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Application of Solid-State NMR To Characterize the Interaction of Gel Inhibitors with Emeraldine Base Polyaniline

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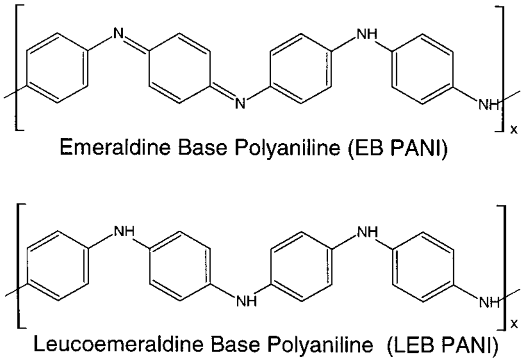
ABSTRACT: The extent and types of changes occurring to polyaniline (PANI) films cast from solutions containing a gel inhibitor were characterized by solid-state NMR (SSNMR). Two secondary amine gel inhibitors, 2-methylaziridine (2-MA) and pyrrolidine (Py), were studied and observed to have very different reactivities with the polymer. ^{13}C and ^{15}N SSNMR data show that pyrrolidine adds to the quinoid ring of ~50% of the repeat units, converting these units from the emeraldine base form to the leucoemeraldine form. The presence of the pendant amine group also disrupts chain packing, increasing the amount of kilohertz regime chain motion in the solid state as determined from the magnitude of $T_{1\rho}$(H). In contrast, 2-MA reacted only slightly with PANI, addition to ~5% of the repeat units, but 0.7 2-MA/repeat unit was physically trapped in the PANI film. The greater reactivity of Py (pK_b = 3) relative to 2-MA (pK_b = 6) is related to the amine's nucleophilicity and orbital arrangement.

Introduction

An understanding of the structure/property relationships in polymers is essential for the preparation of quality materials for today's technological industries. Polyaniline (PANI), one of the oldest known polymers, has distinctive electrical properties for modern applications. Realized and potential applications of PANI include corrosion protection, radio-frequency shielding, batteries, and actuators. However, the widespread commercialization of PANI has been limited due to its poor solubility in common solvents that inhibits easy processing. Spinning fibers from polymer solutions is aided by using highly concentrated solutions, 20 wt % or higher, which yield optimal coagulation properties of the fibers and producing materials that are highly homogeneous with high mechanical strength. While the most common solvent used to make PANI solutions is *N*-methylpyrrolidinone (NMP), PANI solutions as low as 6 wt % in this solvent are unstable and gel in just a few hours, a result of the intermolecular hydrogen bonding between imine and amine nitrogens.[1,2] An alternative solvent system, *N*,*N*′-dimethylpropylene urea (DMPU), has been used, and 10 wt % PANI solutions showed little change in viscosity over 30 h.[3,4] When the PANI concentration is increased to 20 wt %, however, the viscosity changes dramatically over just a few hours.

Recently, we reported that adding a small amount of secondary amines to NMP could significantly enhance the solubility of PANI.[5−7] These gel inhibitors (GI) break up the intermolecular interactions stabilizing the concentrated (up to 30 wt %), high molecular weight PANI/NMP/amine solutions for up to 30 h, making it practical to spin fiber from concentrated PANI solutions.[8] These highly concentrated solutions of high molecular weight PANI yield fibers with excellent mechanical strength and a reduction in macrovoids.[9,10]

Scheme 1



The bulk properties of PANI films processed in the presence of a GI are sensitive to the GI used. High-quality materials are obtained when 2-methylaziridine (2-MA) is used as the GI; however, when pyrrolidine (Py) is used, the PANI films are brittle and they have lost their mechanical integrity.[6] Understanding the chemistry leading to this polymer degradation is then imperative to rationally selecting the proper secondary amine gel inhibitors. An initial study of PANI/Py interactions was conducted by Han et al. under severe conditions.[11] In this case Py was the solvent, and the PANI/Py solution was allowed to stand for 96 h before the solvent was removed at elevated temperatures. A ^{13}C solid-state NMR and FTIR study revealed that the PANI, which had originally been in the half-oxidized emeraldine base (EB) form, was nearly completely reduced to the leucoemeraldine base (LEB) oxidation state (Scheme 1). In addition, some Py remained in the film, proposed to result from covalent attachment to the polymer. A recent study of the impact of a number of secondary amines, including Py, by UV/vis and GPC and under typical processing conditions has again observed reduction of the polymer.[12]

The techniques of UV/vis and ^{13}C have provided insights into the PANI/Py reactivity, but both of these techniques suffer from low resolution. Changes in the PANI oxidation state are monitored by absorbance changes in the UV/vis data and reactivity with the GI

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by shifts in λ_{max}; however, it was not possible to quantify the extent of these reactions.[12] The low ^{13}C chemical shift dispersion in PANI and the peak overlap resulting from the broad line widths observed limits a determination of the extent of reactivity as well as obscuring the presence of additional species. In this study, both ^{13}C and ^{15}N solid-state NMR are used to characterize PANI films processed in the presence of the gel inhibitors 2-MA and Py. With these techniques the polymer oxidation state, the reactions of the polymer with the GI, the extent of the reactivity, and the changes in the polymer morphology and chain dynamics have been characterized and compared for the two different GI's.

Experimental Section

Powder Synthesis. ^{15}N-labeled emeraldine base polyaniline powder ($M_w \sim 60\,000$) was synthesized by dissolving 20 mL of ^{15}N-labeled aniline in 250 mL of 1.0 M aqueous HCl solution. The solution was cooled to 0−2 °C using an ice bath. A solution of 45 g of sodium persulfate dissolved in 250 mL of 1.0 M aqueous HCl was added dropwise to the monomer solution by means of a metered syringe pump over a period of 60 min with vigorous stirring. The reaction was allowed to proceed for an additional 3 h. The ^{15}N PANI·HCl precipitate was collected on a Buchner funnel and washed with several portions of 1.0 M aqueous HCl until the filtrate became colorless. The polymer was then washed with three 100 mL portions of water to remove any oligomeric impurities. The yield was 35%. The green emeraldine salt was converted into the emeraldine base by stirring the precipitate in 500 mL of 1.0 M NH_4OH solution for 1 h. The blue product was collected on a Buchner funnel and washed with 0.1 N NH_4OH until the filtrate became colorless. The EB powder was dried under dynamic vacuum at 10^{-2} Torr for 72 h.

Film Formation. Two 1 wt % solutions of ^{15}N-labeled PANI/NMP/GI were prepared by adding the EB powder to Teflon vials containing ~30 mL of NMP/GI solution. The vials were closed. The mixtures were continuously stirred and heated at 45 °C on a hot plate for 48 h. Free-standing EB films were made by depositing the solution onto watch glasses that were placed inside an oven and dried at 60 °C in air for 72 h to evaporate the NMP/GI solvent. The dried films were immersed in H_2O for 6 h, peeled from the substrate, and air-dried. To remove residual solvent, the samples were methanol extracted over 48 h and then placed in a vacuum oven for 24 h at room temperature. The molar ratio for the 2MA film is 78:1, and the molar ratio for the Py film is 18:1.

NMR. High-resolution ^{13}C (50.4 MHz) and ^{15}N (20.2 MHz) spectra were obtained at room temperature utilizing a 200 MHz (proton) superconducting magnet. Timing and data acquisition were accomplished with a Tecmag/Libra pulse programmer. All data were collected with a "home-built" four-channel HPCN transmission line probe containing a Chemagnetics magic-angle stator. Samples were spun at the magic angle in 7 mm zirconium Chemagnetics Pencil Rotors fitted with Kel-F spacers and drive caps for air pumped spinning. The rotors were supported at both ends with air bearings. A 1 kW Dressler amplifier was used for the proton channel while 1 kW Kalmus amplifiers were used for all other nuclei. Proton decoupling field strength was in the range 85−95 kHz, remaining steady during each experiment. Data manipulation was preformed using MacNMR 5.4 on a PowerPC. ^{13}C and ^{15}N chemical shifts are referenced to HMB ($\delta^{13}C_{methyl} = 17.3$ ppm, $\delta^{13}C_{TMS} = 0$ ppm) and $^{15}NH_4{}^{15}NO_3$ ($\delta^{15}N_{NH_4^+} = 0$ ppm, $\delta^{15}N_{NO_3^-} = 352$ ppm), respectively. All cross-polarization (CP), magic angle spinning, and spin-echo experiments were carried out with the following parameters: proton to carbon CP times were 1 ms at a Hartman−Hahn match of 50 kHz; proton to nitrogen CP times were 2 ms at a Hartman−Hahn match of 40 kHz. $T_{1\rho}$ relaxation times were measured using standard procedures.

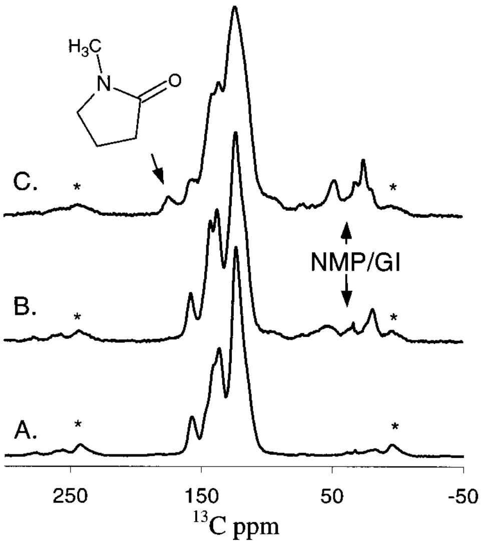


Figure 1. ^{13}C CPMAS spectra of ^{15}N-labeled polyaniline: (A) EB PANI powder, (B) PANI/2-MA film, and (C) PANI/Py film.

Integrated signal intensities from spectra collected under CP/MAS conditions were corrected for the effects of T_{IS} and $T_{1\rho}$(H) by fitting the intensities at increasing CP times to eq 1. In this equation, S is the experimentally measured intensity and S_0 is the corrected intensity, and each peak in the spectrum was fit individually to eq 1.

$$S_0 = \frac{(S/T_{IS})e^{-t/T_{1\rho}(H)} - e^{-t/T_{IS}}}{1/T_{IS} - 1/T_{1\rho}(H)} \qquad (1)$$

Results and Discussion

^{13}C NMR. The ^{13}C CPMAS spectra for the ^{15}N-labeled powder, 2-MA film, and Py film are shown in Figure 1. The peaks in the region from 100 to 165 ppm arise from carbons of the polymer chain. In the PANI/2-MA film, Figure 1B, additional peaks are observed at 16, 35, and 50 ppm that are due to the aliphatic carbons of 2-MA. The GI is also retained in the PANI/Py film (Figure 1C), and the peaks at 30 and 50 ppm are from Py, as well as the solvent; the five peaks at 17, 25, 30, 50, and 175 ppm arise from retained NMP. The GI:PANI molar ratios of 78:1 for the 2-MA film and 18:1 for the Py film were selected as the films made under these conditions result in chemical changes to the polymer at a level that allowed for characterization.

The quantity of retained GI and solvent was determined from integration of the NMR signal intensities, corrected for relaxation effects by using eq 1. The amount of residual 2-MA was calculated by integrating over the peaks in the range of 0−60 ppm and subtracting the integrated area due to the high-field spinning sideband from the polymer signal. The intensity ratio of the low-field to high-field spinning sidebands from the polymer was determined for the polymer, and this ratio was assumed to be the same for the PANI/2-MA film. By using this ratio and the integrated intensity of the low-field spinning sideband, the intensity of the high-field spinning sideband was determined. The GI to PANI ratio for the 2-MA film is 0.7. The amount of pyrrolidine in the sample was determined similarly; however, in this case the results must also be corrected for the presence of NMP. The corrected intensity for the carbonyl signal of NMP was calculated, and the value was multiplied by four to obtain the intensity of the aliphatic carbons of NMP. After subtracting out intensities from NMP and the spinning sideband of the polymer signal, the GI to PANI ratio for the PANI/Py film is 0.5. In addition, there is approximately one NMP molecule retained per PANI repeat unit in the PANI/Py film. The rationale for the retention of NMP in the PANI/Py film is addressed in a forthcoming paper.

The environments of the retained GI and solvent were also investigated. The $T_{1\rho}$(H) for the polymer, gel inhibitors, and solvent are all nearly the same, indicating that there are no independent large-amplitude motions of the additives. Also, the Bloch decay NMR spectra of these materials did not show any new features (data not shown), signifying that there are no liquidlike clusters of these additives located in the PANI films. The interaction of the gel inhibitor and solvent with the PANI is either by covalent attachment or by being physically trapped in the polymer.

A change in the oxidation state of the polymer from EB to LEB (Scheme 1) can be monitored by the change in the intensity of the peak at 160 ppm arising from the carbon of the imine group. A noticeable decrease in intensity of this peak is observed for the PANI/Py film, indicative of reactivity of Py with PANI resulting in reduction of the polymer. In contrast, the ^{13}C spectrum of the PANI/2-MA film is only slightly changed when compared to the PANI powder. A significant loss in resolution is also observed for the PANI/Py film. The broad line widths are not from changes in relaxation parameters but arise from increased structural heterogeneity of the polymer, i.e., changes in chain packing and a variation in chemical structure. Again, there is almost no change in the spectrum from the film with 2-MA present, indicating little change in the structure or composition of the polymer. The ^{13}C spectra show that even with relatively high amounts of 2-MA present during film formation that there is little reactivity between the GI and the polymer, whereas at a substantially lower molar ratio for Py there is a significant amount of GI/PANI interaction. The broad lines and spectral overlap of the ^{13}C spectra prohibit quantifying the details of the interaction of the polymer with the gel inhibitors.

^{15}N NMR. The ^{15}N CP/MAS NMR spectra from as-synthesized PANI powder in the EB oxidation state, PANI/2-MA film, and PANI/Py film are shown in Figure 2. The spectra have peaks at 320 ppm from the imine nitrogens and 60 ppm from the amine nitrogens. The relative concentration of the imine and amine nitrogens was determined from integrated signal intensities after correcting for the effects of T_{IS} and $T_{1\rho}$(H) (Figure 3). The integrated intensity for the imine nitrogens includes the peak at 320 ppm and the corresponding spinning sidebands as well as the peaks near 100 ppm. This grouping of peaks is consistent with the peak assignments discussed below. The PANI powder has an imine-to-amine ratio of 0.8, very close to the expected value of 1.0 for the EB form (Scheme 1); the integrated intensities have an error of ~10%. In the PANI/2-MA film this value decreases slightly to 0.7, indicating that there is little change in the oxidation state of the polymer when in the presence of this GI. A dramatic change in this ratio is observed, however, for the PANI/Py film as it drops to 0.3, a change consistent with ~50% of the quinoid rings being reduced to benzenoid rings. In contrast, in the PANI/2-MA film only ~5% of the rings have been reduced. Similar to the ^{13}C NMR data, the ^{15}N NMR results show that there is a much greater reactivity of the polymer with Py than with 2-MA.

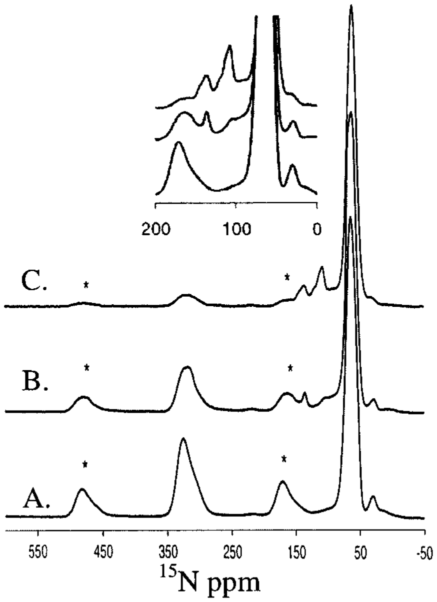


Figure 2. ^{15}N CPMAS spectra of the ^{15}N-labeled EB PANI powder and films with spinning sidebands denoted by an asterisk: (A) polymer powder, (B) PANI/2-MA film, and (C) PANI/Py film.

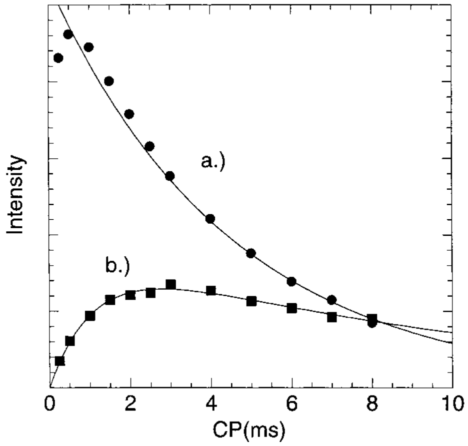


Figure 3. Experimental ^{15}N integrated peak areas as a function of the CP time for ^{15}N-labeled PANI/Py film where (a) is the amine nitrogen signal intensity and (b) is the imine nitrogen signal. The signal intensity at $t = 0$ is determined by a single-exponential fit for the amine nitrogen signal and by eq 1 for the imine nitrogen signal.

In the ^{15}N spectra from the two PANI films new peaks are observed at 140 and 110 ppm; the spectrum for PANI powder does not have any peaks in this region. This is the chemical shift region where peaks from protonated, imine nitrogens are observed when the polymer has been treated with an acid (doped). In the fully doped polymer all imine nitrogens have been protonated, and the ^{15}N NMR signal from the imine nitrogens is very broad, covering ~100 ppm.[13,14] This dispersion in isotropic chemical shifts arises from heterogeneity in the distribution of the positive charge along the polymer chain that is related to the structural heterogeneity of the polymer in the solid state.[15] In the films, however, the peaks at 140 and 110 ppm are quite sharp, consistent with the regions of the polymer giving rise to these signals adopting only a small subset of structures. The line widths for these peaks are also likely reduced by having a more localized positive

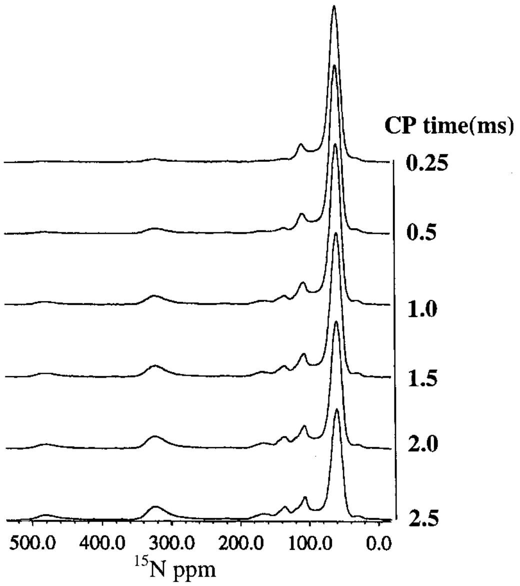


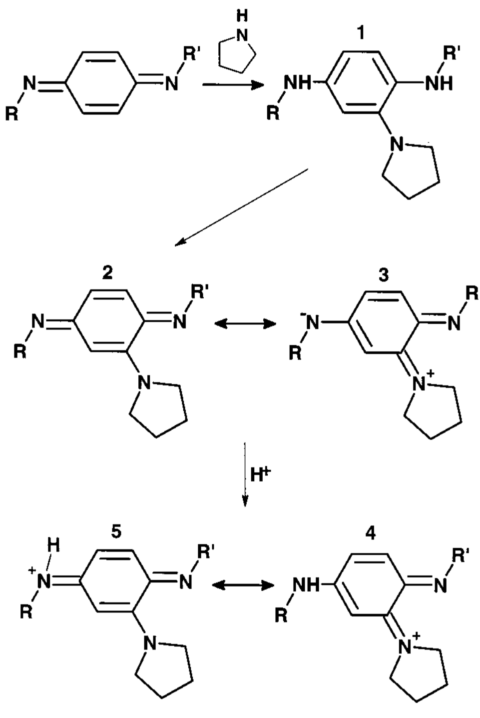
Figure 4. ^{15}N spectra from PANI/Py at increasing CP times.

charge, limiting the heterogeneity in charge distribution within the polymer.

Insights into the chemical species giving rise to these new peaks can be obtained from the rate of cross-polarization from the protons to the nitrogens, T_{IS}. The ^{15}N NMR spectra of the PANI/Py film as a function of CP time are shown in Figure 4. The intensity of the peak at 140 ppm increases at a rate very similar to that observed for the imine nitrogen (320 ppm), so this nitrogen is not covalently bonded to a proton. With a chemical shift of an imine nitrogen carrying positive charge but no N−H bond, the peak at 140 ppm is assigned to imine nitrogens from the polymer that are strongly hydrogen bonded to a GI molecule.

The nitrogen associated with the peak at 110 ppm does have a covalently attached proton, as the T_{IS} value for this peak is very similar to that of the amine nitrogens. Also, the additional upfield shift of this peak is indicative of the nitrogen having some additional amine character; similar assignments have been made previously for the doped polymer.[13] This nitrogen is then carrying positive charge, has a covalently bonded proton, and has some amine character. The proposed structure for the nitrogen site is shown in Scheme 2. Upon attack of the quinoid ring by Py, the quinoid ring is converted to a benzenoid ring, **1**, changing a portion of the polymer from the EB form to the LEB form, consistent with the change in intensity ratio of the imine and amine nitrogens in the ^{15}N NMR data. The films are exposed to ambient atmosphere, and under these conditions it has been observed that LEB PANI is converted to the EB form;[15] the reoxidation generates the substituted quinoid ring, **2**. Resonance structures of this compound show that a partial negative charge is stabilized on the imine nitrogen, increasing its basicity. The presence of protons (water, Py) can then lead to protonation of the nitrogen, yielding an immonium ion, **5**. While the nitrogen in this compound is predominantly a protonated, imine nitrogen, resonance stabilization imparts some amine character.

Scheme 2



The significant differences in the ^{13}C and ^{15}N NMR spectra from the PANI/Py and PANI/2-MA films suggest that the final distribution of the GI's in the PANI films is quite different. As there are 0.5 Py per PANI repeat unit and ~50% of the quinoid rings have been reduced, then nearly all of the Py must be covalently attached to a polymer ring carbon. The relatively low intensity of the peak at 110 ppm in the ^{15}N spectrum from the PANI/Py film, arising from reoxidized substituted benzenoid rings, shows that the reoxidation of the substituted benzenoid ring does *not* occur to a large extent. Assuming that the extent of reoxidation of the reduced polymer with 2-MA attached is similar to that of the PANI/Py system, the majority of the reduced polymer generated in the PANI/2-MA film will remain reduced. As only ~5% of the PANI is reduced in this film, the majority of the 2-MA must be simply physically trapped in the polymer and not covalently attached.

The differences in the reactivity of 2-MA and Py can be related to the electronic structure of the two cyclic amines. The lower pK_b of 2-MA compared to Py (6 vs 3) translates into 2-MA being a weaker nucleophile and less likely to undergo addition to the quinoid ring of PANI. Thus, there is less reduction of the quinoid rings observed when the 2-MA is the GI, ~10% that observed for Py. The ^{15}N NMR signal intensity of the peak at 110 ppm from the PANI/2-MA film should also then be ~10% the intensity seen in the spectrum from PANI/Py. The insert of Figure 2 shows that the signal intensity of this peak in PANI/2-MA is ~1% of the intensity observed in the PANI/Py film. As 2-MA is an analogue of cyclopropane, the orbital structure is best described by the Walsh model.[16] In this model the nitrogen has sp^2 hybridization; however, the unhybridized p-orbital is aligned in the *plane* of the ring. It is then energetically unfavorable for the molecule to form the necessary double bond between the nitrogen of the GI and the carbon of the benzenoid ring shown in Scheme 2 to generate **5**. The site where 2-MA is attached to the polymer benzenoid/quinoid ring has structure **1** or **2** (Scheme 2), and the ^{15}N chemical shift will be 320 or 60 ppm.

Chain Dynamics. The presence of the GI in the PANI films also impacts the chain packing and chain

Table 1. $T_{1\rho}$(H) and $T_{1\rho}$(N) for PANI Powder and Films

material	$T_{1\rho}$(H), ms	$T_{1\rho}$(N), ms
PANI powder	3.7	47
PANI/2-MA film	8.0	92
PABI/Py film	5.2	65

dynamics in the films. Polymer chain dynamics can be probed by measuring $T_{1\rho}$; the magnitude of this relaxation parameter is sensitive to the extent of molecular motion present in the sample with a frequency near that of the radio-frequency field amplitude, 50 kHz in these experiments, with the value of $T_{1\rho}$ increasing as the extent of motion decreases. Previous studies on PANI have shown that the polymer has chain motions occurring with a frequency at or near 50 kHz.[13,17] The $T_{1\rho}$ of the protons, $T_{1\rho}$(H), and the nitrogens, $T_{1\rho}$(N), of the powder, PANI/2-MA film, and PANI/Py film are listed in Table 1. The as-synthesized powder has the largest extent of chain motion, as the powder is simply collected after precipitation from an aqueous aniline solution. The larger $T_{1\rho}$(H) values for the films result from tighter chain packing allowed during slow removal of the solvent. The presence of the Py pendent group located on ~50% of the PANI repeat units disrupts the chain packing in their vicinity, allowing for more chain motion and a decrease in $T_{1\rho}$. In the case of the PANI/2-MA film only a small number of repeat units have an attached 2-MA to disrupt chain packing, leading to tighter chain packing and the largest $T_{1\rho}$. The $T_{1\rho}$(H) values for the GIs in the PANI films are the same as those observed for the polymer. The similarity of the polymer and 2-MA $T_{1\rho}$(H) values indicates that the 2-MA molecules not bonded to the polymer are then tightly packed with the polymer chains.

Conclusion

While the use of secondary amines as gel inhibitors allows for the formation of highly concentrated PANI solutions in NMP, ideal for the spinning solid fibers, the GI selected has a profound impact on the final properties of the polymer. Solid-state NMR characterization of PANI films formed from solutions containing 2-MA as the GI, at levels as high as 78:1 relative to the polymer repeat unit, showed little reactivity with the polymer. However, 2-MA was retained in the PANI film at the level of 0.7 2-MA per PANI, and the GI is physically trapped in the PANI film. In contrast, Py, a stronger base (pK_b = 3 vs 6 for 2-MA), adds to ~50% of the repeat units, reducing them to the LEB form of the polymer. In both films a new species, an immonium ion, was formed at low levels and observed by SSNMR. The presence of the GI also affects the chain dynamics of the polymer. The covalently attached Py disrupts the chain packing in the PANI/Py film, resulting in more chain motion in the low kilohertz regime relative to that observed in the PANI/2-MA film.

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