

IR Spectroscopy of Pristine and Iodine-Doped Permethylpolyazine

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Received September 19, 1995. Revised Manuscript Received November 8, 1995[®]

Mid- and near-IR spectra for pristine and iodine-doped permethylpolyazine ($-\text{[N=C(CH}_3\text{)-C(CH}_3\text{)=N]}_x-$) are reported for both natural isotopic abundance and 100% ^{15}N -enriched samples. For the undoped samples the degree of conjugation along the polymer backbone is fairly small. Upon exposure to iodine, the only changes in the IR spectra are found in the near IR where a very intense band grows in above 4000 cm^{-1} and in the mid-IR where there is development of a weaker, poorly resolved doublet around 1500 cm^{-1} . The strong absorption in the near-IR has none of the characteristics normally associated with gap states and so is assigned to be the tail of the visible, electronic absorption of triiodide. The doping-induced feature in the mid-IR is a doublet; the higher energy band is diminished upon ^{15}N enrichment, while the lower energy peak is unaffected by the isotopic substitution. Complexation of I^+ to the polymer, probably through the imine π bond, is thought to be responsible for the new mid-IR peaks. There is no evidence that the polymer has been oxidized.

Introduction

Polyazines are conjugated polymers that are nitrogen-containing analogues of polyacetylene and can be considered the head-to-head polymer of the imine repeat unit, and this leads to several differences between polyazines and other conjugated polymers. Because of the influence of the nitrogen atoms, polyazines are environmentally stable,^{1–4} have a more complicated electronic structure than many conjugated polymers,^{5–8} and have the potential to act as chelates to metal ions.⁹

Polyazines can be doped with iodine to give conducting materials.^{2,4,10,11} Originally, the spectroscopic data were interpreted in terms of a nitrogen-centered bipolaron charge carrier,^{2,10,11} but this was challenged because theoretical calculations and known properties of nitrenium ions⁷ suggested that this species would be unstable. Subsequent investigation of the UV–vis⁸ and XPS¹² spectra of thin films of methylpropylpolyazine suggested that the polymer chain was not oxidized at all, but the reaction of the polymer with iodine led to a I^+ species bound to the polymer with I_3^- counterions. The work described here is a reinvestigation of the IR spectra of iodine-doped and undoped permethylpolyazine, $-\text{[C(CH}_3\text{)=N-N=C(CH}_3\text{)]}_x-$, using ^{15}N -labeled polymer to establish that there is no IR evidence that the polyazine chain is oxidized when exposed to iodine.

Experimental Section

All reagents and solvents were purchased from Aldrich and, unless otherwise noted, used as received except $^{15}\text{NH}_2^{15}\text{NH}_2\cdot\text{H}_2\text{SO}_4$ which was purchased from Cambridge Isotope Laboratories. Elemental analyses were done by M-H-W Laboratories, Phoenix, AZ. All IR spectra were run at room temperature as KBr pellets on a Perkin-Elmer Model 1650 FTIR instrument between 7500 and 400 cm^{-1} using 2 cm^{-1} resolution.

Polymer Synthesis. Typically, 5.0 g of $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{SO}_4$ (0.038 mol) was added to 5 mL of H_2O . Then 4.07 g of Na_2CO_3 (0.038 mol) was added, and the mixture stirred at room temperature until the CO_2 formation had ceased. Then 40 mL of *n*-butanol was added to the flask. A separate solution of 3.4 mL (0.038 mol) of freshly distilled 2,3-butanedione in 20 mL of *n*-butanol was prepared and added to the hydrazine solution slowly over the course of about 5 min . The entire mixture was then stirred and brought to reflux for 22 h . This was cooled on ice and filtered. The recovered solid was stirred in room-temperature water for about 3 h to remove Na_2SO_4 , filtered, washed with ether, and vacuum dried; yield 3.1 g (100%). Anal. Calcd for $(\text{C}_4\text{H}_6\text{N}_2)_x$: C, 58.51 ; H, 7.37 ; N, 34.12 . Found: C, 58.53 ; H, 7.25 ; N, 34.11 . ^{15}N -enriched samples were prepared similarly using 1.0 g of $^{15}\text{NH}_2^{15}\text{NH}_2\cdot\text{H}_2\text{SO}_4$ as the starting material and the amounts of other reagents adjusted appropriately. In the nonenriched samples, carbonyl end groups were removed by stirring the polymer in excess hydrazine hydrate at room temperature for several hours. This was not done with the enriched samples because the hydrazine hydrate potentially can cause exchange reactions that would lead to removal of ^{15}N from the polymer chain.

Iodine Doping. Normally, 0.30 g of polymer (3.7 mmol repeat unit) was added to a 125 mL Erlenmeyer flask, and a weighed amount of I_2 was added to the flask. This was then corked, and the iodine was allowed to saturate the chamber for about 5 min . Then 10 mL of CHCl_3 was added, the flask recorked, and the mixture stirred for 30 min . This was filtered, washed with CHCl_3 , and air-dried. Typically, 65 – 80% of the iodine atoms were incorporated into the polymer. Four samples of unenriched polymer are reported here. Anal. 0.11 g of I_2 reacted, $(\text{C}_4\text{H}_6\text{N}_2\text{I}_{0.175})_x$, calcd: C, 46.06 ; H, 5.80 ; N, 26.86 ; I, 21.29 . Found: C, 46.66 ; H, 6.51 ; N, 26.38 ; I, 21.54 . 0.51 g of I_2 , $(\text{C}_4\text{H}_6\text{N}_2\text{I}_{0.87})_x$, calcd: C, 24.96 ; H, 3.14 ; N, 14.55 ; I, 57.35 . Found: C, 24.33 ; H, 2.81 ; N, 13.73 ; I, 56.58 . 0.77 g of I_2 , $(\text{C}_4\text{H}_6\text{N}_2\text{I}_{1.12})_x$, calcd: C, 21.42 ; H, 2.70 ; N, 12.49 ; I, 63.38 . Found: C, 17.14 ; H, 2.13 ; N, 9.47 ; I, 63.40 . 0.86 g of I_2 ,

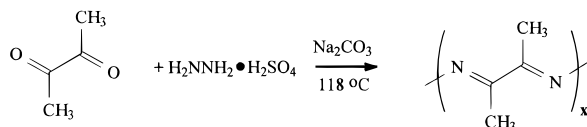
[®] Abstract published in *Advance ACS Abstracts*, December 15, 1995.

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$(C_4H_6N_2I_{1.29})_x$, calcd: C, 19.55; H, 2.46; N, 11.40; I, 66.60. Found: C, 16.66; H, 2.00; N, 9.54; I, 66.54. The poorer analyses for the more heavily doped samples indicate that some degradation of the polymer has occurred. Stoichiometries were estimated using the iodine analysis in each case. One sample of the ^{15}N -enriched polymer was doped with iodine (0.89 g) to give $(C_4H_6^{15}N_2I_{0.74})_x$; the iodine stoichiometry was estimated based in the IR spectrum.

Results

A slightly modified synthesis for polyazines was developed for this work in order to most effectively incorporate ^{15}N into the polymer from the commercially available source of labeled hydrazine sulfate. Previously,^{2,4} the polyazines had been synthesized by preparing a dihydrazone by condensation of a diketone with excess hydrazine hydrate. The dihydrazone, which is a crystalline solid that acts as hydrazine source with an easily measured stoichiometry (necessary for condensation polymerizations), was then reacted with an equimolar amount of a dione to give the polymer.^{2,4} Since this method utilizes the hydrazine source poorly, a polymerization directly from hydrazine sulfate was designed. Attempts at condensing 2,3-butanedione with hydrazine sulfate were ineffective (only oligomers were obtained), but by neutralizing the acid with sodium carbonate, a high yield of the polyazine was obtained:



Incorporation of the labeled nitrogen can then be done directly from the $^{15}NH_2^{15}NH_2 \cdot H_2SO_4$ source with minimal loss of the label. The synthesis leads to primarily carbonyl end groups which, for natural abundance samples, were capped with hydrazine hydrate. The ^{15}N -enriched sample was not treated in this fashion since the amount of exchange caused by hydrolysis of the imine bonds is unknown, and a polymer with 100% ^{15}N enrichment was the goal.

Incorporation of iodine into the polymer was best done in a two-step process. First, the polymer was exposed to iodine vapors for a few minutes, and then solvent was added and the mixture stirred. Without the gas-phase induction period doping was poor and nonreproducible.

The IR spectra between 7500 and 400 cm^{-1} for $(C_4H_6N_2)_x$, $(C_4H_6N_2I_{0.18})_x$, and $(C_4H_6N_2I_{0.87})_x$ are shown in Figure 1. All of the samples have several sharp peaks between 1000 and 2000 cm^{-1} and weak peaks around 3000 cm^{-1} that arise from C–C, N–N, C=N (1000–2000 cm^{-1}), and C–H (3000 cm^{-1}) vibrations in the polymer and are generally independent of the doping level. In contrast, at higher energies a strong, structureless absorption (the features near 3400 and 5200 cm^{-1} vary from sample to sample and are due to water in the KBr pellet) grows in as the doping level increases. This is assigned to the tail of the electronic absorption associated with triiodide, consistent with observations made on thin films of methylpropylpolyazine.⁸ There are no features that indicate the presence of either polaron or bipolaron gap states.

An expanded view of the 1000–2000 cm^{-1} region is shown in Figure 2 for natural abundance and 100% ^{15}N -enriched, undoped polymers. In the unenriched sample

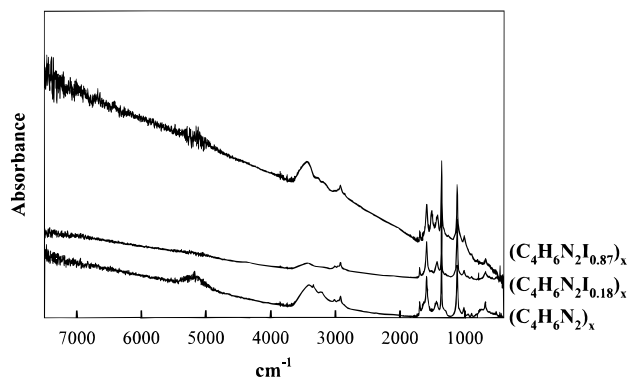


Figure 1. Mid- and near-IR absorption spectra for $(C_4H_6N_2I_{0.87})_x$ (lower spectrum), $(C_4H_6N_2I_{0.18})_x$ (middle spectrum), and $(C_4H_6N_2I_{0.87})_x$ (upper spectrum) between 7500 and 400 cm^{-1} . Samples were prepared as KBr pellets. The variable intensity peaks around 3400 and 5200 cm^{-1} are due to water in the KBr pellet. The intensities of all spectra were normalized to the sharp peak at 1358 cm^{-1} , and the baselines are shifted so each spectrum can be distinguished.

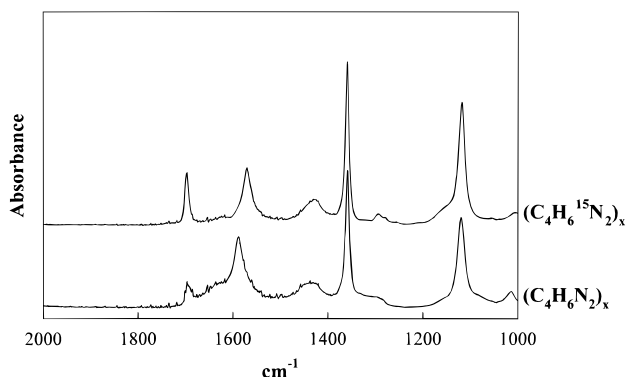


Figure 2. Absorption spectrum of undoped (lower) and ^{15}N -labeled polyazine between 2000 and 1000 cm^{-1} . Samples were prepared as KBr pellets. The intensities of all spectra were normalized to the sharp peak at 1358 cm^{-1} , and the baselines are shifted so each spectrum can be distinguished.

the major peaks are seen at 1700, 1588, 1437, 1359, and 1119 cm^{-1} with a broad shoulder near 1630 cm^{-1} . The features at 1700 and 1630 cm^{-1} are due to carbonyl and amine end groups, respectively. This assignment is supported by the observation that the intense peak at 1700 cm^{-1} and near absence of an absorption at 1630 cm^{-1} in the ^{15}N -enriched sample which was not treated with hydrazine, similar to the spectrum of the natural abundance polymer (not shown) prior to treatment with hydrazine. The intensity of the 1630 cm^{-1} peak suggests $M_n \sim 2000$ –3000.² The absorption at 1588 cm^{-1} is the only feature that shifts significantly upon enrichment with ^{15}N , to 1570 cm^{-1} , and is assigned to the anti-symmetric imine stretch in the polymer (for a pure harmonic oscillator the predicted frequency is 1563 cm^{-1}). The broad peak at 1437 cm^{-1} shifts slightly to 1430 cm^{-1} and is somewhat narrower upon ^{15}N enrichment. This suggests that there are two contributions to the feature, one of which is associated with a nitrogen motion. Thus, this is assigned to be a mixture of a C–CH₃ antisymmetric deformation and a chain C–C vibration weakly coupled to the nitrogen atoms. The most intense feature in the spectrum is found at 1358 cm^{-1} and does not shift with ^{15}N enrichment. This is assigned to the C–CH₃ symmetric deformation and, because of the invariance of both peak position and lineshape, is used as an

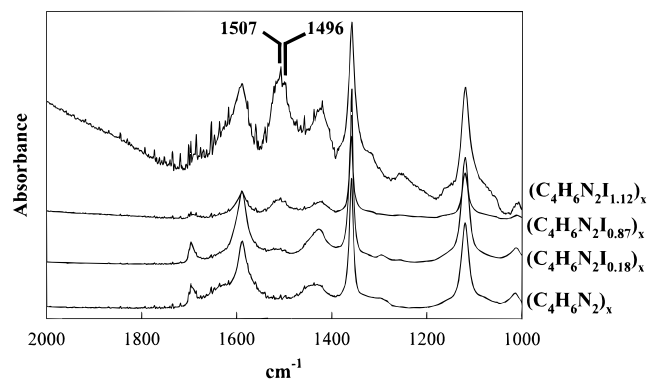


Figure 3. Absorption spectrum of $(\text{C}_4\text{H}_6\text{N}_2)_x$, $(\text{C}_4\text{H}_6\text{N}_2\text{I}_{0.18})_x$, $(\text{C}_4\text{H}_6\text{N}_2\text{I}_{0.87})_x$, and $(\text{C}_4\text{H}_6\text{N}_2\text{I}_{1.12})_x$ between 2000 and 1000 cm^{-1} . Samples were prepared as KBr pellets. The intensities of all spectra were normalized to the sharp peak at 1358 cm^{-1} , and the baselines are shifted so each spectrum can be distinguished.

internal standard for all the spectra reported here. Finally, the peak at 1119 cm^{-1} shifts to 1117 cm^{-1} in the ^{15}N -enriched sample, the same within experimental error. This peak was originally thought to arise from an N–N stretch^{2,13} but that assignment is certainly in error. More likely, in comparison to polyacetylene,^{14,15} this is due to a chain C–C stretching vibration.

Upon exposure to iodine, the 1000–2000 cm^{-1} region changes very little in terms of peak positions or relative intensities of the major absorptions, as demonstrated in Figure 3. The only exception to this is the presence of a new feature around 1500 cm^{-1} that grows linearly with the amount of iodine in the sample. Close examination of the absorption shows that it is a doublet with maxima at 1507 and 1496 cm^{-1} . As shown in Figure 4, the low-energy peak does not shift with ^{15}N enrichment while the higher energy absorption is diminished. This suggests that the vibration associated with the 1507 cm^{-1} peak involves a nitrogen atom, while the 1496 cm^{-1} absorption arises only from carbon atoms. Since the other peaks in the spectrum do not lose intensity, it seems likely that the new features are not associated with the vibrations found in the pristine polymer. Since any vibrations involving iodine atoms are not likely to resonate at this high of an energy, the doping-induced absorptions are assigned to arise from vibrations formally forbidden in the undoped polymer. These vibrations gain intensity by the symmetry lowering caused by the presence of the iodine atoms although the specifics of the interaction between the polymer and the iodine are not elucidated.

Thin films of methylpropylpolyazine can be compensated with anhydrous ammonia.⁸ However, attempts to compensate these iodine-doped materials with gaseous ammonia were unsuccessful. Although copious reaction was evident when the iodine containing polymers were exposed to NH_3 , no spectroscopic changes could be detected in the IR region. It is assumed that the observed reaction occurred between surface iodine and ammonia and that the ammonia could not effectively diffuse into the bulk powder, at least over the course of the reaction times used (overnight).

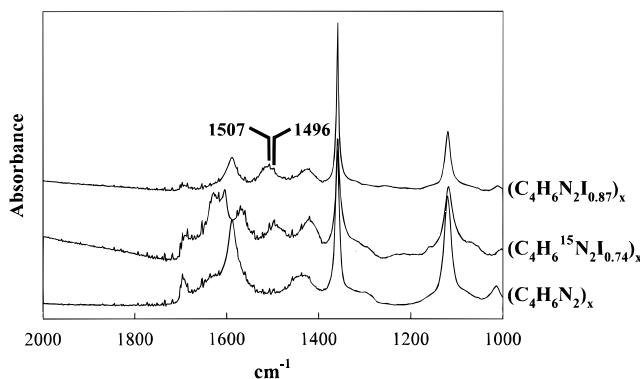


Figure 4. Absorption spectrum of $(\text{C}_4\text{H}_6\text{N}_2)_x$ (lower spectrum), $(\text{C}_4\text{H}_6^{15}\text{N}_2\text{I}_{0.74})_x$ (middle spectrum), and $(\text{C}_4\text{H}_6\text{N}_2\text{I}_{0.87})_x$ (upper spectrum) between 2000 and 1000 cm^{-1} . Samples were prepared as KBr pellets. The intensities of all spectra were normalized to the sharp peak at 1358 cm^{-1} , and the baselines are shifted so each spectrum can be distinguished. The peaks near 1630 cm^{-1} in the middle spectrum are due to end groups of degraded polymer.

Discussion

Assuming the undoped polymer is in the *anti*-E-*anti*-E conformation^{2,10} (the notation refers to the conformations of the N–N and C–C single bonds and the two C=N bonds in the repeat unit; this is analogous to the all-trans form of polyacetylene) the local symmetry is C_{2h} . Because of the inversion symmetry, only 15 fundamental vibrations are expected, and this is consistent with the low number of absorptions observed in the pristine polymer.

The degree of conjugation along the polymer chain is relatively small, in agreement with other assessments reported in the literature.^{2,16} This conclusion is reached for two reasons. First, the C=N antisymmetric stretch at 1588 cm^{-1} is quite close to the frequency expected for an isolated imine bond (1610–1630 cm^{-1}); the slight reduction in frequency implies a small amount of conjugation. Second, as evidenced by the comparison of the natural abundance and ^{15}N -labeled spectra, the C=N antisymmetric stretch moves to a frequency that is close to that predicted by a simple harmonic oscillator while the C–C chain vibrations are all invariant. This implies that the degree of coupling of the imine bond to the rest of the chain is relatively small.

The nature of the doping process has generated some controversy. Originally, a bipolaron with charges centered on the nitrogen atoms ($-\text{N}^+-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{N}^+$, formally nitrenium ions) was proposed.^{10,11} This was consistent with the typical behavior of conducting polymers where oxidation occurs from the π system and explained the 1500 cm^{-1} doping-induced absorption as arising from the C=C in the bipolaron unit. The prolonged lifetime of the usually unstable nitrenium ions was rationalized to arise from the delocalization of the bipolaron over 4–5 repeat units. On the basis of theoretical calculations, previously known nitrenium chemistry, and alternate interpretations of the spectroscopic data, this was challenged.⁷ Instead, a cumulene type unit ($-\text{C}(\text{CH}_3)=\text{N}^+=\text{N}-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{N}=\text{N}^+=\text{C}(\text{CH}_3)-$ for this polymer) was proposed as the charge carrier, effectively having the oxidation from the nitro-

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gen lone pair. However, the calculations suggested that this type of dication should also be reactive. Recent evidence implies that neither interpretation is correct.^{8,12} The doping-induced doublet near 1500 cm⁻¹ is also found in oligomers with chain lengths too short to support a bipolaron.¹² Further, XPS spectra suggest the presence of I⁺ as the cationic species in these polymeric complexes.¹⁷ Thus, the most reasonable explanation is that the polymer chain is not oxidized at all (or, at least, the degree of charge transfer is small). Rather, the iodine disproportionates into I⁺ and I₃⁻ (the presence of triiodide has been confirmed by both UV and Raman spectra¹²) with the role of the polyazine to stabilize the iodonium ion. Similar behavior is known when I₂ reacts with pyridine.¹⁸ The doping-induced vibrations at 1507 and 1496 cm⁻¹ then probably arise from repeat units with I⁺ complexed to the imine bond: the 1507 cm⁻¹ absorption is likely to arise from an imine bond (perhaps the symmetric stretch forbidden in the uncomplexed polymer) since this peak diminishes in the ¹⁵N-labeled sample while the 1496 cm⁻¹ must be due to a chain C–C vibration. While the nature of the complexation of the iodonium to the nitrogen could be either σ (through the N lone pair) or π (through the imine π bond), the proposed interpretation of the doping induced vibrations

favors the π complexation since this would have a bigger effect on C–C bonds. However, further studies will be required to confirm this conclusion.

Finally, if the polyazine is not oxidized, then the reported conductivity must occur through the iodine atoms. The maximum conductivities in these systems are $\sim 10^{-2}$ S/cm^{2,10} and this is comparable to other iodine-doped nonconjugated polymers,^{19–23} especially the iodine-doped polyisoprenes (that the charge transport in iodine-doped polyazines is analogous to that in the iodine-doped polyisoprenes has been previously suggested⁷) which have been shown to have conductivity centered through the polyiodide chains.^{22,23} Thus, it seems that the complexation reaction takes precedence in the polyazines, probably because the imine bonds are too localized to be oxidized by iodine, and that charge transport occurs through the triiodide or other higher polyiodides.

CM9504394

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