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Molecular Origin of Solvent Resistance of Polyacrylonitrile

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ABSTRACT: We report on the first in-situ sum frequency generation (SFG) spectroscopy characterization of polyacrylonitrile (PAN) interfacial interactions with air, sapphire, water, and heptane. Using the shift in the resonance frequency of CN at various interfaces, we demonstrated that PAN interacts with the surface hydroxyl of sapphire substrate through the lone pair orbital of nitrogen in the "end-on" configuration (σ-H bond). We also demonstrated that the CN−CN interaction is the main reason for the superior chemical resistance property of PAN. At room temperature the interaction between the polymer chains is much stronger than the interaction between the polymer and solvent molecules including water and heptane. At high temperatures, however, the interaction between the nitrile groups of the polymer weakens, making interaction possible between the nitrile groups and the surface hydroxyls of the substrate and water. These results provide an important insight as to why acrylonitrile when copolymerized with butadiene to form nitrile rubber results in one of the best known synthetic oil-resistant rubber.

1. Introduction

Acrylonitrile monomer is used in synthesizing polyacrylonitrile (PAN) and as a comonomer with butadiene is used in the synthesis of the best known oil-resistant polymer, nitrile rubber.[1−5] The oil-resistant property of nitrile rubber has been attributed to the acrylonitrile content,[1] to the high dipole moment of the CN groups, and to its affinity to form strong intra- and intermolecular bonds. It has been suggested that the CN triple bond can interact using two available molecular orbitals.[6−8] The first one is the lone pair orbital of the nitrogen, and the second one is the π orbital of the triple bond CN. The interaction via the lone pair orbital of the nitrogen atoms results in a positive (blue) shift of the CN stretch vibration. In contrast, if the interaction occurs via the π orbital, then a negative (or red) shift of the nitrile CN stretch has been observed. The strong polarity of the CN groups in PAN results in very unusual properties. For example, the CN−CN interactions (dipole−dipole interactions) in PAN are so strong that only a limited amount of solvent can break these interactions. Additionally, the microstructure of PAN is suggested to have a low degree of crystallinity and a very high melting point.[6,9−11]

The current IR assignments and the shifts in the peak positions with environment for CN are available using a small molecule analogue such as acetonitrile.[7,12−16] The CN infrared stretching vibration band occurs at 2253 cm^{-1} in acetonitrile liquid, and the position of this band changes from 2253 to 2257 cm^{-1} upon interaction with various solvents.[15] Much stronger blue shifts have also been reported when CN groups of acetonitrile interact with δ-Al_2O_3 surfaces (2300 and 2328 cm^{-1}).[12] Limited spectroscopic data are available for PAN because of its limited solubility. Andreeva and Burkova[17] showed that the CN peak position shifts from 2242 to 2236 cm^{-1} upon heating PAN from room temperature to above the glass transition temperature of PAN (85−100 °C). More unusually, a large red shift of the CN frequency (2050 cm^{-1}) has also been reported for PAN upon exposure to water at high temperature and pressure.[6,18] It has been suggested that at these temperatures and pressures the CN−CN interactions are broken and PAN forms a one-phase system. The shift in the frequency of the CN band was reversible, indicating that these changes in the CN bands cannot be due to possible chemical reaction.

It is important to study the CN interactions to understand the unusual properties of PAN. In this paper, we have taken advantage of surface-sensitive IR−visible sum frequency generation (SFG) spectroscopy to study buried PAN interfaces. SFG is a second-order nonlinear optical process and is directly sensitive to the orientation and density of molecules at the interface.[19] According to the dipole approximation, the generation of SFG photons is forbidden in centrosymmetric bulk and permitted only at interfaces where inversion symmetry is broken.[19] The surface selectivity of SFG is important in probing the interfacial structure without the measurements being swamped by the signals generated in the bulk, which is a common problem encountered in using Raman and IR techniques. Additionally, the SFG conversion is resonantly enhanced when the infrared frequency overlaps with the molecular−vibrational modes that are both Raman- and infrared-active. The position and the magnitude of these resonance peaks provide chemical and orientation information on the molecules at the buried interface. SFG spectroscopy makes it possible to study the CN band at PAN/air interface and in contact with sapphire (Al_2O_3),[20,21] and nonpolar (heptane) and polar (water) liquids, without the difficulty of solubilizing PAN in a different solvent. Here, we have undertaken the study of PAN/liquid interfaces using SFG as a first important step toward understanding the superior oil-resistance properties of PAN and polyacrylonitrile rubbers.

2. Experimental Section

2.1. Sample Preparation. Reagent dimethyl sulfoxide (DMSO), heptane, and polyacrylonitrile (M_w = 22 600 g/mol)

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were purchased from Aldrich Chemical Corp. and used as received. Water was distilled and deionized using a Milli-Q system (18 MΩ). Differential scanning calorimetry (DSC) at heating and cooling rates of 10 °C/min was used to measure the thermal transitions of polymer. The DSC results indicate that the first thermal transition was at 101 °C, typically associated with the glass transition temperature (T_g), and a second transition between 140 and 150 °C, in close agreement with the previously reported values.

A 4 wt % solution of polyacrylonitrile (PAN) solution in DMSO was used for preparing the films for SFG measurements. To ensure complete dissolution of the polymer into the solvent, the solution was left to rest for a minimum of 12 h. From the solution, a PAN film was spread on a sapphire prism surface (equilateral sapphire (Al_2O_3) prism with optical axis in the plane of the surface) using a spin-coater at a rotational speed of 2400 rpm for 15 s. The thickness of PAN films was 400 nm (determined using spectroscopic ellipsometer). The sapphire prism was cleaned prior to the coating of polymer using an ultrasonic bath of DMSO, rinsed with ethanol and heptane, and then dried and cleaned using a plasma cleaner.

The coated prism was then annealed in a vacuum oven to remove the traces of DMSO used to spin-coat the PAN. The duration and the temperature of heat treatment were varied in each experiment and will be discussed in the Results and Discussion section. To study the polymer/liquid interface, a stainless steel flow cell was used. The cell was disassembled prior to each experiment and cleaned with ethanol and heptane and then placed in the oven at 250 °C for 15 min. The cell was then cooled to room temperature and plasma-treated for 1 min. The coated prism was clamped onto the cell. A Teflon spacer was used to ensure adequate sealing between the prism and the cell.

2.2. SFG Measurements. SFG measurements were carried out at room temperature in PPP polarization (infrared, visible, and sum frequency beams were set and detected in P polarization, where the *E* field of light is in the plane of incident). Infrared pulses (1−2 mJ, 10 ns pulse duration, 0.2 cm^{-1} bandwidth, and 10 Hz repetition rate) tunable from 2100 to 2300 cm^{-1} and visible pulses (532 nm, 1−2 mJ, 0.2 cm^{-1}, 10 Hz) were focused and overlapped on the PAN-coated sapphire prism.[21,22] The incident angles of 1°, 42°, 10°, and 10° were used to probe the polymer/sapphire, polymer/air, polymer/heptane, and polymer/water interface, respectively. These angles were chosen based on the refractive index of the materials and are similar to the critical angles for total internal reflection determined using Snell's law.[21,23,24] The SFG beam generated from the surface of the sample was detected using a photomultiplier (the details are provided elsewhere[22]). To eliminate any effect of the infrared spectral features, the SFG data were normalized by the power of the infrared beam. Vibrational features such as frequency, bandwidth, and amplitude of each vibrational modes were determined by fitting the spectra using a Lorentzian model.

3. Results and Discussion

3.1. PAN Structure at Sapphire Interface. Figure 1A shows the FTIR spectrum of bulk PAN. The resonance feature at 2242 cm^{-1} is assigned to the symmetric stretch of CN. The nitrile CN stretching absorption band between 2237 and 2243 cm^{-1} has been reported previously.[25] In this paper, the value of 2242 cm^{-1} is used as the spectroscopic reference for bulk PAN. To characterize the interfacial nitrile group of PAN, the SFG spectrum from 2100 to 2300 cm^{-1} is shown in Figure 1B for the PAN/sapphire interface at 20 °C. The film was annealed for 8 h at 90 °C and 4 h at 120 °C, well above T_g of the PAN. The interfacial CN resonance frequency was detected at 2254 cm^{-1}, which is blue-shifted 12 cm^{-1} from the bulk spectrum, indicating a strong interaction between the sapphire substrate and the polymer at the interface.

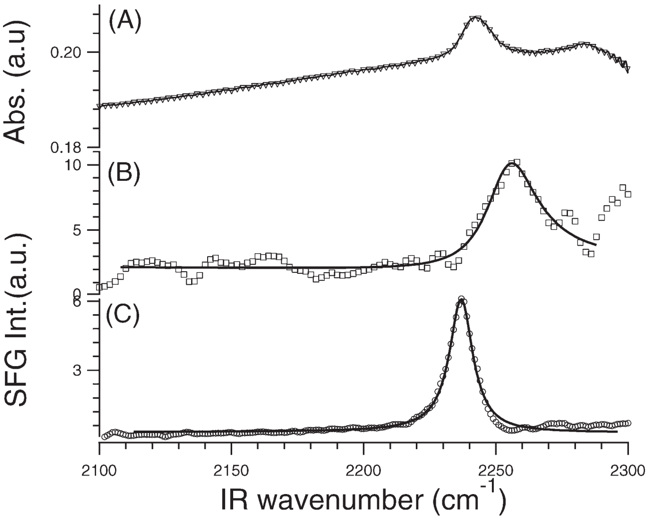

Figure 1. (A) FTIR spectrum of PAN bulk, (B) SFG spectrum in PPP polarization at the sapphire/PAN interface after the PAN film is annealed at 90 °C for 8 h followed by a second heating at 120 °C for 4 h, and (C) SFG spectrum of sapphire/PAN interface in PPP polarization. The sapphire was annealed at 750 °C for 36 h before spin-coating the PAN. The sapphire/PAN samples were annealed at 90 °C for 8 h and 120 °C for 4 h in a vacuum oven before the SFG experiments at room temperature. The solid lines in (B) and (C) are fits using a Lorenztian equation. The solid line in (A) is a fit using a Gaussian function to identify the position of the IR peak.

The significance of CN frequency shift has been extensively investigated using acetonitrile[7,12−16] and to a limited extent for PAN.[6,17,18] Blue and red shifts of the nitrile stretching absorption band are possible for both acetonitrile and PAN. The direction of the shift is diagnostic of the interaction of nitrile with surrounding molecules. It is understood that CN side groups have an intriguing capability to interact via either the lone pair orbital of the nitrogen "end-on" leading to an hypsochromic (positive or blue) shift of the CN stretching vibrational frequency or to interact via a "side-on" coordination leading to a bathochromic (negative or red) shift of the CN stretching vibrational frequency.

Before interpreting the reasons behind the shift of the CN peak at the PAN/sapphire interface, it is necessary to identify the functional groups on the sapphire surface that are interacting with the CN groups of PAN. There are two possible reactive sites on the sapphire surface, namely surface hydroxyl groups and unsaturated aluminum cations.[12] The nitrile groups can interact with the hydroxyl groups through hydrogen bonding or via an electron donor−acceptor interaction with aluminum cations of aluminum oxide (sapphire). To distinguish between these two possibilities, the number of surface OH groups was reduced by heating the sapphire at 750 °C for 48 h (we will refer to this specific condition as heat-treated sapphire). The effectiveness of the heat treatment in reducing the number density of the hydroxyl groups on the sapphire surface was previously demonstrated using SFG spectroscopy.[26] Following the heat treatment, the PAN was spin-coated on the sapphire prism and annealed at 90 °C for 8 h and 120 °C for 4 h. Figure 1C shows the SFG spectrum in the CN region after reducing the hydroxyl groups on the sapphire surface. For the heat-treated sapphire/PAN interface, the CN resonance feature of PAN is at 2237 cm^{-1}, which is significantly lower than the CN stretching vibration for CN groups at the PAN/sapphire interface. The above results indicate that the surface hydroxyl groups on the sapphire substrate play an important role

Table 1. CN stretching Vibrational Assignments (Units of cm^{-1}) as a Function of Dielectric Constants

	dielectric constants						
	1	1.92	4.9	10.36	20.7	36.34	78.39
compound 1, CH_3CN	2271	2268	2264	2262	2261	2261	2261
compound 2, $CH_3CHCNCH_3$	2253	2250	2245	2243	2242	2241	2241
compound 3, $CH_3CH_2CHCNCH_2CH_3$	2250	2246	2242	2240	2239	2238	2237

in the interaction between the sapphire and the CN groups in PAN.

To understand whether the CN groups are interacting with the surface OH groups via "end-on" (also referred as σ-H bond) or "side-on" (also referred as π-H bond) interactions, the vibrational assignment of an isolated CN group in PAN is needed. This is a complex issue because the only known reference is the IR assignment of the CN groups in the bulk PAN at 2242 cm^{-1} that has CN groups already interacting strongly with each other. We have used the Gaussian03 package (B3LYP/6-311G++(3df,2pd) method/basis set) to determine the CN vibrational assignments for three model compounds shown in Table 1 (see Supporting Information for additional details).[8] Compound 3 (1,1-diethyl cyanide, $CH_3CH_2CHCNCH_2CH_3$) represents a model for PAN molecule with a vibrational resonance of 2250 cm^{-1} at dielectric constant of 1 (i.e., free CN). The position of this peak shifts to 2238 cm^{-1} for a CN group that is surrounded by a medium of dielectric constant corresponding to that of the bulk PAN (32−35[27]), which is similar to the values observed experimentally. However, this agreement may be coincidental because the Gaussian calculations presented here do not take into account the directional CN−CN interactions. On the basis of the assignment of the free CN group at 2250 cm^{-1}, we can conclude that the CN peak at 2254 cm^{-1} for PAN in contact with sapphire substrate is blue-shifted and is due to the CN molecules interacting with the surface hydroxyl groups using the lone pair orbital of the nitrogen.

3.2. The Role of Annealing above and below T_g in Controlling CN Interactions. Interestingly, some unusual effects on the annealing temperature of the PAN films were observed. Figure 2 shows the SFG spectrum of the PAN/sapphire interface that was annealed only at 90 °C for 8 h. The interfacial CN resonance features were detected at 2236 cm^{-1} instead of 2242 cm^{-1} in the bulk and 2254 cm^{-1} as observed for the PAN/sapphire interface in the presence of the surface OH. The position of the PAN peak is now similar to that observed for PAN in contact with the heat-treated sapphire prism. These results indicate that annealing above T_g is important in forming the "end-on" interactions with the surface hydroxyl groups.

The SFG spectrum in the region from 2800 to 3100 cm^{-1} was measured to study the methylene stretching vibrations. Figure 3A shows the SFG spectrum of the heat-treated sapphire/PAN interface for films that were annealed at 90 °C for 8 h and 120 °C for 4 h. The SFG spectrum was fitted using three resonant features at 2870, 2930, and 2950 cm^{-1}, based on the IR assignments (2800−3000 cm^{-1}) reported in the literature.[28] The resonance structures at 2870 and 2950 cm^{-1} are assigned to the symmetric and asymmetric methylene stretching modes and the 2930 cm^{-1} resonance is due to a stretching mode of the CH group.[28] The spectrum for the heat-treated sapphire (without surface OH) is very different from the SFG spectrum of the sapphire/PAN interface annealed at 120 °C for 4 h (with surface OH), shown in Figure 3B. It is important to note that the spectral features in Figure 3A are not due to the solvent DMSO, which was used in spin-coating because the annealing at 90 °C for 8 h and 120 °C for 4 h under vacuum was sufficient to remove the trace amount of DMSO from these thin PAN films.

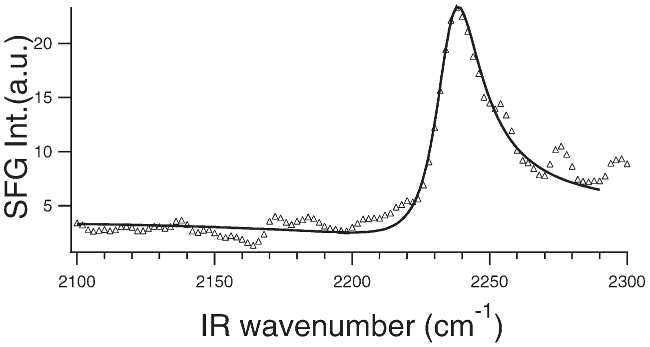

Figure 2. SFG spectrum of PAN in PPP polarization in the CN region at the sapphire/PAN interface after the PAN film is annealed at 90 °C for 8 h. The solid line is a fit using a Lorenztian equation.

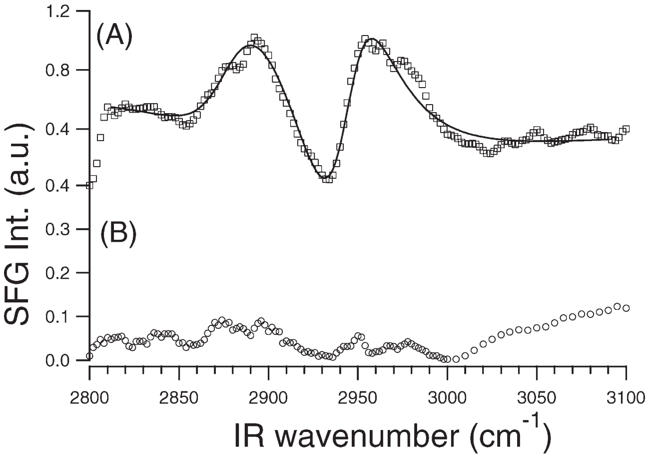

Figure 3. (A) SFG spectrum of PAN in PPP polarization at the heat-treated sapphire/PAN interface. The PAN films were annealed at 90 °C for 8 h and 120 °C for 4 h after spin-coating on a heat-treated sapphire prism (750 °C for 36 h). (B) SFG spectrum of PAN in PPP polarization after annealing at 90 °C for 8 h and 120 °C for 4 h at the sapphire/PAN interface. Both these spectra are shown in the CH stretching region.

These annealing experiments reveal two important points. First, the heating above T_g at 120 °C is important in forming the "end-on" bond with surface hydroxyl groups. In addition, there is a considerable rearrangement of the molecular structure of PAN after annealing the samples at 120 °C. Andreeva and Burkova[17] have demonstrated that the PAN molecules unwind after heating above 150−180 °C, at temperatures well above those used in this work. We postulate that upon annealing and in the presence of surface hydroxyl groups the interfacial CN side groups reorient to interact with the substrate hydroxyl surface. The disappearance of the SFG peaks of methylene and CH signals upon annealing is consistent with this hypothesis. The annealing temperature to rearrange the PAN chains at 120 °C is far lower than the dissociation of CN interactions observed in the PAN bulk at 150−180 °C.[10,17] The differences in the annealing temperatures between the bulk and the sapphire interface could be

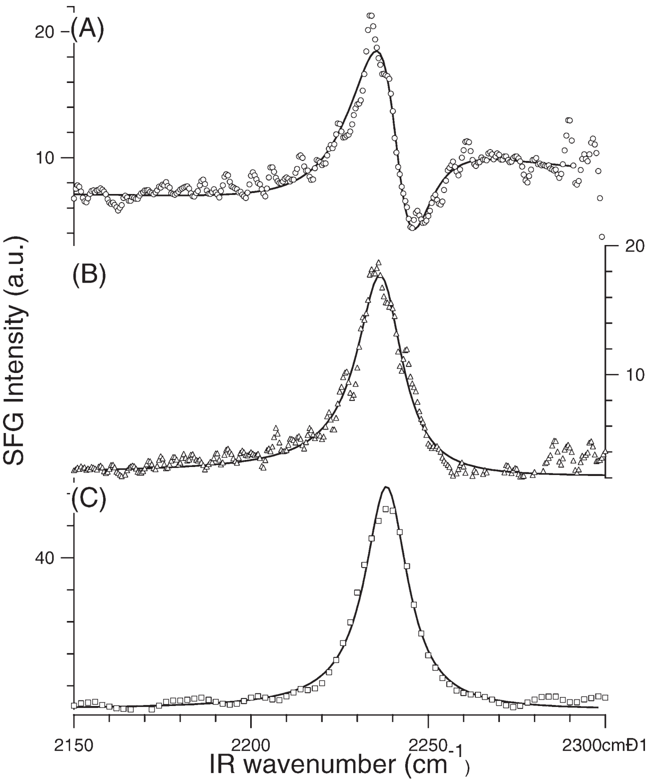

Figure 4. SFG spectra of PAN in PPP polarization at the (A) PAN/air, (B) PAN/water, and (C) PAN/heptane interfaces collected from 2150 to 2300 cm^{-1}. The solid lines are the fits using a Lorenztian equation.

due to the enthalpic forces driving the interactions between the hydroxyl and the CN groups.

3.3. Probing PAN/Liquid Interfaces. To understand the interaction of CN groups with polar and nonpolar solvents, the molecular structure of PAN at water/PAN and heptane/PAN interfaces was studied using SFG. Heptane was used as a model liquid to simulate a linear hydrocarbon oil to shed light on the oil-resistant properties of PAN and NBR (nitrile butyl rubber). The interest in studying water stemmed from an earlier work by Goodman,[18] where they had observed a reversible red shift by 200 cm^{-1} after exposure of PAN to water under high temperature and pressure.

Figure 4A shows the SFG spectrum of the PAN/air interface. Fitting analysis of the spectra reveals two resonant features in the SFG spectrum. The peak at 2238 cm^{-1} and the second peak at 2242 cm^{-1} with an opposite phase with respect to the 2238 cm^{-1} peak. The detection of two CN stretching frequencies indicates the existence of two environmentally different nitrile groups at the surface of the film. Multiple vibrational peaks have been reported before between 2100 and 2245 cm^{-1} for CN bearing compounds.[12]

Upon the injection of water, the binodal surface population of CN groups become uniform and only one CN vibrational band is observed at 2237 cm^{-1} (Figure 4B). The CN band in contact with water is red-shifted by 1 and 5 cm^{-1} with respect to the two original bands at 2238 and 2242 cm^{-1}, respectively. Because Goodman had observed a very large red shift by dissolving PAN at high temperatures and pressure, we have also measured the SFG spectrum for PAN/water interface in the range between 2000 and 2100 cm^{-1}, as shown in Figure 5. No discernible peaks in the SFG spectra in this range were observed, indicating that high temperature and pressure are required to break the CN−CN bonds and form CN−OH interactions. These results are also consistent with the SFG data for PAN/sapphire interface, where the shift in the CN peak was observed only after the samples were heated to 120 °C.

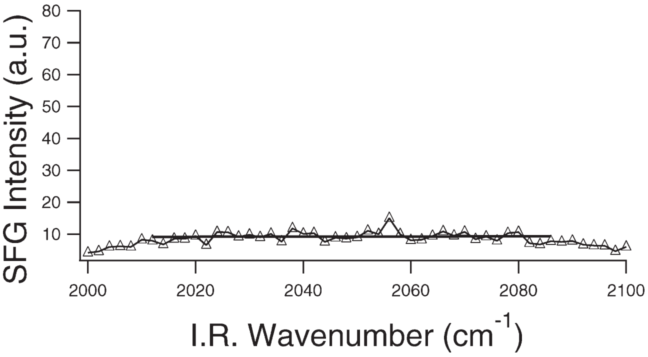

Figure 5. SFG spectrum in PPP polarization for the PAN/water interfaces collected between 2000 and 2100 cm^{-1}. This spectrum was collected using the SFG laser system at Akron that uses a 800 nm visible laser (1 kHz and pulse width of 1−2 ps) and mixes with tunable IR generated using an OPA (1 kHz and pulse width of 1−2 ps).

Figure 4C shows the SFG spectrum for PAN in contact with heptane. Interestingly, upon the injection of heptane, a similar spectrum is collected at the PAN/heptane interface where only one vibrational band is detected at 2238 cm^{-1}. It is surprising to observe the insensitivity of the CN peak to its environment considering the past results where the position of the CN peak of acetonitrile is dependent on the solvent polarity. The physical picture we postulate is that the CN groups at the PAN surface have a strong interactions with its neighboring CN groups creating an environment that is not much different from that in the bulk. This is supported by the observation of the CN peak at PAN/air interface at 2238−2242 cm^{-1}, similar to that in the bulk. By not observing any blue shifts after adding water indicates that this interaction has to be strong and difficult to perturb by the addition of high dielectric constant liquid. Additionally, if the CN groups were solvated with heptane molecules, then we should have observed the peak at 2246.3 cm^{-1} because the CN molecules would be surrounded by lower dielectric constant heptane liquid (Table 1). The similarity between both the PAN/water and PAN/heptane spectra and the subtle differences from the PAN/air spectrum indicate that the polar and apolar solvents may affect the molecular arrangements of CN groups; however, they are not strong enough to break the CN−CN interactions at room temperatures.

4. Conclusions

Here, the first in situ sum frequency generation spectroscopy characterization of PAN at various interfaces is reported. It was demonstrated that the CN−CN interactions are very strong at room temperature and prevail upon exposure to solvents such as water and heptane. The CN peak blue-shifts after annealing the PAN films at 120 °C in contact with sapphire surface, indicating an "end-on" interaction of OH groups with the lone pair orbital of CN. These results have important implications in understanding the solvent resistance properties of PAN and NBR rubber.

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Supporting Information Available: Details of Gaussian calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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