

Electronic Spectroscopy of Poly(propylmethylazine)

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Poly(propylmethylazine) $[\text{N}=\text{C}(\text{R}_1)-\text{C}(\text{R}_2)=\text{N}]_x$, $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{CH}_2\text{CH}_2\text{CH}_3$, PMPAZ) and a permethylpolyazine (MMPAZ)-PMPAZ copolymer series with varying amounts of propyl substitution has been studied by UV-vis spectroscopy in solution and UV-vis-NIR as thin films and I_2 -doped thin films. The presence of the propyl group allows for limited solubility in some organic solvents but does not affect the approximate C_{2h} symmetry of the conjugated π backbone indicative of substantial σ - π separability. Due to the two imine bonds in the repeat unit the electronic manifold contains two high-lying filled bands and two low-lying empty bands. The pristine polymers all exhibit a $\pi \rightarrow \pi^*$ multiplet arising from the conjugated azine moiety with maxima observed approximately at 280 and 320 nm arising from transitions to the lower energy conduction band. A bandgap of 3.0 eV has been assigned by extrapolation of the low-energy band edge and an approximate energy diagram of the π manifold is proposed. The iodine-doped PMPAZ thin-film spectrum is dominated by the I_3^- signature and is accompanied by a pronounced vacuum-UV band edge while the $\pi \rightarrow \pi^*$ multiplet is diminished and no longer discernible. Compensation with ammonia regenerates the conjugated azine manifold.

Introduction

Extended linear systems containing conjugated double bonds have been extensively investigated for over 50 years.¹ Conjugated polymers, the current manifestation of this form, have been shown vigorous renewed interest since the discovery that polyacetylene (PA) can be oxidized or reduced into highly conducting states.² The resulting field of conducting polymers has exploded in the past 15 years due to a concerted push by chemists, physicists, and material scientists to understand and harness charge storage and transport in these unusual materials. Electronic spectroscopy has been a very powerful method for

characterizing the electronic manifolds of conjugated polymers and probing for the signatures of charge-carrying species.

Numerous other conjugated systems³ are currently being investigated for commercial potential; a combination of π -system conductivity coupled with environmental stability and industrial processibility is desired. Several of these polymers modify an all-carbon conduction pathway with geometric restraints, such as polypyrrole⁴ and polythiophene,⁵ while others utilize aromatic rings, for example, poly-*p*-phenylene.⁶ Another important strategy is to incorporate a heteroatom into the π -conduction network which has resulted in, for example, polyaniline⁷ and polyazine (PAZ).⁸ All of these conjugated polymers have

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enhanced environmental stability and can be doped into conducting states. However, since all of these polymers lack structural degeneracy, the charge carriers are required topologically to be polarons and bipolarons instead of the solitons found in PA. Polarons and bipolarons exhibit a pair of states at intragap energies. The absorption associated with the lower energy polaron or bipolaron state is typically found in the NIR regime.^{3c}

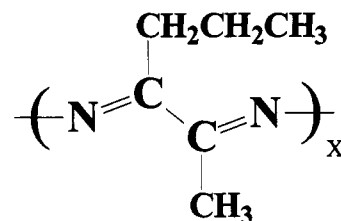
Polyazine ($[N=C(R)-C(R)=N]_x$, PAZ) is a direct analog of PA. PAZ is formally isoelectronic with PA and has a similar all-trans or zig-zag geometry. Due to the head-to-head linkage of the imine moiety in PAZ, the repeat unit must contain two π bonds, which is the simplest system that can generate an electronic manifold with four bands, two filled valence bands and two unfilled conduction bands. In addition, the electronegativity of the nitrogen heteroatom limits the delocalization of the π network and should result in a decreased bandwidth relative to PA. Theoretical calculations at both the extended Hückel and the Hartree-Fock level predict these four narrow bands with a bandgap more than twice as large as PA.^{8a,b,d,o}

Presently, permethylpolyazine (MMPAZ) is the most studied polyazine. IR,^{8c} solid-state NMR,^{8g,h} and X-ray diffraction⁸ⁿ have confirmed an all-trans structure with extended conjugation. Iodine-doped pressed pellets of MMPAZ have reached room-temperature conductivities of 0.1 S cm^{-1} ^{8c} and solid-state ¹⁵N NMR has characterized the charge-carrying bipolaron as the unprecedented dinitrenium ion.^{8m} However, MMPAZ is an intractable yellow powder which is insoluble in typical solvents and decomposes before reaching its melting point,^{8c} and consequently, the electronic spectral information is unobtainable by standard UV-vis techniques.

The addition of alkyl substituents is the easiest way of improving solubility and, hence, the processibility of an organic polymer as demonstrated by the success achieved

with polythiophene^{5f,g,i,j,9} and polyaniline¹⁰ derivatives. With the introduction of statistically alternating propyl group substitution on the PAZ chain, the polymer easily dissolves in chloroform and other organic solvents. As the degree of propyl substitution is decreased, the solubility drops as well. Nevertheless, even at the lowest levels of propyl substitution (<2%) the polymers retain limited solubility. Therefore, PMPAZ and the MMPAZ-PMPAZ copolymer series can be cast into optical-quality thin films which readily allows the examination of the solid-state electronic properties of these materials.

PMPAZ with statistically alternating propyl and methyl groups has previously been studied by IR and NMR spectroscopy.^{8j}



Comparisons of the IR vibrational frequencies and NMR chemical shifts of PMPAZ with its monomer, 2,3-hexanedione dihydrazone and with MMPAZ indicate that there is very little difference in the geometry between them. This structural similarity demonstrates that PMPAZ is also a linear polymer in an all-trans ground-state conformation. Extensive conjugation of the π backbone is revealed by a low-energy imine stretch at 1587 cm^{-1} and deshielded NMR resonances (vs the monomer) especially in the imine region.

Polyazines are unusual conjugated polymers because they are formed by a condensation polymerization rather than the more typical oxidative methods. Because of this, the only saturated defects possible are amino alcohols,^{8k,l} which are easily detected by both NMR and IR methods. No evidence for conjugated defects has been found for alkyl-substituted polyazines, consistent with mechanistic studies of the polymerization of these polymers.⁸ⁱ

PMPAZ also appears to maintain its structural integrity after oxidative doping with iodine. The IR spectrum of doped PMPAZ is virtually unchanged except for a new double-bond resonance at 1505 cm^{-1} which is attributable to the generation of dinitrenium bipolarons. Therefore, PMPAZ is a stable polymer which provides easy access to the solid-state electronic manifold characteristic of the conjugated PAZ π network.

Experimental Section

The samples in this study were prepared by a procedure previously described in the literature.^{8c} By varying the amounts of 2,3-hexanedione and 2,3-hexanedione dihydrazone relative to 2,3-butanedione and 2,3-butanedione dihydrazone, respectively, a series of polyazines with various ratios of propyl to methyl side groups were obtained.^{8j} A generalized polymer can be represented as $[(C_6H_{10}N_2)_y(C_4H_6N_2)_{1-y}]_x$ so that y is the fraction of propyl-

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methyl repeat units in the polymer chain and $1 - y$ is the fraction of permethyl repeat units. Therefore, a PAZ designated $y = 1.00$ would contain 100% $-(C_6H_{10}N_2)-$ units and would have statistically alternating propyl and methyl groups. The six poly(propylmethylazine) used in this study were $y = 0.0325, 0.0605, 0.127, 0.232, 0.500,$ and 1.00 , which yields a range of propyl group percentages from less than 2% up to 50%. GPC analysis was used to determine the degree of polymerization of the polymers.

Solutions. PMPAZ and all of the copolymer series were dissolved in N_2 -degassed chloroform (Fischer reagent grade used as received). The solubility of the $y = 1.00$ sample was moderate (≈ 0.1 M) but diminished substantially (2 or more orders of magnitude) for the low- y samples. Solution spectra were recorded between 1100 nm and the $CHCl_3$ cutoff at 240 nm (1.1–5.2 eV). The $CHCl_3$ solutions were found to follow Beer's law up to saturation or to a concentration of 0.1 M, whichever was smaller.

PMPAZ was also examined spectroscopically as solutions of methylene chloride (Fischer Optima), carbon tetrachloride (Fischer reagent grade), tetrahydrofuran (Fischer HPLC grade), acetonitrile (Burdick & Jackson UV grade), diethyl ether (Baker anhydrous reagent grade), hexane (Fischer Optima), 1-propanol (Fischer reagent grade), 2-propanol (Fischer reagent grade), and methanol (Fischer Optima). All solvents were used as received, and the solution spectra were recorded from 600 nm down to the respective UV cutoff of each solvent.

Films. The thin-film samples were prepared by spin-casting chloroform (Burdick & Jackson or Fischer Optima used as received) solutions of the polymers onto optical quality quartz slides (NSG Precision Cells). The $y = 1.00, 0.500, 0.232,$ and 0.127 solutions used were approximately 2×10^{-2} M. Saturated solutions of the $y = 0.0325$ and 0.0605 were used and required multiple applications of polymer solution to spin-cast films of appreciable thickness ($A > 0.2$). The films were a light yellow-brown in color and possessed an "oil-slick sheen" to reflection. Film thicknesses were determined by dissolving a $2 \text{ mm} \times 10 \text{ mm}$ area (the focal area of the spectrometer on the sample) of representative films in chloroform and then using the molar absorptivity to determine concentration. This coupled with the repeat unit molecular weight and density yielded the volume of the original sample. Film spectra were recorded between 2500 and 190 nm (0.50–6.5 eV).

Doping. The polymer films cast on quartz slide substrates were placed in a sealed glass chamber physically separated from a layer of iodine crystals (Baker & Adamson resublimed reagent grade used as received) covering the bottom. The films were allowed to react with the I_2 vapor at room temperature (21–26 °C) for various lengths of time. The films quickly adsorbed I_2 and began to darken after a few minutes. Spectra characteristic of doped PMPAZ were obtained after 30–60 min. After several hours the films were a very dark brown, almost opaque, while the quartz substrate remained free of any measurable I_2 deposition. Spectra were taken immediately upon removal from the doping chamber and at various time intervals afterwards.

Instrumentation. The UV-vis spectra were recorded between 1100 and 190 nm (1.1–6.5 eV) on a Perkin-Elmer $\lambda 2$ spectrophotometer at room temperature operating in the double-beam absorbance mode calibrated vs a HO_2 standard and utilizing the 2-nm curve-smoothing function.

The NIR spectra were recorded between 1100 and 2500 nm (0.50–1.1 eV) on a Pacific Scientific Model 6250 spectrophotometer.

The Raman spectra were obtained with a Spex 1401 double-monochromator equipped with an EMI 9558A photomultiplier tube operated at -20 °C in the photon-counting mode. Incident 514.5-nm radiation from a Lexel Model 95 Ar^+ ion laser which delivered 70 mW at the sample served as the source. An $f1.7$ camera lens collected and focused the scattered light onto the entrance slit of the monochromator. The polymers were examined as spinning powder samples.

The GPC was performed on an instrument utilizing a Waters M6000 pump with a 2 mL/min flow rate of THF, a Rheodyne injector with a 6- μ L injection loop, a Waters Ultrastaygel 10^3 Å column in series with a Polymer Laboratories Gel 10^4 Å column, and a Schoeffel UV Detector set at 280 nm. The system was calibrated using a series of polystyrene standards (Scientific Polymer Products, Inc.).

PMPAZ - MMPAZ Solution

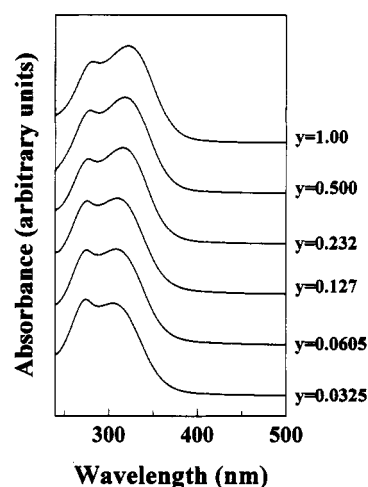


Figure 1. UV-visible solution spectra of PMPAZ and the PMPAZ-MMPAZ copolymer series, $[(C_6H_{10}N_2)_y(C_4H_8N_2)_{1-y}]_z$, between 240 and 500 nm in chloroform.

Conductivities were measured at 27 Hz on thin films using a home-built instrument as described previously.^{8c} The maximum resistance measurable on this instrument is about $10^8 \Omega$.

Results and Discussion

In previous studies the PAZ chain lengths have been estimated by end-group analysis and NMR peak ratio experiments which left some question as to the reliability of these evaluations. GPC was used to determine molecular weights in this investigation, and the outcome was consistent with the earlier results. Typical $y = 1.00$ samples had chromatographic maxima corresponding to $M_n \sim 8200$ (DP = 75) while one preparative batch had $M_n \sim 2800$ (DP = 25). The $y = 0.500$ and $y = 0.232$ had maxima at $M_n \sim 6700$ (DP = 61) and $M_n \sim 3600$ (DP = 33), respectively. The GPC results on samples with lower propyl concentration, however, yielded maxima at $M_n \sim 1400$ reflecting the limited solubility of the longer chain polymer in THF. Nevertheless, the results clearly show that the samples used in this study are sufficiently long to exhibit full polymeric conjugation and to develop quasi-continuous one-dimensional electronic bands.

Solutions. The majority of work in this study was performed using chloroform as the solvent due to a small solute-solvent interaction, spectroscopic access to the prominent $\pi \rightarrow \pi^*$ transitions and the relative ease of dissolution, especially for the low- y value copolymers. All of the PMPAZ chloroform solution spectra (Figure 1 and Table 1) in this study exhibit two strong absorptions in the UV and are consistent with the $y = 1.00$ PMPAZ spectrum previously reported.^{8j} The experimental results are compiled in Table 1. The absorption peaks are centered at approximately 275–280 nm which is designated as the high-energy band (HE) and at 310–320 nm denoted as a low-energy band (LE) and are the result of allowed $\pi \rightarrow \pi^*$ transitions with molar absorptivities on the order of 1×10^4 L/mol-cm. The LE peak is dominant in the solution spectra with the HE transition appearing as a partially resolved shoulder.

The spectra generated by PMPAZ and the series of PMPAZ-MMPAZ copolymers are very similar except for small variations in absorbance maxima and the relative intensity of HE to LE. Both the HE and LE maxima blue

Table 1. Spectroscopic Results for Solutions and Thin Films of $[(C_6H_{10}N_2)_y(C_4H_6N_2)_{1-y}]_x^a$

	y					
	0.0325	0.0605	0.127	0.232	0.500	1.00
λ_{max} (log ϵ)	275 (3.92)	276 (3.89)	Solution ^b 276 (3.920)	278 (3.959)	280 (3.960)	282 (3.936)
λ_{max} (log ϵ)	308 (3.92)	311 (3.910)	311 (3.944)	317 (4.021)	319 (4.029)	321 (4.004)
			Pristine Films			
λ_{max} (log α)	270	271 (4.62)	272	278 (4.46)	277	276 (4.23)
λ_{max} (log α)	324	321 (4.60)	313	329 (4.49)	323	321 (4.18)
			Doped Films ^c			
λ_{max}	298	299	299	295	293	295
λ_{max}	368	367	367	367	364	364

^a λ_{max} values are in nm, ϵ values are in L/mol-cm and α values are in cm^{-1} . ^b Chloroform. ^c Pumped to remove all unreacted I_2 .

PMPAZ - Thin Film vs. Solution

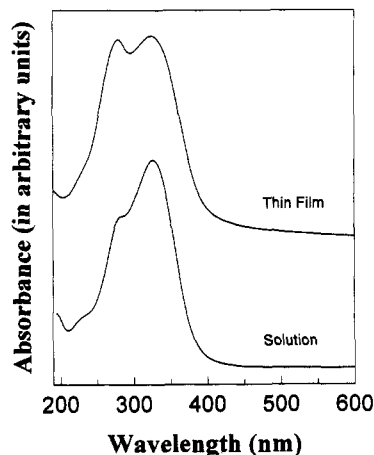


Figure 2. Comparison of the PMPAZ thin-film spectrum vs solution (hexane) between 195 and 600 nm.

shift slightly as the number of propyl groups is decreased. Therefore, an estimate of the absorption maxima for the limiting case with all-methyl substitution, the intractable MMPAZ, can be made by graphical extrapolation. The permethyl limit is evaluated to be 274 nm for the HE maximum and 305 nm for the LE absorption. This shift of absorbance maxima may be due to either electronic or geometric factors. Typically, longer chain alkyl groups cause conjugated polymers to become less delocalized since the substituent group causes twists along the polymer chain. The results here indicate that the planarity of the conjugated backbone is essentially unaffected by the bulky propyl group. Alternately, since a propyl group is a slightly better electron donor relative to methyl, the increased inductive effect from more propyl groups would lower the energy of the $\pi \rightarrow \pi^*$ transition. However, the shift in absorbance energy is not due to a polymer chain length effect. Examination of a series of permethyl azine oligomers demonstrates that spectral convergence occurs by four repeat units¹¹ which is easily surpassed by the lowest molecular weight samples used in this study.

The solution spectra obtained in other solvents on the $y = 1.00$ polymer are consistent with the chloroform data. The extended spectral window of some of the solvents such as hexane (Figure 2), reveal a low-intensity shoulder (SH) at approximately 230 nm and the beginning of a vacuum-UV band edge (VE). Both of these bands are also assigned as $\pi \rightarrow \pi^*$ transitions.

Thin Films. The PMPAZ thin-film optical spectrum also contains the characteristic $\pi \rightarrow \pi^*$ multiplet (Figure

2). The HE peak is found at approximately 275 nm and the LE maximum is located at 320 nm with the band edge tailing into the visible accounting for the yellow color of the films. The absorptivity values, α , are in the range of $10^4 cm^{-1}$, which confirms that the transitions are allowed. Similar to the solution spectra, the only other discernible features between 190 and 2500 nm are the low-intensity shoulder at approximately 225 nm and a hint of a band edge at the vacuum limit. The VE is less defined in the thin film, suggesting a blue shift of this transition in the solid state.

It is known that polyazine powders readily occlude solvents,^{8h} but there appears to be little or no residual chloroform in the films after the initial evaporation during casting. Once the films look dry to the eye (<1 min), the chloroform-free PMPAZ spectrum is established down to 190 nm. Even drying under vacuum for several weeks is ineffective in changing the appearance or spectra of the films. The films are reasonably robust and do not begin to degrade in the presence of air and moisture for many months. However, PMPAZ has been shown to be photochemically active,¹² and the thin films will degrade upon prolonged exposure to UV light.

When the solution and thin-film spectra are compared, it is evident that there is little change in the energy maxima or in the shape of the $\pi \rightarrow \pi^*$ absorption bands except for a change of the intensity of the LE band relative to HE (Figure 2). The HE peak is much more prominent and, in some cases, dominant in the films. The spectral similarity between the thin film and solution suggests weak interchain coupling in the solid state. Therefore, the electronic spectra in PMPAZ is generated essentially by a one-dimensional intrachain electronic manifold. PA has shown a distinct electronic anisotropy between the on-chain axis and the two other perpendicular interchain dimensions in highly aligned films. Direct measurement of the solid-state electronic anisotropy in PMPAZ films has been unsuccessful to date, despite attempts to form aligned films.

There is also very little change between the film spectra of the PMPAZ-MMPAZ copolymer series (Figure 3 and Table 1). However, as the amount of propyl substitution decreases, the film thickness obtainable from spin-casting also diminishes and is readily attributed to the increased difficulty in processing polymers with low solubility. The $y = 1.00$ PMPAZ thin films exhibit slight HE dominance to slight LE dominance among samples from six separate synthetic preparations. Changing the end groups from

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PMPAZ - MMPAZ Thin Films

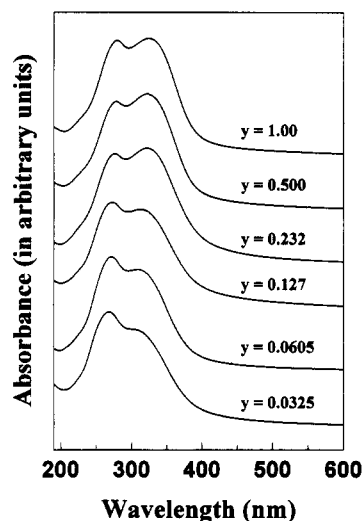


Figure 3. UV-visible thin-film spectra of PMPAZ and the PMPAZ-MMPAZ copolymer series, $[(C_6H_{10}N_2)_y(C_4H_6N_2)_{1-y}]_x$, between 190 and 600 nm. The thin films were spin-coated from chloroform solutions onto optical quartz substrates.

carbonyl to amine has no discernible effect on the spectrum. There is also a variation in the intensities of the HE band relative to the LE band as the number of propyl groups is varied. The $y = 0.127$, $y = 0.0605$, and $y = 0.0325$ copolymers display the prominence of the HE peak, while the $y = 0.500$ and $y = 0.232$ samples, similar to the solutions, show the LE peak dominant. The spectral appearance of an individual sample can sometimes be perturbed by modifying the casting conditions. This variation is attributed to an unknown solid-state effect but most likely relates to packing factors.

Although the absorption maxima of the film spectra fluctuate slightly for the different y value polymers, the deviations in wavelength are not proportional to the propyl substitution, unlike the blue-shift pattern which is observed for the solution spectra on the same series. Therefore, it can be concluded that propyl substitution of the carbon sites in the polymer has an insignificant influence upon the π -electronic manifold and that the thin-film spectrum of PMPAZ is representative of the conjugated PAZ system. However, although the propyl substitution has been shown to have no appreciable electronic effect upon the conjugated π system, the measurable conductivity of doped PMPAZ drops to less than 10^{-6} S cm^{-1} .^{8j} This plunge in bulk electrical transport is attributed to decreased intermolecular coupling as interchain packing distances are increased in the film by the bulkier propyl groups. However, this lower conductivity may be due to the asymmetry of the bipolaron as proposed in the random dimer model.¹³

The repeat unit, $(C(R)=N-N=C(R))_x$, in the planar, zig-zag structure can be assigned to the C_{2h} point group. The similarity of the PMPAZ thin film spectrum with the spectra of the entire PMPAZ-MMPAZ copolymer series implies that C_{2h} is an adequate approximation for all the polymers examined. Due to its symmetry, each repeat unit contributes two bonding-antibonding pairs of states into the electronic manifold. These states develop into four closely spaced electronic bands in the polymer (Figure

PMPAZ Energy Level Diagram

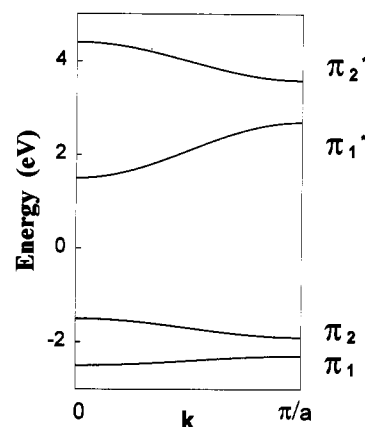


Figure 4. Energy level diagram derived for poly(propylmethylazine) thin films. The Fermi level is arbitrarily assigned 0 eV. The bandwidth of π_1 ($W(\pi_1)$) = 0.2 eV, $W(\pi_2)$ = 0.4 eV, $W(\pi_1^*)$ = 1.2 eV, $W(\pi_2^*)$ = 0.8 eV. The band gap (BG, $\pi_2 \rightarrow \pi_1^*$) = 3.0 eV, the valence bandgap (VG, $\pi_1 \rightarrow \pi_2$) = 0.4 eV, and the conduction bandgap (CG, $\pi_1^* \rightarrow \pi_2^*$) = 0.9 eV. For illustrative purposes the bands are approximated by a cosine function.^{8a}

4) which is an unusual electronic manifold for one-dimensional polymers with extended conjugation. The π_1 and π_2 bands are completely filled and the π_1^* and π_2^* are empty. Transitions from the two π valence bands to the π_1^* conduction band account for the LE and HE bands which are prominently observed in the spectra, whereas transitions to the π_2^* band are observed as the SH and VE. The $n \rightarrow \pi^*$ should be of much lower intensity and are most likely buried under the $\pi \rightarrow \pi^*$ multiplet.¹⁴ The absorption bands are relatively narrow for linear polymers with extended conjugation but is consistent with decreased dispersion of the electronic states associated with the incorporation of nitrogen atoms in the polymer backbone.

The lowest level transition is unambiguously $\pi_2 \rightarrow \pi_1^*$. A bandgap of 3.0 eV is assigned by graphical extrapolation of the band-edge inflection point tangent. The HE absorption band is ascribed as $\pi_1 \rightarrow \pi_1^*$ for two reasons: first, selective irradiation of LE or HE resulted in a different excited state as evidenced by different photoproducts,¹² so that the spectral shape is not due to variations in the density of states across the $\pi \rightarrow \pi^*$ transition, and second, theoretical predictions place π_2^* at substantially higher energy than π_1^* .^{8a,b,d} Although the SH band is in the expected location of monomeric imine $n \rightarrow \pi^*$ absorptions,¹⁴ the oscillator strength is much too high for this forbidden transition and exposure of PMPAZ to strong acids in nonaqueous solvents effected no change on the observable spectrum. Thus, SH is assigned to $\pi \rightarrow \pi^*$ and reiterates the substantial σ - π separability. The fourth transition, $\pi_1 \rightarrow \pi_2^*$, is anticipated well into the vacuum-UV and is consistent with only observing the beginning of a band edge at the high-energy spectral limit.

With the assignments given above, the bandwidths can be estimated if the absorption edges for each transition can be obtained. This can be done by deconvoluting the spectra assuming that the distribution of conjugation

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(14) (a) Robin, M. B.; Simpson, W. T. *J. Chem. Phys.* **1962**, *36*, 580. (b) Bonnett, R.; David, N. J.; Hamlin, J.; Smith, P. *Chem. Ind.* **1963**, *82*, 1336. (c) Bonnett, R. *J. Chem. Soc.* **1965**, 2313. (d) Vocelle, D.; Dargelos, A.; Pottier, R.; Sandorfy, C. *J. Chem. Phys.* **1977**, *66*, 2860. (e) Sandorfy, C. *J. Photochem.* **1981**, *17*, 297.

lengths in the polymer are regular. Although GPC results show that PMPAZ is not monodisperse, the polymers in the samples measured all have chain lengths well in excess of 10 repeat units. By looking at a series of increasing chain length oligomers, we have observed that the polymer spectrum is fully developed after about four repeat units (eight double bonds).¹¹ All of the samples measured in this study exceed this lower limit so that the polydispersity is not an issue for finding the absorption edges. However, because of the polydispersity no details concerning the nature of the electronic bands between the band edges can be obtained.

Although complete deconvolution of the observed thin-film spectra was not successful, the two major peaks (LE and HE) could be reasonably well described by two Gaussians with peak positions and linewidths fairly independent of the model used. This allows us to estimate not only the bandgap but also the gaps between the other electronic states by graphically extrapolating both the lower and upper edges for LE and HE (LE lower edge = 3.0 eV, upper edge = 4.6 eV; HE lower edge = 4.0 eV, upper edge = 5.0 eV). Further, we have assumed that the upper edge for SH and the lower edge for VE coincided at the observed spectral minimum, 5.9 eV. With this information all but one of the bandwidth and bandgap parameters can be determined; we have assumed that the lower energy filled valence band is one half the width of the upper valence band on the basis of semiempirical calculations^{8a,b,d,o} and is, therefore, assigned a bandwidth of 0.2 eV. Even if this assumption is incorrect, it introduces no more than 0.2–0.3 eV of error into the bandwidth estimates which is about the same as the error in the graphical extrapolation.

In assigning the band-edge transitions, care must be taken to note the shapes of the bands as required by the symmetry of the repeat unit. Thus, while the LE band edges correspond to the transitions from the top of the π_2 band to the bottom of the π_1^* band ($k = 0$) and from the bottom of π_2 to the top of π_1^* ($k = \pi/a$) for the bandgap and the high-energy band edge, respectively, HE is assigned such that the low-energy edge (4.0 eV) is from the bottom of π_1 to the bottom of π_1^* ($k = 0$) and the high-energy edge (5.0 eV) is from the top of π_1 to the top of π_1^* ($k = \pi/a$). Similarly, the SH edge at 5.9 eV is from $k = 0$ and the VE edge is from $k = \pi/a$. Any other assignment leads to negative bandwidths. The results of these calculations are given in Figure 4. All of the electronic bands are quite narrow which is consistent with the observation that the delocalized electronic structure of polyazine is fully developed by four repeat units.¹¹

Doped Thin Films. The PMPAZ and PMPAZ-MMPAZ copolymer films were doped by contact with I_2 vapor in a sealed container for various lengths of time. The experimental results of the entire polymer series were identical. The films acquired a noticeable rust tint due to surface adsorption of iodine within minutes of being placed in contact with the vapor. After a few hours of exposure to iodine in the vapor chamber, the films became a very deep brown. The intensity of color was proportional to the polymer film thickness which is evidence that the oxidant is diffusing into the polymer lattice rather than layers of iodine merely adsorbing on the surface.

Studies on other conjugated polymers have elucidated that the doping process follows diffusion kinetics similar

PMPAZ Thin Film - Pristine and Doped

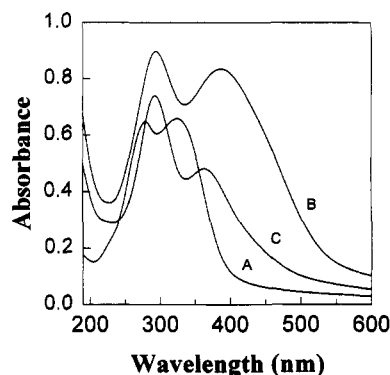


Figure 5. UV-visible spectra of a $\gamma = 1$ PMPAZ thin film. A, the pristine thin film; B, freshly iodine doped film; C, " I_2 -free" iodine doped film (after pumping to remove unreacted I_2).

to the intercalation of graphite. In PA films,¹⁵ for example, at low dopant levels the iodine adsorbs onto the surface of the polymer fibrils. At higher I_2 concentrations, the linear moieties I_3^- and I_5^- are formed as the polymer is oxidized. These anions then diffuse into channels between the polymer chains. The doping is inhomogeneous due to the random nature of diffusion. We are assuming a similar behavior for the doping of PMPAZ films. In situ doping experiments reveal a lag time of 3 or 4 min before any substantial I_2 adsorption occurs, followed almost immediately by the rapid growth of the I_3^- signature.

Exposure to I_2 vapors causes the PMPAZ films to undergo a drastic change in their electronic spectra (Figure 5B). As the redox reaction occurs, the $\pi \rightarrow \pi^*$ multiplet of the pristine film is replaced by a single, narrower band centered at 295 nm. In addition, a new broad band is generated with a maximum varying between 380 and 400 nm depending on the extent of I_2 exposure and a sweeping tail well into the visible which accounts for the dark color of these materials. This new band is the superposition of an absorption at approximately 365 nm and a broad, unresolved feature at roughly 450 nm which can be inferred from the asymmetric shape of the peak. This shoulder intensity decreases under vacuum with a corresponding blue shift of the λ_{max} and reappears upon further exposure to iodine vapors and, thus, can be attributed to free I_2 .

It can take up to several weeks of pumping to remove the excess I_2 and reach the equilibrium concentration of dopant in the films which exposes the intrinsic doped PMPAZ UV-vis spectrum (Figure 5C and Table 1). However, the " I_2 -free" doped film remains stable under pumping indicating a much stronger ionic lattice than is observed in iodine doped PA. The peak at 364 nm, as well as the band at 295 nm, are the principal absorptions expected for the I_3^- species and are assigned to the $^1\Pi_u$ and $^1\Sigma_u^+$ transitions of triiodide, respectively.¹⁶ Unlike the physically adsorbed molecular iodine, the triiodide species is strongly bound to the polymer. The only other important spectral transfiguration is the evolution of a prominent vacuum-UV shoulder.

The presence of a linear triiodide anion is confirmed by a peak at 110 cm^{-1} in the Raman spectrum of I_2 -free doped

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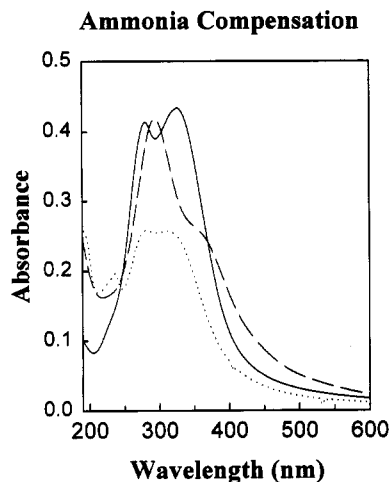


Figure 6. NH_3 compensation of an iodine-doped $y = 1$ PMPAZ thin film. (—) the pristine thin film spectrum; (---) the I_2 -free doped thin film; (···) the same film after $\text{NH}_3(\text{g})$ compensation.

PMPAZ.^{16b,17} No other Raman peaks are seen between 100 and 200 cm^{-1} , indicating that asymmetrical triiodide and higher polyiodides, such as I_5^- and I_7^- , are notably absent.

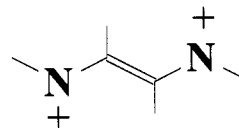
Nondegenerate conjugated polymers are expected to have polaron or bipolaron excitations after doping. The absence of unpaired electrons in doped PAZ eliminates the possibility of polarons in this system.^{8m} Since the I_3^- spectra dominate the UV and presumably are masking the transitions associated with the polymer chain, we searched for the low energy bipolaron transition in the NIR region. Unexpectedly, no bipolaron signatures were observed. This suggests that either the oxidation leads to products that are not bipolarons or that in this complicated electronic system the intensities of the intragap transitions do not follow the same pattern as found in simpler systems such as polypyrrole^{4c,d} or polythiophene.^{5c,d,h}

To test the reactivity hypothesis, we reacted the I_2 -free doped thin films with NH_3 gas. This led to virtually immediate compensation. As shown in Figure 6 upon $\text{NH}_3(\text{g})$ exposure, the optical spectrum returns to that of the pristine film at wavelengths greater than 250 nm, albeit at lower intensity. The new absorptions found in the compensated films below 250 nm are due to reaction products between ammonia and triiodide, presumably iodoamines. This was confirmed by reacting NH_3 with $(\text{CH}_3)_4\text{NI}_3$ in hexane, which gave the same features below 250 nm and was transparent above 250 nm. The lowered intensity of the polymer spectrum after compensation is presumably due to some decomposition that occurs, but it is unclear if the decomposition transpires during doping or dedoping. Upon further exposure to iodine the compensated films redope very quickly to levels equal or greater than those observed during the initial doping.

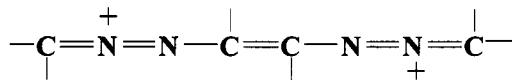
Correlation of the optical spectra with the electrical conductivity was attempted. Unfortunately, because of the thinness of the PMPAZ films (~ 0.1 – $0.5 \mu\text{m}$) the

resistance of all the samples exceeded our capabilities to measure. This means that the conductivity of all the films was less than $10^{-3} \text{ S cm}^{-1}$. The low conductivity is consistent with previous measurements on pressed pellets^{8j} where the room-temperature conductivity was found to be less than $10^{-6} \text{ S cm}^{-1}$. Given the much higher conductivity of iodine-doped permethylpolyazine, this was attributed to poor charge transport between chains that are forced farther apart by the bulky propyl groups^{8j} although the asymmetry of the repeat unit may also be responsible for the lower mobility of the charge carrier along the polymer backbone.¹³

The structure of the oxidized state of polyazines is under some dispute. Based on the IR and solid-state NMR spectra,^{8m} it was originally proposed that the charge carrier was a dinitrenium ion, depicted as the localized structure shown.



Stabilization of this chemically unusual species occurs because of the delocalization of the charge over three to four repeat units, as suggested by semiempirical quantum calculations^{8a,d} and the nature of the charge bearing states in other conducting polymers (e.g., the positively charged soliton in PA extends over ~ 14 C atoms¹⁸). In contrast, high level ab initio calculations performed by Dudis et al.¹⁹ suggest that the initial oxidized state of polyazine is a diazo-like structure;



which is not a bipolaron created from the extended π band but arises from oxidation from the nitrogen lone pair. (It should be noted that these calculations were performed on a 10-atom chain which may not be long enough to support a bipolaron structure and that gas-phase calculations ignore lattice effects.) This diazo structure is then proposed to further react to give N_2 and acetylenes. However, we experimentally observe the doped films to remain stable for months. The results presented here do not corroborate either structure. The dinitrenium bipolaron is expected to give a low-energy transition in the NIR that is not observed, although this may be associated with the complex electronic structure in this material. However, the, at least partial, reversibility of the doping process as well as the prominent vacuum-UV band edge are consistent with bipolaron formation. It may be feasible that shorter length oligomers present in the samples are irreversibly oxidized via the diazo-like intermediate, but the reversibility also demonstrates that a less damaging process must also occur. Previous IR studies^{8c,f,j,k} have conclusively shown that the polymer backbone remains intact upon doping and there is no spectroscopic evidence

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for the conjugated diazo moiety or decomposition products in the IR or UV-vis. Moreover, a doping study of controlled chain length permethyl oligomers demonstrates that only the monomer and dimer decompose upon exposure to I₂ vapors while the tetramer and longer oligomers oxidize in the same fashion as the polymers examined here.¹¹ Clearly, 10 atoms may be adequate to model the structure of a conjugated linear polymer but are insufficient to describe the electronic properties.

Conclusion

The propyl groups on PMPAZ allow for sufficient solubility in organic solvents to cast thin films and has allowed us to study the optical spectroscopy of these conjugated polymers. The nature of the alkyl group (methyl vs propyl) has a relatively small effect on the electronic structure of the polyazines. The symmetry of the repeat unit dictates that four electronic bands are formed from the π orbitals in this polymer and estimates

of the bandwidths and bandgaps have been made. The filled valence bands are quite narrow while the empty conduction bands are wider. The bandgap between the highest filled band and the lowest unfilled band is quite large, ~ 3.0 eV.

Iodine doping of PMPAZ significantly alters the optical spectrum. New absorptions arise that are attributed to I₃⁻, a conclusion confirmed by resonance Raman spectroscopy. Most notably, the doping process can be reversed, at least partially, by compensation with NH₃. This results suggests that the doping gives rise to bipolarons, although the low-energy NIR signatures are not observed. Further experiments are required to resolve this conundrum.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.