

Polydifluoroacetylene, Polychlorofluoroacetylene, and Polydichloroacetylene

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Received November 5, 1998

Polymerization of fluorinated and chlorinated acetylenes has received little or no attention to date despite the potential for discovery of new materials with unusual optical, electrical, and chemical properties.^{1–6} The challenges of synthesizing and handling the parent difluoro-, fluorochloro-, and dichloroacetylenes, which are notoriously explosive even at cryogenic temperatures (in the case of fluorinated acetylenes)^{7–10} and pyrophoric upon exposure to very small amounts of air,^{11–17} have probably limited preparative work in the area. We report the preparation and characterization of the first tractable polymeric materials derived separately from difluoroacetylene, fluorochloroacetylene, and dichloroacetylene.^{18,19}

Cryogenic polymerization (or chemical vapor deposition onto substrates) of highly unstable difluoroacetylene²⁰ from -196 to -95 °C leads to formation of a new fluorocarbon polymer (polydifluoroacetylene; PDFA) with a bulk stoichiometry of $C_{1.00}F_{0.93-0.97}$ measured by elemental analysis. This air-sensitive, deep-red material has very different structural, spectroscopic, and physical properties than those of well-known carbon monofluoride materials derived from graphite and fluorine at high temperatures (graphite fluorides).^{21–25} Angle-resolved X-ray photoelectron spectroscopic (XPS) measurements on thin films deposited on quartz indicate an F/C ratio which decreases toward the surface:

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- (18) Although the synthesis of the polymer of dichloroacetylene was allegedly claimed in two patents (refs 19a–b), the published preparative methods are irreproducible. The PDCA polymer in this work does not have similar properties to those described and decomposes irreversibly in the presence of catalysts claimed to generate the polymer.
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0.86(2), 0.89(2), and 0.96(2) at 20, 50, and 90 Å penetration depths, respectively. High-resolution C_{1s} XPS measurements (Figure 1 top) indicate the material contains a distribution of fluorocarbon structural moieties (2% $\pi-\pi^*$ shake-up satellite, 19% CF_2 , 43% CF , 25% C_β , 11% CH_x ; C_β = beta shifted carbon), suggestive that redox disproportionation occurs readily on the pathway to forming the isolable metastable film. The peak at 293.5 eV could also be attributed to a small percentage of $-CF_3$ groups, but the red color and air sensitivity of the films support primary assignment as a $\pi-\pi^*$ shake-up satellite. The C_β peak is assigned to nonhalogenated carbon atoms whose binding energies are shifted due to vicinal halogen substitution (e.g. $\underline{C}-CX$).²⁶

Cryogenic polymerization of chlorofluoroacetylene leads to a new polymer (polychlorofluoroacetylene; PCFA) which has a stoichiometry of $C_{2.00}Cl_{1.01}F_{1.00}$. Characterization of PCFA by GPC, ^{13}C NMR, ^{19}F NMR, IR, and UV/vis spectroscopies indicates that the highly polydisperse material ($M_w/M_n = 5.04$ and 6.39 for two fractions with different chloroform solubility) has a polyunsaturated chain structure composed primarily of repeating $-CF=CCl-$ units. The IR spectrum shows a relatively intense set of $C=C$ modes at 1673 and 1632 cm^{-1} . A group of broadened doublets around 150 ppm ($^1J_{C-F} = ca.270-280$ Hz) and a collection of overlapping broad resonances centered at 110.5 ppm are the only significant peaks observed in the ^{13}C NMR spectrum (Figure 2).²⁷ High-resolution C_{1s} XPS measurements on a pellet of the PCFA polymer (Figure 1 middle) indicate that it contains a greater percentage of monohalogenated carbon (2% $\pi-\pi^*$ shake-up satellite, 13% CX_2 , 36% CCl , 37% CF , 5% C_β , 9% CH_x) relative to the PDFA polymer, suggestive that redox disproportionation occurs to a lesser extent.

Dichloroacetylene resists thermal polymerization in condensed or gas phases. Polymerization of dichloroacetylene in benzene (25 °C), catalyzed by $MoCl_5$ gives a white insoluble solid ($C_{1.00}Cl_{0.99}$) in 94% yield.^{28–30} The spectroscopic properties of this air-stable material are consistent with a nonplanar, polyunsaturated backbone of *cis*-dichloro stereochemistry at each double bond.^{31–33}

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(26) Elemental analysis and time-of-flight SIMS experiments show that there is very little hydrogen in the film; thus, the beta-shifted carbon (C_β totaling 25%) is either unsaturated or bonded to oxygen. Because oxygen totaled less than a few percent on average, the former is more consistent with the observations. The CH peak grows with increasing exposure to atmospheric moisture.

(27) Data for polychlorofluoroacetylene: ^{19}F NMR ($CHCl_3$) (δ , description, peak width, assignment, relative area) -89.5 (br s, 350 Hz fwhm, 20%), -91.4 (br s, 35 Hz fwhm, 14%), -91.8 (br s, 20 Hz fwhm, 42%), -92.9 (br s, 40 Hz fwhm, 15%), -94.5 (br s, 30 Hz fwhm, 9%); ^{13}C NMR ($CHCl_3$) (δ , description, assignment, relative area) 152.0 (br d, $^1J_{C-F} = 281$ Hz, $=CF$, 18%), 151.3 (br d, $^1J_{C-F} = 274$ Hz, $=CF$, 25%), 150.7 (br d, $^1J_{C-F} = 270.0$ Hz, $=CF$, 57%), 112–109 (broad-overlapping singlets or doublets, $=CCl$, 95% vs total of 152–150 region). Anal. Calcd for C_2ClF C, 30.57; H, 0.00; Cl, 45.22; F, 24.20. Found C, 29.89; H, 0.00; Cl, 44.49; F, 23.66. IR (KBr, cm^{-1}) 1673 (s, br), 1632 (s) ($C=C$); 1260 (vs), 1045 (vs) 1026 (vs) ($C-F$); 784 (s) ($C-Cl$). Weak bands were also observed at 1162, 975, 908, 834, 671, and 458 cm^{-1} . UV/vis (CH_2Cl_2 ; 0.08 mg mL^{-1}) $\lambda_{max} = 292, 350$ nm ($A_{292} = 2.02$; $A_{350} = 0.59$).

(28) The polymerization of 1-chloro-aryllalkynes by $MoCl_5$ has been reported.²⁹

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(31) Data for polydichloroacetylene: ^{13}C MAS NMR 126 (s, ca. 600 Hz fwhm). Anal. Calcd for CCl_2 C, 25.29; Cl, 74.72; Found C, 25.44; Cl, 74.83. IR (KBr, cm^{-1}) 1626 (mw), 1562 (vw), 1157 (s), 850 (vs), 801 (vs) 612 (vw), 571 (w). Raman (solid, cm^{-1}) 1664 (vs), 1575 (m), 1175 (m), 383 (m). UV/vis (thin film) $\lambda_{max} = 220, 270$ nm, ($A_{220}/A_{270} = 1.1$).

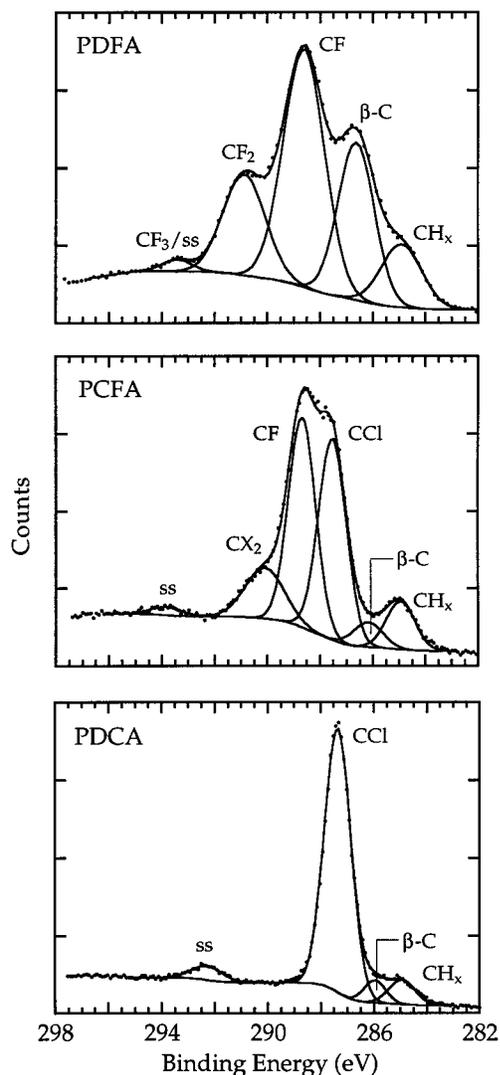


Figure 1. XPS C_{1s} spectra (55° takeoff angle) for a PDFA thin film on quartz (top), PCFA pellet (middle) and PDCA pellet (bottom). Peak fits show the contribution of hydrocarbon (CH_x), beta-shifted carbon (β -C), carbon bonded to one halogen atom (CCl and CF), carbon bonded to two halogen atoms (CX_2 and CF_2), and the π - π^* shake-up satellite (ss) to the C_{1s} spectrum for each sample.

A pellet of the free-standing polymer shows no CX_2 carbon by C_{1s} XPS (Figure 1 bottom) in contrast to the fluorinated polymers, but still shows a strong π - π^* shake-up satellite.

Thermogravimetric studies on PDFA and PDCA show they have comparable thermal stability under Ar, with a 10% mass loss temperature for PDFA of $425^\circ C$ versus $468^\circ C$ for PDCA ($10^\circ C\ min^{-1}$ heating rate). While PDFA shows only a broad exotherm associated with mass loss (predominantly C_6F_6), PDCA demonstrates striking thermal behavior (Figure 3), exhibiting a sharp exotherm centered at $413^\circ C$ ($1.46\ kJ\ g^{-1}$) and a sharp endotherm centered at $669^\circ C$ ($1.61\ kJ\ g^{-1}$). Both peaks are consistent with highly cooperative structural rearrangements or phase transitions. The onset of mass loss beginning around $430^\circ C$ is coincident with a broad exotherm ($667\ J\ g^{-1}$) expected for the observed reductive dechlorination of the parent polymer; a

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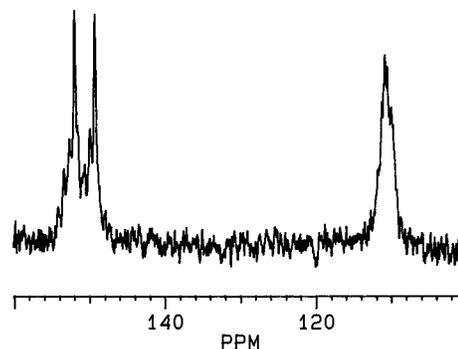


Figure 2. ^{13}C NMR spectrum (coupled to F) for the chloroform soluble fraction of polychlorofluoroacetylene.

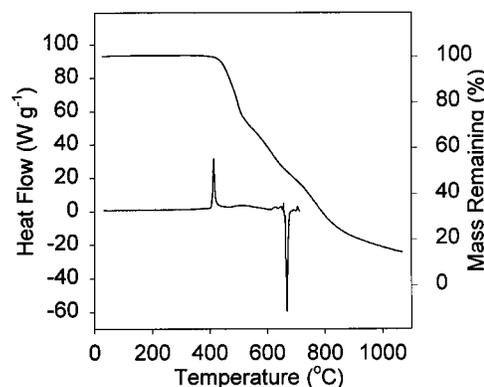


Figure 3. Overlaid TGA (top) and DSC (bottom) thermograms for polydichloroacetylene.

noncrystalline carbon char (glassy carbon-like based on broad Raman peaks at 1588 and $1349\ cm^{-1}$)³⁴ is obtained at temperatures exceeding $400^\circ C$ (in vacuo). Mass loss from PCFA (10% by $350^\circ C$) is primarily in the form of $(C-X)_n$ chlorofluorocarbon gases. Fluoro substitution on a polyunsaturated backbone clearly favors kinetic pathways for decomposition that retain strong C–F bonds and the C(+1) oxidation state.

Comparison of the UV/vis spectra of the three polymers shows that a thin film of PDFA (freshly made) has significantly red-shifted lowest energy absorbance values ($\lambda_{max} \approx 269$ and $340\ nm$ with a very broad tail extending out to $630\ nm$) relative to a solution of PCFA ($\lambda_{max} = 292\ nm$ in dichloromethane) and a thin film of PDCA ($\lambda_{max} = 220$ and $270\ nm$). The presence of fluorine in the polyunsaturated polymers not only red-shifts the electronic spectra, but also significantly enhances the air and light sensitivity relative to chlorine substitution.³⁵

The structural, spectroscopic, and chemical properties of the three polymers show that increasing fluorine substitution on the acetylene monomers promotes structural rearrangement upon polymerization and greatly enhances reactivity of the polymers toward oxygen, water, and light.

Acknowledgment. Support from the University of Illinois at Chicago and the University of Illinois Campus Research Board is gratefully acknowledged.

Supporting Information Available: Procedures for synthesis of the polymers, spectroscopic and physical characterization data, details for XPS studies of thin films (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA983840A

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