

Electrochemical Sensor for Nitrobenzene using π -conjugated Polymer-embedded Nanosilver

Victor M. Kariuki^a, Sohaib A Fasih-Ahmad^a, Francis J Osonga^a and Omowunmi A. Sadik^{a,*}

^aDepartment of Chemistry Center for Advanced Sensors & Environmental Systems (CASE)
State University of New York at Binghamton P.O Box 6000 Binghamton, NY, 13902

Supporting Information

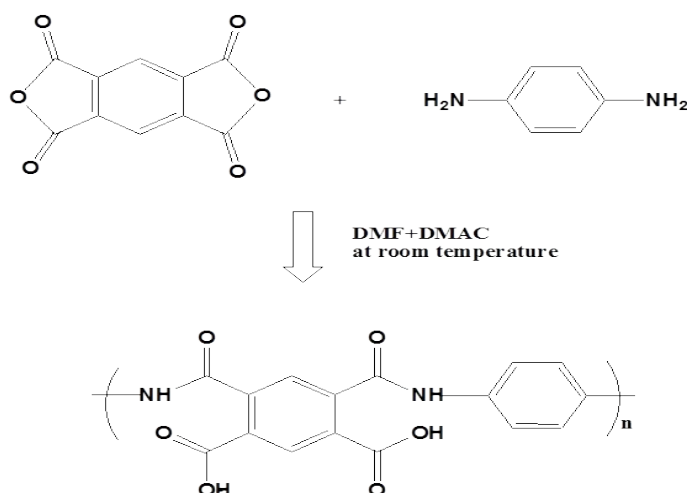


Figure S1: Schematic showing synthesis and structure of PAA polymer

Figure S2: NMR Characterization

The dry PDA-PAA membrane was dissolved in DMSO- d_6 and subjected to ^1H NMR, ^{13}C NMR, ^1H -correlation spectroscopy(COSY) and ^1H - ^{13}C -heteronuclear single quantum coherence(HSQC). A BRUKER AM 600 spectrometer operated by TopspinTM 3.0 NMR software was used for spectra.

¹H NMR

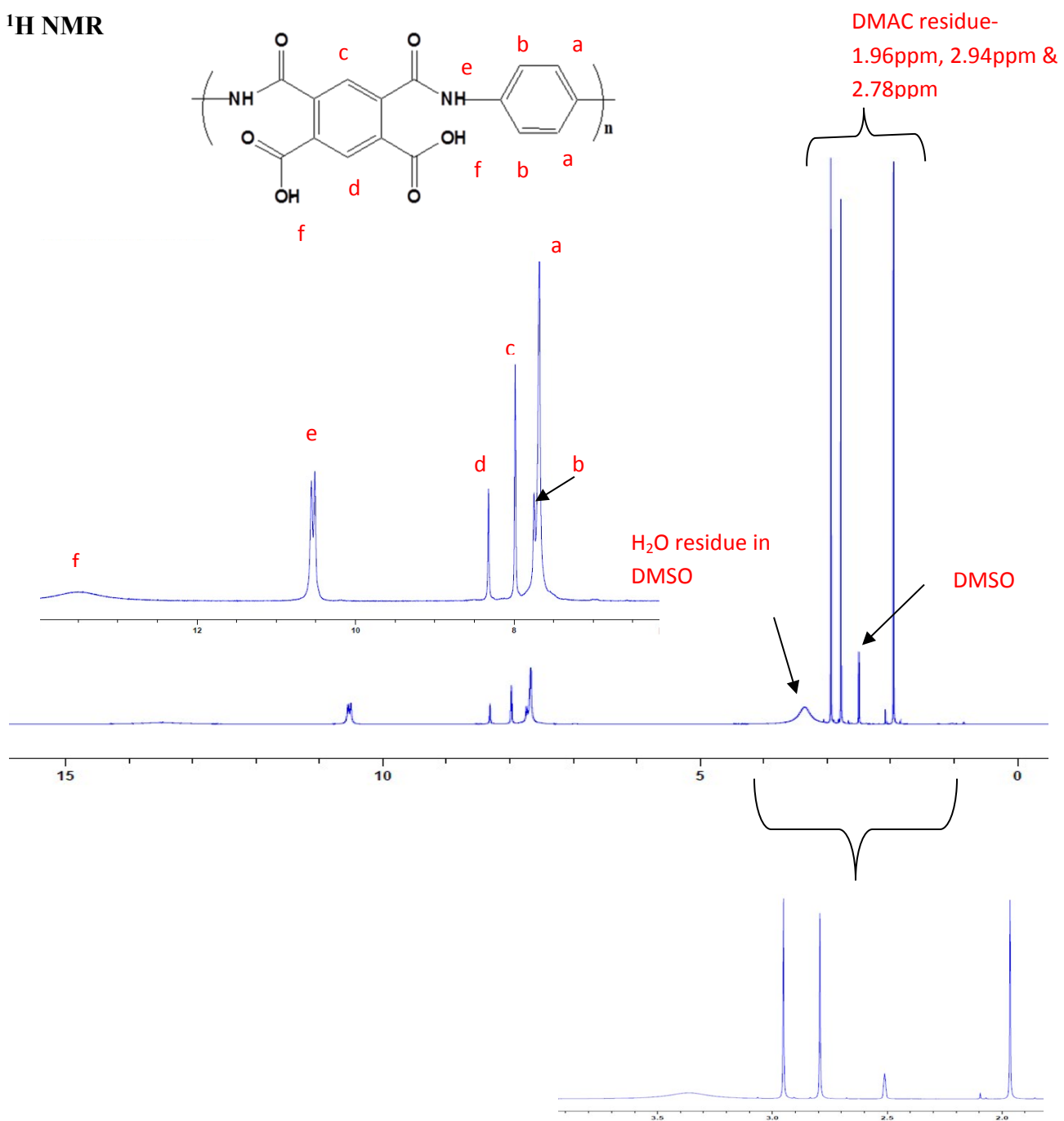


Figure S2-A: ¹H NMR spectrum of PAA in DMSO-d₆

The chemical structure of the PAA was confirmed by ^1H NMR analysis (**Fig S2 A**). A broad signal was identified at 13 ppm chemical shift. This signal was assigned to the protons from COOH groups which are included in the PDA-PAA. The signals at 10.5 ppm are assigned to the protons from NH groups of amide units presented from the dianhydride structures and the new amide unit created from the reaction of the diamine and the dianhydride in PAA structure. The aromatic protons were identified in the 7 and 9 ppm ranges

^1H NMR of PAA at some instance revealed additional peaks in the aromatic region as highlighted below. These peaks are as a result of existence of multiple conformations of polymer within the solution. The aromatic protons are between 6.5 ppm to 8.5 ppm. However, according to ^1H - ^{13}C HSQC, there are only 6 carbons with aromatic protons

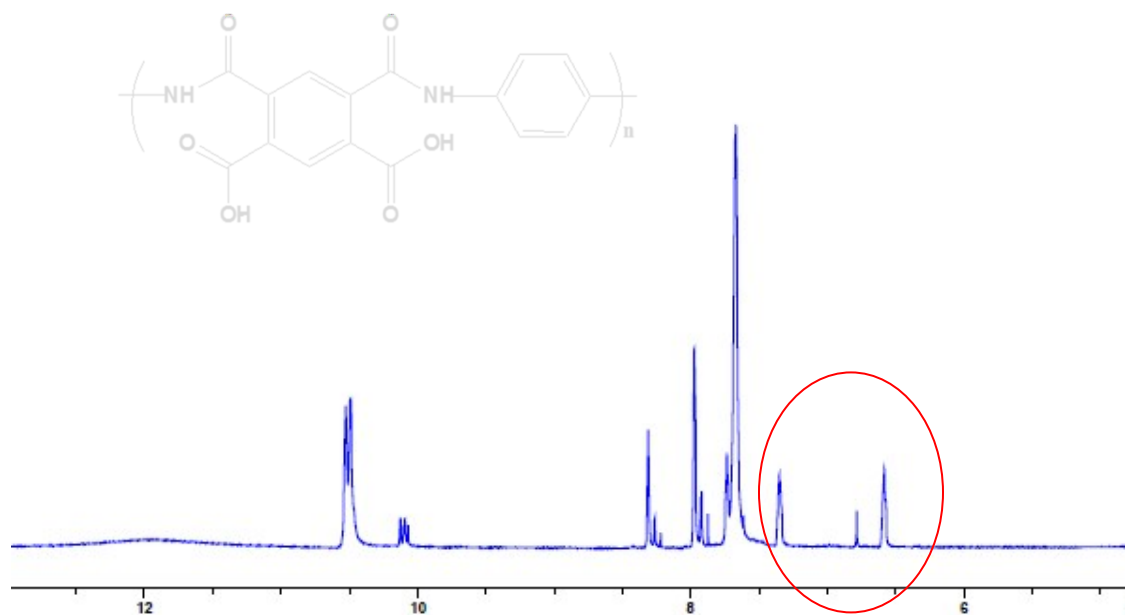


Figure S2-B: ^1H NMR spectrum of PAA in DMSO- d_6 showing extra peaks, evidence of existence of different polymer conformations in solution.

^{13}C NMR

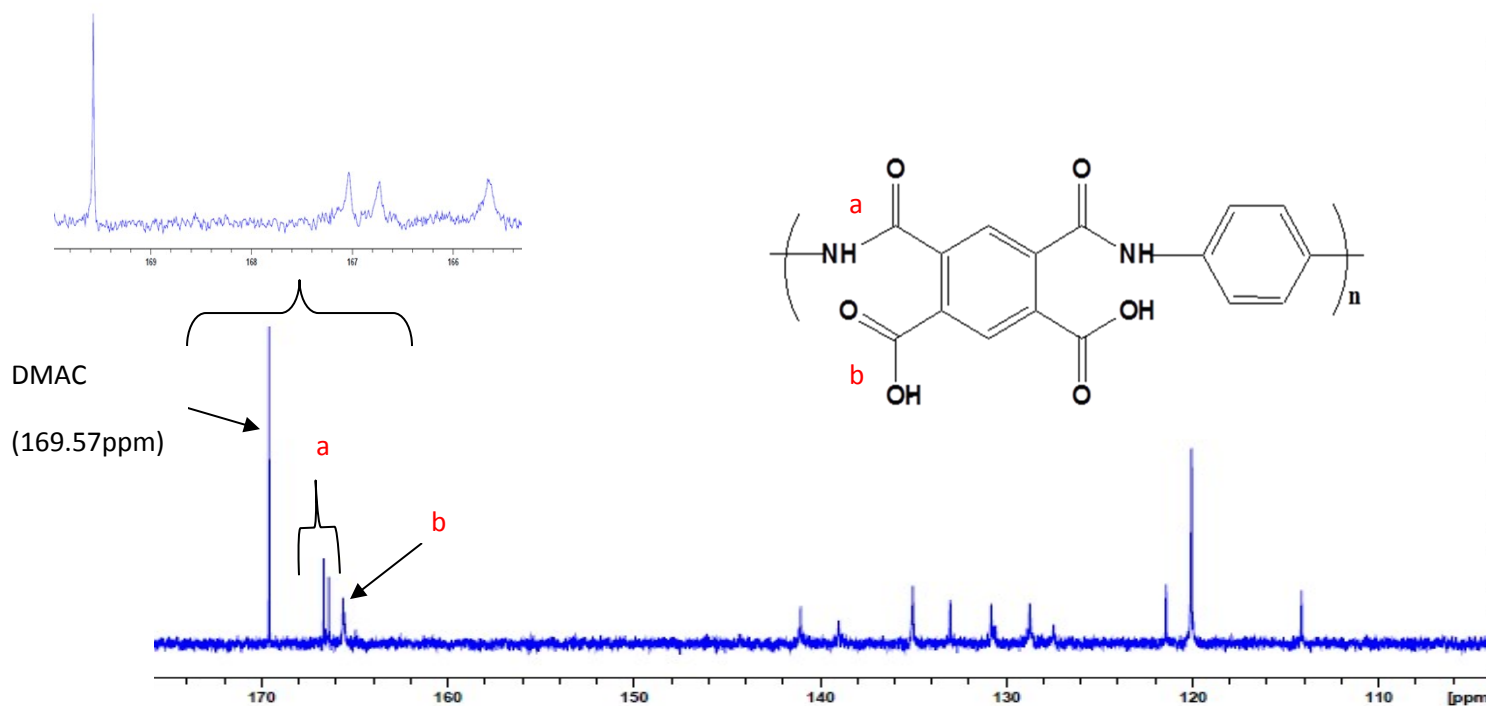
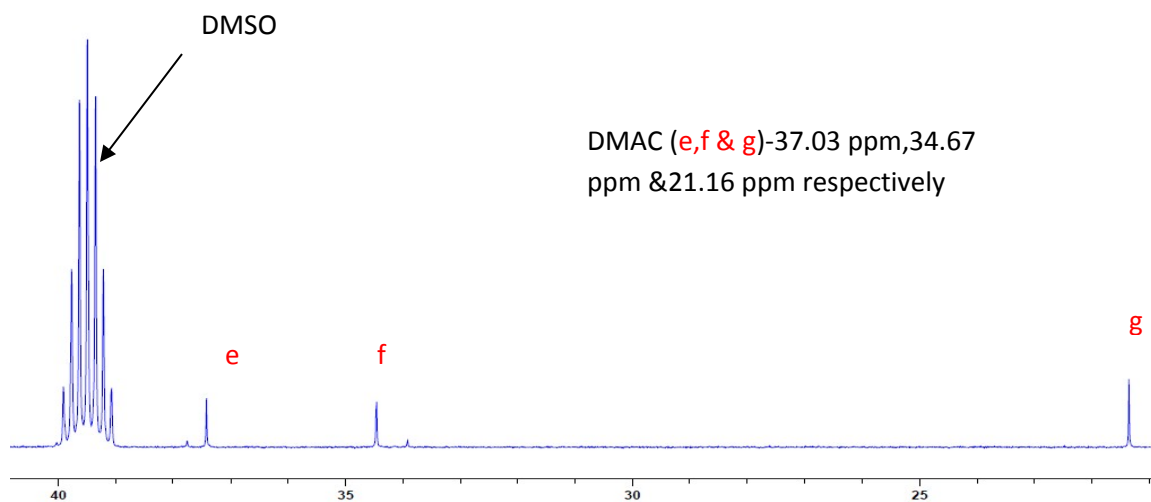


Figure S2-C: ^{13}C NMR of PDA-PAA polymer in DMSO-d₆ (Low field region)

The peaks between 122-130 ppm belong to carbons with aromatic protons. The peaks between 132ppm -142ppm belong to non-proton containing aromatic carbons of PAA. The presence of more than one amide carbonyl carbon (167.03ppm and 166.73) confirms presence further the presence of more than one polymer conformation.



FigureS2-D: ^{13}C NMR of PAA in DMSO- d_6 (Upfield region) showing the DMSO peaks and DMAC peaks.

DMAC is the solvent in which the polymer was prepared. Appearance of DMAC peaks in the ^{13}C spectra shows that even after drying the sample prior to dissolution in DMSO, there was residual solvent in polymer membranes.

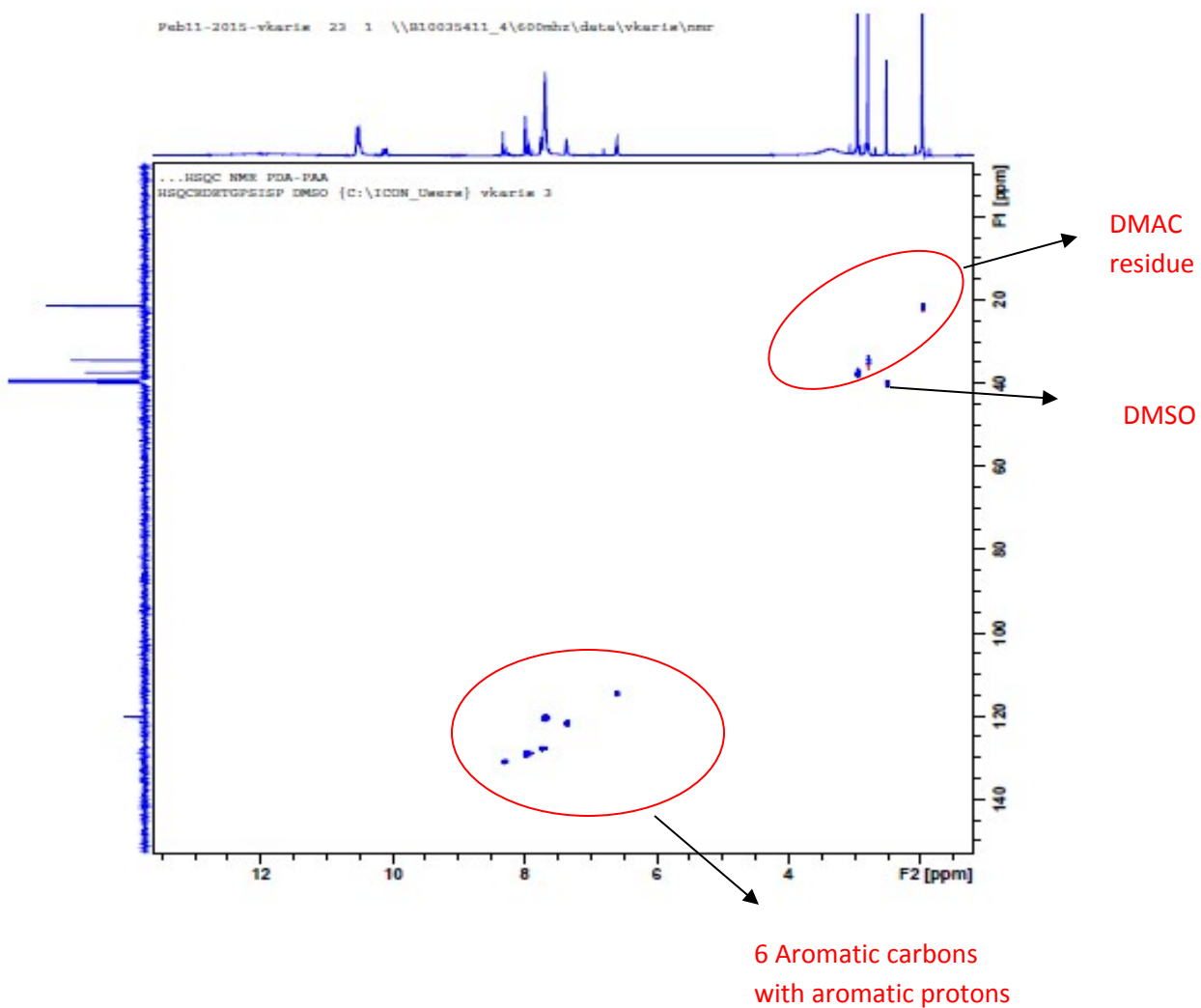


Figure S2-E: Heteronuclear single quantum coherence (HSQC) spectroscopy of the ^1H - ^{13}C system of the polymer

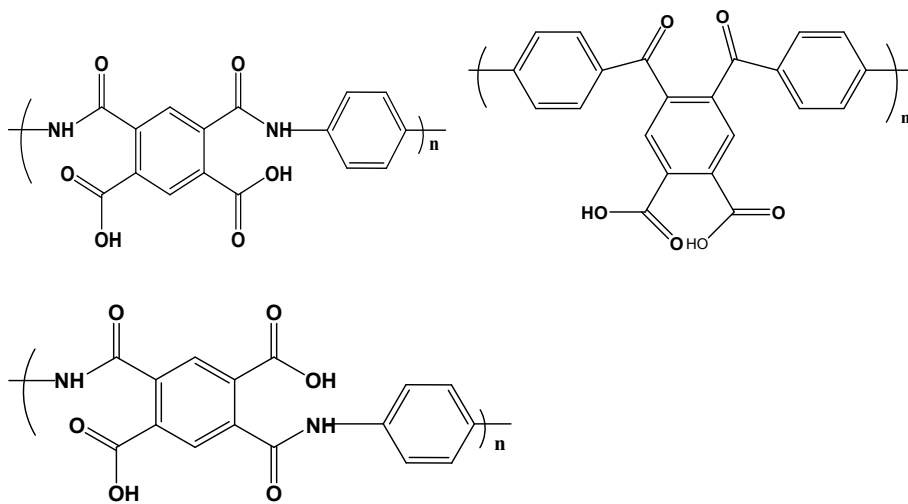


Figure S2-F: Possible conformations of the PAA polymer elucidated from NMR characterization.