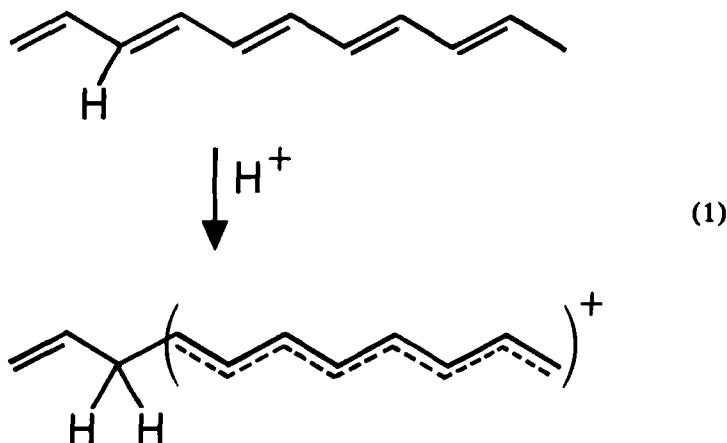


Figure 5 Transmission IR of undoped and lightly HF doped $(CH)_x$

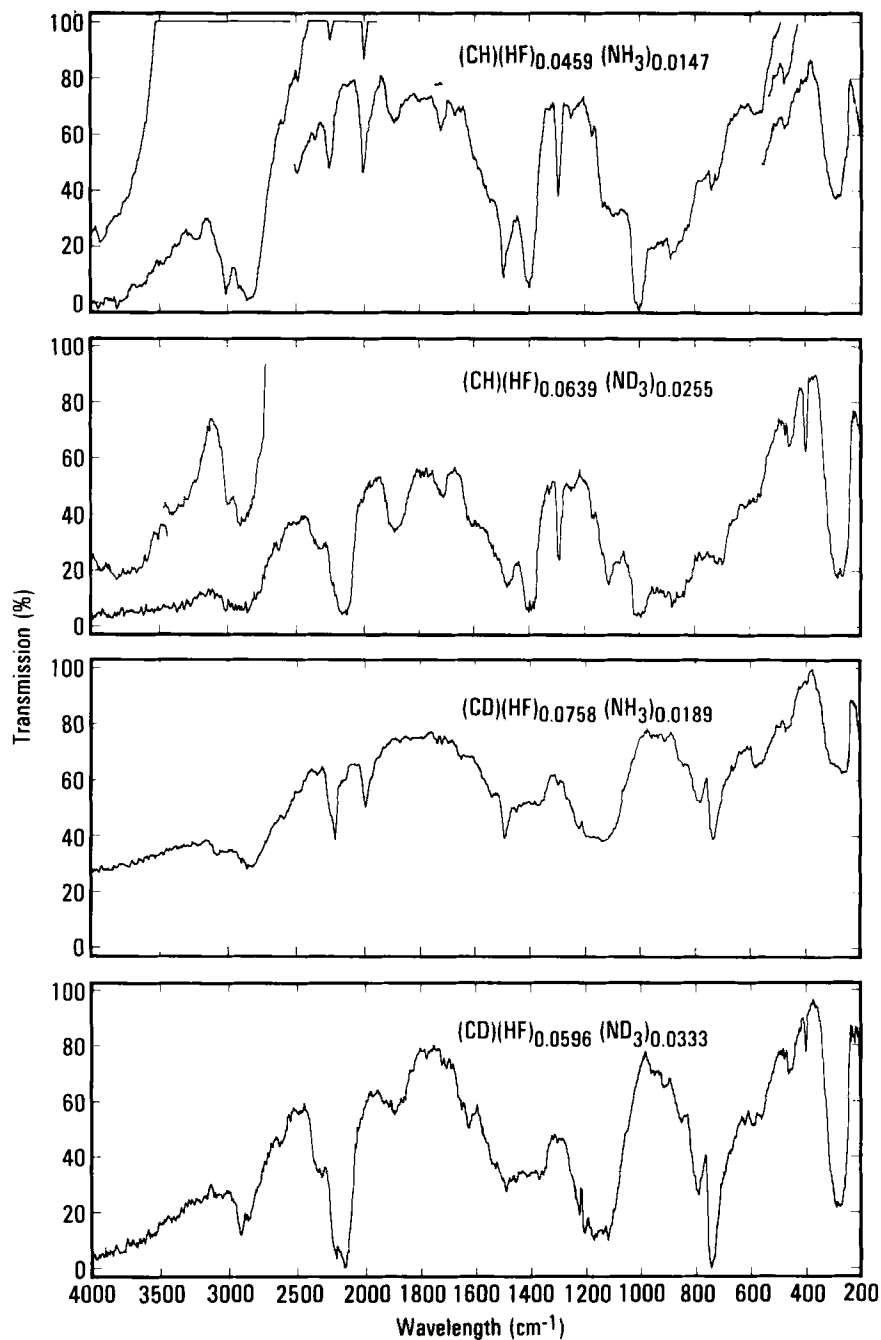
This result can be rationalized by examining the effect of adding a proton to one double bond of polyacetylene (Equation 1). Effectively



this reaction cuts the polyacetylene chain into two segments. As drawn, the region to the left of the reaction site is essentially a shorter but otherwise unchanged $(\text{CH})_x$ chain. The region to the right is a delocalized carbonium ion formally identical to the ion believed to be generated by oxidative doping. Thus it is reasonable that the infrared spectra of polyacetylene doped by oxidants and by proton acids should be quite similar, particularly since vibronic enhancement of the absorptions arising from the charged regions causes these peaks to dominate the infrared spectra of doped samples.¹⁷⁻¹⁹ The protonated sites, of course, interrupt the conjugation along the polymer backbone and, in sufficient quantity, would be expected to seriously degrade the ability of the chain to support charge transport. The extent of the 1,3 overlap of the π -orbitals immediately adjacent to the defect, and the ability of electrons to tunnel through this site remain unknown quantities.

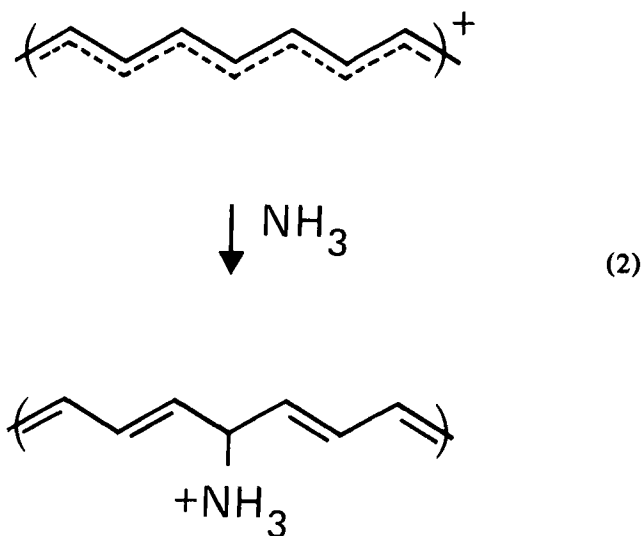
Because the more heavily doped samples are opaque in the infrared, transmission IR cannot be used to obtain information about the molecular structure of these materials. However, indirect information can be obtained by treating the doped samples with ammonia, a procedure which returns the polymer to an insulating state and allows infrared examination of the resulting material. Figure 6 shows the IR spectra of $(\text{CH})_x$ and $(\text{CD})_x$ samples after successive treatment with HF and NH_3 or ND_3 . Remnants of the broad peaks characteristic of the doped

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T. C. CLARKE *et al.***Figure 6** IR spectra after ammonia treatment

polymer suggest that the ammonia reaction may have been incomplete, but several interesting conclusions can be drawn from these spectra. None of the four spectra show any peaks associated with *cis*-polyacetylene, but prominent features at $\sim 1000\text{ cm}^{-1}$ in the $(\text{CH})_x$ and $\sim 740\text{ cm}^{-1}$ in the $(\text{CD})_x$ indicate the presence of *trans* material. This observation is consistent with previous reports that *cis*- $(\text{CH})_x$ is converted to *trans* on doping.⁸

A second significant feature of these spectra is the strong 2000 cm^{-1} peak in both the $(\text{CH})_x$ and $(\text{CD})_x$ samples after NH_3 treatment. Nakanishi has shown that primary aliphatic amine hydrochlorides have a band at $2100\text{--}1900\text{ cm}^{-1}$, but that this band is not present in the corresponding free amine.²⁰ The absorptions near 1600 and 1500 cm^{-1} are also characteristic of primary ammonium salts. This evidence suggests that addition of the ammonia to the oxidized polyacetylene occurs, localizing the positive charge on the ammonium group (Equation 2).



The absence of the 2000 cm^{-1} band in the ND_3 treated samples agrees with this interpretation. Elemental analyses also reveal that the nitrogen containing species cannot be washed out with water, supporting the idea that the bulk of the nitrogen is bound to the polymer chain and not present as ammonium fluoride.

In samples treated with ND_3 a peak near 2900 cm^{-1} is also observed, indicative of saturated C-H stretches. This signal is stronger in the $(\text{CH})_x$ samples, presumably because protonation of the undeuterated

polymer creates two sp^3 carbon-hydrogen bonds as opposed to one in the case of $(CD)_x$. No vinyl C-H stretches are observed in the $(CD)_x$ sample in the region above 3000 cm^{-1} , showing that exchange by a protonation-deprotonation mechanism does not occur.

The spectra of the ammonia treated samples change dramatically with time. After storage in sealed containers in a dry box for two weeks, the 2000 cm^{-1} peak in the NH_3 samples disappears. A new band appears at 1650 cm^{-1} , characteristic of an R- NH_2 bend. This suggests that the ammonium ion has been transformed into a primary alkyl amine with loss of HF. This change is accompanied by strong features in the sp^3 C-H stretching region at 2900 and 2850 cm^{-1} . Again no evidence for hydrogen exchange at vinyl positions is observed.

The ability of HF to act as an effective polyacetylene dopant might at first seem puzzling, since ion cyclotron resonance data indicate that HF is a weaker acid in the gas phase than either HCl or HBr.²¹ The coordination of the fluoride anion with additional HF, however, provides an additional driving force which is absent for the other hydrogen halides. Formation of the bifluoride anion alone is exothermic by 37 kcal/mole .¹⁶

In summary, we find that HF is capable of raising the conductivity of polyacetylene to high levels by what must be a protonation mechanism. Subsequent reaction with ammonia leads to localization of positive charge on the resulting primary ammonium ion.

ACKNOWLEDGMENTS

We thank the 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 project. We also thank M. Druy and T. Woerner for their help in preparing the 3.2% *trans* sample.

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