CHEMISTRY of
MATERIALS

VOLUME 6, NUMBER 5 MAY 1994

Communications

Characterization of "Highly Conducting" Polyacetylene

Georgia A. Arbuckle,[*] Nancy M. Buecheler,[†] and Kathleen G. Valentine[‡]

Department of Chemistry, Rutgers University
Camden, New Jersey 08102
Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received December 8, 1993
Revised Manuscript Received February 8, 1994

The large increase in conductivity observed when polyacetylene is exposed to iodine vapor has fascinated scientists since the late 1970s.[1] When conductivities in the metallic regime were reported by Naarmann et al.[2] and Tsukamoto,[3] interest in this conducting polymer was rekindled. As 10^5 S/cm is the highest reported conductivity for any organic conducting polymer, a greater understanding of the factors that influence the high conductivity in polyacetylene is critical. One of the factors contributing to the high conductivity was thought to be the amount of sp^3 sites in the sp^2 chain. The sp^3 content was reported[2b] to be lower in N-$(\mathrm{CH})_x$ than in traditional Shirakawa polyacetylene (or S-$(\mathrm{CH})_x$) (0% vs 4%) as determined by ^{13}C CPMAS NMR. Other factors may include the bulk density or the morphology of each polyacetylene. The physical differences would presumably affect the electronic properties of the conducting polymer. However, N-$(\mathrm{CH})_x$ is remarkably similar electronically to S-$(\mathrm{CH})_x$.[4]

There have been extensive attempts to reproduce these highly conducting polyacetylene films by many research groups.[3,5,6] Therefore, to compare these polyacetylene materials, we have synthesized and characterized S-$(\mathrm{CH})_x$ (Shirakawa polyacetylene[1]), N-$(\mathrm{CH})_x$ (Naarmann et al.[2]), and ν-$(\mathrm{CH})_x$ (Tsukamoto[3]). Many syntheses of both free-standing and thin films of S-$(\mathrm{CH})_x$, N-$(\mathrm{CH})_x$, and ν-$(\mathrm{CH})_x$ were carried out.[7,8] We report here the characterization of the undoped free-standing films by ^{13}C CPMAS NMR, FTIR, and elemental analysis as well as the conductivity of iodine-doped, stretched and unstretched films.

Naarmann et al.[2] prepared their highly conducting polyacetylene, referred to in the literature as New or N-$(\mathrm{CH})_x$, using the Ziegler–Natta catalyst which is used in the original Shirakawa polyacetylene. However, silicone

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[*] To whom correspondence should be addressed at Rutgers University, Camden, NJ 08102.

[†] Current address: Department of Chemistry, Temple University, Philadelphia, PA 19122.

[‡] Current address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.

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oil[9] was used as the catalyst solvent, and the catalyst was aged by heating to 120 °C for 2 h. Tsukamoto was not able to reproduce such a metallic polyacetylene,[3] and better results were observed when Decalin (decahydronaphthalene) was used as the solvent. In this preparation, the catalyst is heated to 200 °C, and the polymerization occurs under reduced acetylene pressure. We have followed the procedures described in the literature[10] for each type.[1-3] In addition, high-purity acetylene[11] was used for all syntheses. Since the type of silicone oil was presumed to be critical,[9] ABIL AV 1000 silicone oil was obtained.[12]

Several syntheses of each type of polyacetylene were characterized by elemental analysis,[13] ^{13}C CPMAS NMR, FTIR, and SEM. Each of our preparations were self-consistent. Although all three types use the Ziegler–Natta catalyst and high-purity acetylene gas, we prepared three distinctly different polyacetylene materials due to the changes in catalyst pretreatment. The well-known fibrillar morphology of S-$(CH)_x$ was clearly observed by SEM. In contrast, both N-$(CH)_x$ and ν-$(CH)_x$ are much more densely packed.[2,3] SEM confirms that the three materials are topologically distinct.[14]

S-$(CH)_x$ is the easiest to handle. Several washes in pentane or toluene are sufficient to obtain a good elemental analysis.[13] However, extensive washing of N-$(CH)_x$ (for up to 10 days), still produces a polyacetylene that may contain residual catalyst (*vide infra*). Methanol is used to remove more catalyst (see elemental analyses in ref 13), but no elemental analysis of N-$(CH)_x$ is as close to ideal as S-$(CH)_x$. The elemental analyses indicate residual catalyst present in ν-$(CH)_x$.

NMR studies were performed to compare the relative amount of sp^3-hybridized carbons in the otherwise completely sp^2-hybridized polyacetylene chain. The sp^3 groups may be due to methyl and methylene end groups and/or cross-links in the polymer. The relative sp^3 content of N-$(CH)_x$ and S-$(CH)_x$ was reported to be related to the conductivities after doping.[2b] This assumes that the sp^3-hybridized units interrupt the conjugated chain. Residual catalyst would also result in methyl and methylene type resonances but not necessarily lower conductivity after doping.

Figure 1 shows the room-temperature ^{13}C NMR spectra for the three polyacetylene materials.[15] For all, the expected sp^2-hybridized carbon resonances are found at 128.1 ppm for cis and 137.6 ppm for trans (relative to external reference TMS).[16-18] A typical spectrum of the as-synthesized *cis*-S-$(CH)_x$ isomer is shown in Figure 1a. A small amount of the trans isomer is present. Figure 1b was obtained by isomerizing the *cis*-S-$(CH)_x$ to *trans*-S-$(CH)_x$ by heating at ~150 °C in vacuum for ~1 h. No resonances are observed due to methylene groups or methyl end groups. Within the detection limits of this technique,

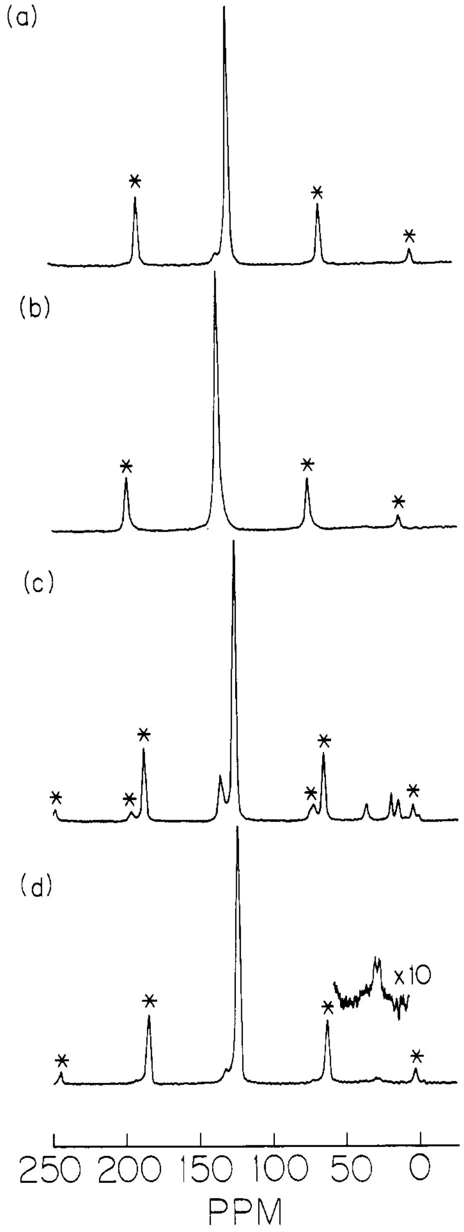

Figure 1. The 67.8-MHz carbon-13 CPMAS NMR spectra of polyacetylene: (a) S-$(CH)_x$, high cis content; (b) S-$(CH)_x$ isomerized to trans isomer; (c) N-$(CH)_x$, high cis content; (d) ν-$(CH)_x$, high cis content. Spectra were recorded on a 270-MHz wide-bore JEOL spectrometer equipped with a Doty 7-mm variable-angle sample spinning probe. Cross polarization was used with high-power ^{1}H decoupling. The Hartmann–Hahn contact time was 1 ms with a recycle time of 5 s. Approximately 2500 scans were collected from a 50–100-mg sample. The spin rate was ~4 kHz. The asterisks denote spinning sidebands.

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[9] The type of silicone oil used by Naarmann to obtain high-conductivity polyacetylene was Tegiloxan AV-1000 (Wacker Chemie, Theodore Goldschmidt Chemical Corp.).

[10] Discussions with Naarmann, Theophilou, and/or Tsukamoto provided further information about the details of each method of synthesis. For example, "several hours" used in refs 3a and 3b was actually 7 h.

[11] High-purity acetylene gas (99.9998% C_2H_2) was obtained from Koatsu Gas Kogyo Co., Ltd., Japan by Iwatani Int.

[12] Correspondence with Wacker Chemie, Theodore Goldschmidt Chemical Corporation, Germany, indicates that Tegiloxan AV-1000 is marketed in the USA by Goldschmidt Chemical Corp., Hopewell, VA, as ABIL AV 1000.

[13] Analyses were performed on a Perkin-Elmer 240 C elemental analyzer. Calculated (ideal): %C, 92.26; %H, 7.74. Total %C+H, 100.00 Found: S-$(CH)_x$: %C, 89.14; %H, 7.71, ash 1.66% (as percent of initial sample weight); N-$(CH)_x$ (washed in toluene only) %C, 85.03; %H, 8.04, ash 7.2%; N-$(CH)_x$ (washed in toluene and anhydrous methanol) %C, 87.57; %H, 7.93, ash 2.0%: ν-$(CH)_x$ (washed in toluene and anhydrous methanol) %C, 82.55; %H, 7.44, ash 6.6%.

[14] A detailed analysis, including SEMs, of the differences between the thin films of each type is in preparation.

[15] All samples were synthesized and handled under vacuum or in an argon filled dry box. Polyacetylene films were cut into small pieces (<0.25 cm^2) and loaded into a saphire rotor in a Vacuum Atmospheres drybox and transferred to the spectrometer in an argon-filled container. The rotor was spun over dry nitrogen at ~4 kHz.

[16] Maricq, M. M.; Waugh, J. S.; MacDiarmid, A. G.; Shirakawa, H.; Heeger, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7729.

[17] Gibson, H. W.; Pochan, J. M.; Kaplan, S. *J. Am. Chem. Soc.* **1981**, *103*, 4619.

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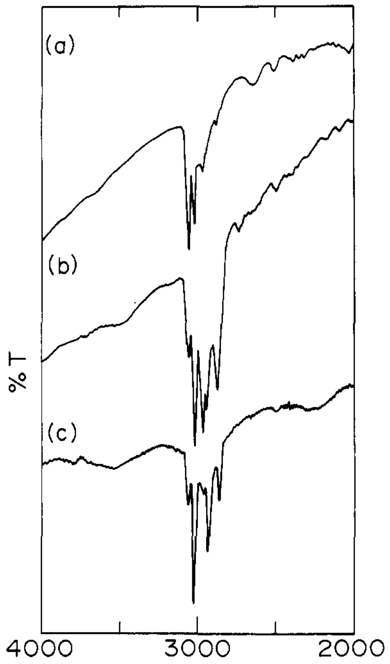

Figure 2. FTIR spectra of polyacetylene: (a) S-(CH)$_x$, as-polymerized at −78 °C; (b) N-(CH)$_x$, as-polymerized at room temperature; (c) ν-(CH)$_x$, as-polymerized at −70 °C. Spectra were recorded on a Perkin-Elmer 1760-X spectrophotometer under nitrogen purge. Approximately 32 scans were collected.

<1% sp^3 carbons are found in S-(CH)$_x$ contrary to previous reports.[2b,19]

In contrast, parts c and d of Figure 1 indicate that methyl and methylene groups are present in N-(CH)$_x$ and ν-(CH)$_x$. The sp^3 content in N-(CH)$_x$ was as high as 9%. In Figure 1c, the resonances at 40 and 20 ppm are methylene carbons; the 15 ppm resonance is typical of methyl end groups. Methylene carbon resonances are also found in ν-(CH)$_x$ as shown in Figure 1d at ~30 ppm.

The FTIR spectrum of N-(CH)$_x$ shown in Figure 2b supports the NMR results. C–H stretches from sp^3-hybridized carbon are found at 2959, 2929, and 2871 cm^{-1}. The FTIR spectrum of ν-(CH)$_x$ in Figure 2c also illustrates sp^3 C–H stretches in the 2960–2850-cm^{-1} region. For comparison, cis-rich S-(CH)$_x$ is shown in Figure 2a with only the expected sp^2 C–H stretches at 3044 and 3012 cm^{-1}, in agreement with the NMR spectrum of S-(CH)$_x$ in Figure 1a and elemental analyses.

To investigate whether the sp^3 content may be due to catalyst residue remaining in the polymer, as was suggested by FTIR studies of N-(CH)$_x$,[6,20] NMR spectra were taken after exposing each polyacetylene sample to air for 24 h. The main cis and trans resonances remained while the methyl and/or methylene resonances were absent. This agrees with the hypothesis that titanium and/or aluminum catalyst sites are hydrolyzed by air exposure with the corresponding loss of organic residues that contain sp^3-hybridized carbons. No residual catalyst is detectable by these analyses in S-(CH)$_x$. Catalyst residue in N-(CH)$_x$ and ν-(CH)$_x$, even after extensive washing, is consistent with the lower total C + H content.[13] The ash residue may be due to titanium and/or aluminum from the Ziegler–Natta catalyst that remains in the film.

Table 1. Conductivities of I$_2$/CCl$_4$-Doped Polyacetylene Films

		conductivity (four probe, S/cm)		
type of (CH)$_x$	l/l_0	high	low	avg[a]
S-(CH)$_x$	1[b]	379	337	3.6 × 10^2
H-(CH)$_x$	1	1035	762	8.5 × 10^2
ν-(CH)$_x$	1	417	132	2.9 × 10^2
S-(CH)$_x$	2.5[c]	499	412	4.5 × 10^2
N-(CH)$_x$	2	3648	1746	2.5 × 10^3
N-(CH)$_x$	3	3180	2255	2.8 × 10^3
N-(CH)$_x$	4	5440	2314	4.2 × 10^3
ν-(CH)$_x$	2	980	694	8.4 × 10^2
ν-(CH)$_x$	3	1153	1074	1.1 × 10^3
ν-(CH)$_x$	4	3838	1182	2.2 × 10^3

[a] Average conductivities limited to 2 s.f. for all reported values due to thickness measurement limitations. [b] l/l_0 = 1 indicates unstretched polymer. [c] Maximum stretching possible for S-(CH)$_x$. Average thickness of film before stretching: S-(CH)$_x$ ~75 μm; N-(CH)$_x$ ~50 μm; ν-(CH)$_x$ ~2 μm.

If the sp^3 sites present in N-(CH)$_x$ and ν-(CH)$_x$ are due to catalyst residue, the higher amount of sp^3-hybridized carbon found in these polyacetylenes would not necessarily result in lower conductivity. Conductivity would be influenced only by the amount of sp^3 units present in the polymer, if they existed as cross-links in the chain. Since cross-links would not be removed by air exposure, any sp^3 units other than those due to the catalyst are below the detection level of these techniques. *It is important to note that complete removal of catalyst residue is not necessary to obtain high conductivity in N-(CH)$_x$ and ν-(CH)$_x$.*

The relative amounts of stretching and conductivities after iodine doping[21] of the three polyacetylene materials are given in Table 1. The conductivities of both stretched and unstretched S-(CH)$_x$ agrees with previous studies. Comparing the unstretched samples, N-(CH)$_x$ is the most conducting (8.5 × 10^2 S/cm). N-(CH)$_x$ and ν-(CH)$_x$ stretch[22] much more readily than S-(CH)$_x$, up to 4 times their original length. The highest conductivity was found for N-(CH)$_x$ stretched to 4 times its original length (average 4.2 × 10^3 S/cm). This is in agreement with the values reported for N-(CH)$_x$ stretched 4 times after washing and iodine doping.[2b] The "high" conductivities reported for N-(CH)$_x$ (up to 10^5 S/cm) were for N-(CH)$_x$ supported on a polybutadiene film stretched 4 times while wet with catalyst.[2b] The film was then washed and iodine doped. We are investigating stretching the film prior to washing as well as using acidic methanol.

A reviewer questioned the role of molecular weight. The molecular weight of S-(CH)$_x$ has been determined by radioquenching.[23] The amount of dopant required for the sharp increase in conductivity to occur varies with molecular weight from ~8 × 10^{-5} for M_n = 500 to ~7 ×

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(19) Wind, R. A.; Duijvestijn, M. J.; Vriend, J. *Solid State Commun.* **1985**, *56*, 713.

(20) In ref 6, absorptions in the 2980–2875-cm^{-1} region were removed by exposure to oxygen for 24 h. Mass spectroscopy confirmed that organic fragments such as $(C_3H_7)^+$, $(C_2H_3O)^+$, $(C_4H_9)^+$, and $(CH_3O)^+$ were eliminated when N-(CH)$_x$ was heated from 50 to 285 °C.

(21) Polyacetylene film is doped for 1 h in a saturated solution of iodine in carbon tetrachloride. The films were washed in carbon tetrachloride and dried in a current of argon. Four-probe conductivity measurements are made using a nanovoltmeter. Doping and conductivity measurements were performed in an argon-filled glovebag.

(22) Although N-(CH)$_x$ and ν-(CH)$_x$ could be stretched dry, better results were found if the films were wet with either toluene or cumene/toluene during stretching.

(23) Chien, J. C. W.; Karasz, F. E.; Schen, M. A.; Hirsch, J. A. *Macromolecules* **1983**, *16*, 1694.

10^{-4} for M_n = 11 000.[24] Since the M_n of N-$(CH)_x$ and ν-$(CH)_x$ has not been reported, a comparison between the three types of polyacetylene cannot be made. However, the relationship between conjugation length and conductivity may be more critical than molecular weight. The conjugation length in polyacetylene has been approximated using resonance Raman spectroscopy (RRS). Somewhat surprisingly, a longer conjugation length has not been found for N-$(CH)_x$ or ν-$(CH)_x$ as compared with S-$(CH)_x$.[2,3] A RRS investigation of the three polyacetylenes synthesized for this study is in progress.

We conclude, that the differences in conductivity between S-$(CH)_x$, N-$(CH)_x$, and ν-$(CH)_x$ are not due to the amount of sp^3 sites present in each. The higher conductivities possible for N-$(CH)_x$ and ν-$(CH)_x$ are likely related to their ease of alignment. The residual catalyst may be acting as a plasticizer. However, even comparing the unstretched films, N-$(CH)_x$ is the most conducting, indicating a difference in the polyacetylene synthesized by this method. Differences between the three materials observed by SEM agree with the higher bulk densities reported[2,3] for N-$(CH)_x$ (ca. 0.85–0.90 g/cm^3) and ν-$(CH)_x$ (ca. 1.1 g/cm^3) in comparison with the open fibrillar nature of S-$(CH)_x$ (ca. 0.4 g/cm^3).[25] The denser materials result in higher conductivity after doping. However, they require a longer time to achieve maximum conductivity. The rate of doping is different for each of the polyacetylene materials,[26] with a slower doping rate found for the denser polymers. Other differences between these materials are under investigation. There is no doubt that these "highly conducting" materials will continue to be of interest in the future.

Acknowledgment. The JEOL 270 NMR spectrometer is supported by NSF Grant CHE-89-09587. Acknowledgement is made to Xue Qin Wang for SEM performed at the LRSM Electron Microscopy Central Facility at the University of Pennsylvania, which is supported by NSF-MRL (Grant DMR91-20668). This work was supported by Research Corporation, Pew Science Program in Undergraduate Education, and the Research Council of Rutgers University. G.A.A. acknowledges a Henry Rutgers Research Fellowship from Rutgers University.

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