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Synthesis, Characterization, and Iodine Doping of a Soluble Polyazine: The Propyl Methyl Substituted Derivative

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Reaction of 2,3-hexanedione with 2,3-hexanedione dihydrazone leads to a polyazine that is soluble in organic solvents. This synthetic method gives a polymer with statistically alternating methyl and propyl substituents on the carbon atoms along the chain. Like the previously reported permethyl polyazine, IR spectra suggest that the propyl methyl polymer is a linear chain with double bonds in the *E* conformation and single bonds in the anti (or s-trans) conformation. IR, UV–vis, and NMR spectra all imply that extensive conjugation exists along the polymer backbone. The high-resolution ^{13}C NMR spectrum shows the presence of two types of sequences of propyl and methyl groups along the polymer chain. Iodine doping of this polyazine leads to a charge-transfer product with no measurable electrical conductivity. An iodine titration of the polymer allows an estimate of the equilibrium constant for the charge-transfer reaction of 800 M^{-1}.

Introduction

The study of conducting polymers has been of great interest in the past few years.[1] The prototype example of a conducting polymer is polyacetylene,[2] which has the simplest π system that can be easily oxidized or reduced into a conducting state. Unfortunately, from an applications point of view, polyacetylene suffers the disadvantages of being neither processable nor environmentally stable.

Polyazines, $(N{=}C(R)C(R){=}N)_x$, are formally isoelectronic to polyacetylene but, because of the nitrogen heteroatoms, are not reactive in air. Like other polymers with extended π systems, polyazines can be oxidized into a conducting state.[4,5] When R = H, the polyazine is not a simple linear, conjugated polymer; although a soluble material has been reported,[4] this polymer has not been thoroughly investigated. When R = CH_3 (the permethyl polyazine), a well-defined linear polymer free of defects is found that can be doped with iodine to give powder conductivities as high as 0.1 Ω^{-1} cm^{-1}. Unfortunately, this latter polymer is rather intractable, decomposing rather than melting at elevated temperatures and is insoluble in any solvent.

One method of improving the processability of conducting polymers is to add long-chain alkyl side groups to the polymer backbone to improve the solubility of the polymer in organic solvents. This approach has been especially successful for polythiophene derivatives.[5] The synthetic chemistry for the formation of polyazines is quite amenable to this approach of improving the properties of this conducting polymer system, as well. To this end, the polyazine with statistically alternating propyl and methyl substituents on the carbon atoms has been prepared. This had the desired effect of inducing organic solubility for the polymer, but at the expense of removing the high conductivity of this material when doped with iodine. This report details the synthesis and properties of the propyl methyl derivative of polyazine.

Experimental Section

2,3-Hexanedione and hydrazine hydrate were purchased from Aldrich. Solvents were reagent grade and used as received. Melting points were recorded on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

$C_6H_{14}N_4$ (2,3-Hexanedione Dihydrazone). A modification of the previously described procedure was used.[3] A solution of 15 mL of hydrazine hydrate (0.31 moles) and 0.2 mL of glacial acetic acid was stirred at room temperature in an Erlenmeyer flask. To this was added dropwise 3.4 mL (0.030 mol) of *freshly distilled* 2,3-hexanedione over about 5 min. This solution was allowed to stir at room temperature for 45 min and then cooled on ice for 1.5 h. The white product was then vacuum filtered, yield 4.2 g (0.030 moles, 100%). This can be recrystallized from cyclohexane, although it is generally not necessary. The dihydrazone is quite sensitive toward hydrolysis and must be kept dry and cool; mp 56–58 °C. Anal. Calcd for $C_6H_{14}N_4{\cdot}0.17C_6H_{12}$: C, 53.87; H, 10.33; N, 35.80. Found: C, 54.03; H, 9.96; N, 36.00. ^{1}H NMR ($CDCl_3$) δ 5.36 (s, 2 H, NH_2), 5.29 (s, 2 H, NH_2), 2.37 (t, 2 H, CH_2), 1.81 (s, 3 H, CH_3), 1.35 (m, 2 H, CH_2), 0.84 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 151.5, 147.6, 24.4, 18.4, 14.2, 8.3.

$(C_6H_{10}N_2)_x$. A round-bottomed flask was charged with 3.0 g (0.021 mol) of freshly prepared 2,3-hexanedione dihydrazone, 20 mL of dimethyl sulfoxide (DMSO), and 0.5 mL of glacial acetic acid. This was warmed to 50 °C. A solution of 3.0 mL (0.026 mol) of *freshly distilled* 2,3-hexanedione (a slight molar excess of the dione is used because even freshly distilled 2,3-hexanedione does not appear to be analytically pure, but distillation does remove contaminants that inhibit the polymerization) in 5 mL of DMSO was added dropwise over about 5 min to the stirred dihydrazone solution. During the addition the temperature rose to about 80 °C. After the dione addition was completed, the entire reaction mixture was then warmed to about 115 °C and maintained at this temperature for 40 h. The mixture was then cooled to 0 °C on an ice bath, vacuum filtered, and washed with cold cyclohexane. The yellow product was placed in a Soxhlet extractor and extracted with methanol to remove low molecular weight products. The remaining product was then air dried, yield 1.4 g (0.013 mol based on the repeat unit, 31%); mp 110–140 °C, melting to a red liquid but without apparent decomposition (i.e., no loss of gases). Anal. Calcd for $(C_6H_{10}N_2)_x$: C, 65.42; H, 9.15;

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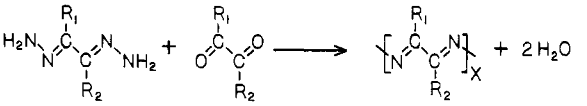
N, 25.34. Anal. Calcd for $CH_3C(O)(C_6H_{10}N_2)_{50}C(O)CH_2CH_2CH_3$: C, 65.37; H, 9.14; N, 24.91. Found: C, 65.06; H, 9.10; N, 24.80. ^1H NMR ($CDCl_3$) δ 2.65 (br), 2.11 (s), 2.08 (s), 1.51 (br), 0.93 (br); ^{13}C NMR ($CDCl_3$) δ 160.4, 159.6, 155.8, 154.8, 29.2, 28.9, 20.5, 20.2, 14.6, 14.5, 13.9, 13.1, 13.0.

I_2 Doping of the Polymer. Since the polymer is readily soluble in chloroform, any level of "doping" could be achieved by simply weighing the amount of the two reactants, mixing in chloroform, and removing the solvent by evaporation. For example, 87.5 mg (7.94×10^{-4} mol) of the polymer and 67.4 mg (2.66×10^{-4} mol) of I_2 were dissolved in 15 mL of $CHCl_3$, stirred for 10 min, and then aspirated to dryness to give $(C_6H_{10}N_2I_{0.67})_x$. There is a fair amount of free iodine present in these samples that is lost over time, so measurements were all made on freshly doped materials. For the heavily doped samples, the product typically was a shiny, black, brittle, thick film that could be readily scraped off the wall of the evaporating flask. Materials with general formula $(C_6H_{10}N_2I_y)_x$ were made with y = 0.067, 0.14, 0.18, 0.34, 0.42, 0.49, 0.67, 0.75, 0.87, 1.01, and 1.36.

Instrumentation. All IR spectra were run at room temperature as KBr pellets on a Perkin-Elmer 281B infrared spectrophotometer between 600 and 4000 cm^{-1}. NMR spectra were run on a Bruker AM300 spectrometer at 300 MHz, with all spectra referenced to TMS. Electrical conductivities were measured on pressed pellets using the Van der Pauw technique on an instrument built by Research Specialities, Chicago, IL, as previously described.[3] UV-vis spectra were run on either a Cary 210 or a Varian DMS90 spectrophotometer.

Results

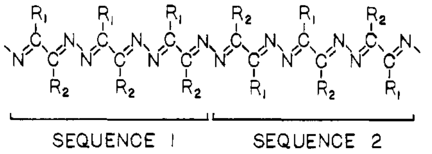
Synthesis. The synthetic procedure for methyl propyl substituted polyazine is the same as we previously developed for the permethyl substituted polymer (eq 1),



$$H_2N{-}N{=}C(R_1){-}C(R_2){=}N{-}NH_2 + O{=}C(R_1){-}C(R_2){=}O \longrightarrow {-}[N{=}C(R_1){-}C(R_2){=}N]_x{-} + 2\,H_2O \quad (1)$$

where $R_1 = R_2 = CH_3$ for the permethylpolyazine (MMPAZ) and $R_1 = CH_3$ and $R_2 = CH_2CH_2CH_3$ for the propylmethylpolyazine (PMPAZ). The reaction appears to be general for any alkyl substituent groups. The addition of the propyl groups at alternate carbon atoms along the chain has the desired effect of inducing solubility in organic solvents: the polymer is soluble to the tens of millimolar level in common organic solvents such as chloroform, methylene chloride, ether, or toluene but has a more limited solubility in alcohols. The effect of the propyl group is further noted in the thermal behavior of PMPAZ: the polymer melts at relatively low temperature (110–140 °C), reacting to form a red liquid but, apparently, not decomposing. This contrasts to MMPAZ, which decomposes with significant gas evolution at quite high temperature (316 °C). The product of the melting process has not yet been determined.

The synthetic scheme used here gives half methyl substituents and half propyl substituents but does not control the sequence of these alkyl groups. As shown in the schematic below, two sequences of substitution patterns



can exist. One has methyl and propyl groups alternating across the N–N bond (sequence 1), while the other has methyls adjacent and propyls adjacent across the N–N bond (sequence 2). As the polymer forms, a diketone approaches the hydrazone end of the growing chain and either carbonyl (distinguished by having either a methyl or propyl attached) can form the new imine linkage. The nearest alkyl substituent on the macromolecule is fairly remote, so little, if any, steric selectivity would be anticipated. Thus, the two types of sequences should be about equal in number.

The elemental analysis of PMPAZ gives an indication of the molecular weight of the polymer. The observed carbon to nitrogen ratio of 3.059 is indicative of two points: first, an infinite chain length has not been approached, since an infinite chain must have a C/N ratio of 3.000; second, the end groups must be predominantly carbonyl since hydrazone end groups would give C/N ratios less than 3. Using a chain length of 50 monomer units (molecular weight of about 5500) and all carbonyl end groups (this is consistent with the excess of dione used in the synthesis) gives a good fit to the experimental analysis. This is in accord with the chain length of about 45 monomer units found for MMPAZ found from elemental analysis,[3] IR end group analysis,[3] and solid-state NMR.[6]

The iodine "doped" polymers were synthesized simply by dissolving both reactants in chloroform, stirring at room temperature, and then removing solvent. Reaction appeared to commence immediately upon addition of the oxidant. At low iodine levels the doped product has a burnt orange color, while at high doping levels the product is black. At the high iodine levels, the product could be recovered off of the evaporating flask walls as a shiny, brittle, thick film. Although no iodine odor was present, the doped polymers do lose iodine upon standing. This is in contrast to the iodine-doped MMPAZ polymers which have been obtained only as dispersed powders and do not lose iodine, even under vacuum.[3]

Electrical Conductivity. No measurable conductivity was found on any of the doped PMPAZ samples; the apparatus has a lower limit of 10^{-6} Ω^{-1} cm^{-1}. In contrast, the iodine-doped MMPAZ polymers were conductive powders, reaching values as high as 0.1 Ω^{-1} cm^{-1} in highly doped samples. Clearly, the propyl group has a large effect on the conductivity properties of polyazine.

It is possible that the propyl group is affecting the oxidative chemistry of the azine chain. To test this prospect, two experiments were tried. Cyclic voltammetry of PMPAZ solutions (chloroform and acetonitrile using both glassy carbon and platinum working electrodes) and thin films on ITO glass showed no electroactivity between −0.5 and +1.25 V vs Ag/AgCl. To test if this result was due to electrode kinetics, TCNQ was reacted with a chloroform solution of PMPAZ. TCNQ has about the same one-electron oxidation potential as iodine but does not undergo the wide variety of chemistry found for iodine. Further, TCNQ is known to react oxidatively with MMPAZ.[7] No reaction was found to occur between TCNQ and PMPAZ. These results imply that iodine is not oxidizing the propylmethylpolyazine, explaining why no significant charge transport is found.

IR Spectroscopy. The IR spectrum of 2,3-hexanedione dihydrazone (HDDH, shown as the lower spectrum in Figure 1) is very similar to the IR spectrum of 2,3-butanedione dihydrazone (BDDH).[3] Resonances associated with N–H vibrations are seen near 3300, 1630, and 700 cm^{-1} for both HDDH and BDDH; the only major difference between the two materials is observed in the 3300-cm^{-1} region, where BDDH has two peaks and HDDH has three peaks. This is a reflection of the fact that the two NH_2 groups in HDDH are not the same, whereas in BDDH the

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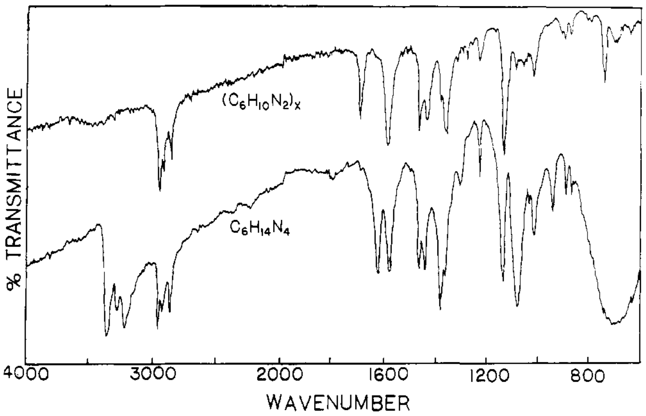

Figure 1. Infrared spectra of 2,3-hexanedione dihydrazone (lower spectrum) and propyl methyl polyazine (upper spectrum) between 600 and 4000 cm^{-1} recorded as KBr pellets.

amino moieties are equivalent. Both HDDH and BDDH have a strong C=N resonance near 1580 cm^{-1}, somewhat lower than typically observed for carbon–nitrogen double bonds, indicating the conjugation of the two imine bonds. The dihydrazones differ slightly in the nature of the C–C absorptions at 1440 and 1355 cm^{-1}: in BDDH the 1440-cm^{-1} band is a broad, barely resolved doublet, and the 1355-cm^{-1} band is very sharp; in HDDH the 1440-cm^{-1} region has a clearly resolved and sharp doublet, while the 1355 cm^{-1} is broader and has observable shoulders. These are effects due to the propyl group. A strong, sharp, unassigned doublet exists near 1100 cm^{-1} for both compounds that is characteristic of monomeric species (oligomers and polymers only show a singlet in this region). Finally, the C–H stretching region in these two compounds show significant differences: HDDH has three very sharp and well-resolved bands while BDDH has two rather weak, ill-defined bands.

The comparison of the IR spectra of the two dihydrazones are rather similar, with the small differences noted above. This strongly suggests that the structure of the two compounds is also very similar. In BDDH, where the structure is known from an X-ray crystallographic study,[3] the double bonds are in the *E* conformation and the conformation about the single bond between the imine bonds is anti (s-trans); likewise the structure of the 2,3-hexanedione dihydrazone is also likely to have *E* imine bonds and an *anti*-C–C bond. The steric reasons that lead to this geometry in BDDH are even more pronounced in HDDH, since the propyl group is larger than the methyl group.

The IR spectra of HDDH and PMPAZ are compared in Figure 1. The main differences between the two spectra are the loss of the N–H resonances, the collapse of the doublet into a singlet near 1100 cm^{-1}, and the rise of a carbonyl band at 1690 cm^{-1} in the polymer spectrum. Since N–H groups can only be at chain ends, it is expected that the N–H resonances should be weak for a long chain molecule; further, since the end groups appear to be mainly carbonyls (as evidenced by both the IR and elemental analysis), it is not surprising that the N–H bands are completely absent. The carbonyls can be capped with hydrazine hydrate to give a polymer spectrum devoid of both carbony and N–H resonances; in analogy to the end-group analysis performed on the IR spectra of MMPAZ oligomers and polymers,[3] this suggests a chain length of at least 45 repeat units for PMPAZ, consistent with the conclusion drawn from the elemental analysis. The similarity between the monomer and polymer spectrum also indicates that the geometric structure does not change drastically upon polymerization, i.e., the *E* double bond and anti single bond (s-trans) conformations are retained in the polymer structure.

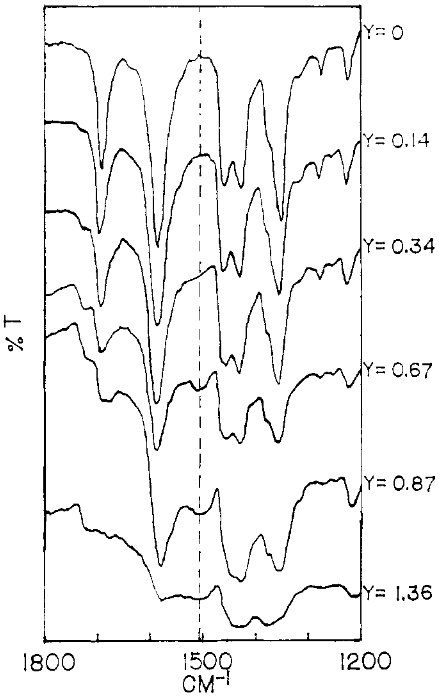

Figure 2. Infrared spectra of iodine doped propylmethylpolyazine, $(C_6H_{10}N_2I_y)_x$, as a function of iodine level, *y*, between 1200 and 1800 cm^{-1} recorded as KBr pellets.

Upon reaction with iodine, the IR spectrum of PMPAZ changes rather little, suggesting that the integrity of the polymer structure is maintained upon doping. Two effects are observed: a new band is seen at 1505 cm^{-1} and, especially at high iodine levels, the resolution of the original vibrational bands is diminished. This is similar to what is observed in the IR spectra of iodine-doped MMPAZ, with one notable difference:[8] in the MMPAZ case, a broad, intense band centered at 4000 cm^{-1} or above, attributed to a free electron absorption, appears upon iodine doping; this band does not appear in the 4000–600-cm^{-1} range in any iodine-doped PMPAZ, suggesting the absence of a mobile charge carrier, consistent with the conductivity results. The growth of the 1505-cm^{-1} band as a function of doping level is shown in Figure 2. The increasing intensity of the 1505-cm^{-1} band and the loss of resolution with increasing doping level is clearly demonstrated. This new absorption is in the double-bond region and has been previously attributed to a bipolaronic type defect,[8] either including a C=C or N=N double bond. Since PMPAZ does not appear to be oxidized by iodine, this peak cannot arise from a bipolaron. Thus, the origin of the 1505-cm^{-1} peak is unknown.

NMR Spectroscopy. The proton spectrum of HDDH can be readily assigned by using the splitting patterns and the spectra of BDDH; the results are given in Table I. The carbon spectrum of HDDH (shown as the top spectrum in Figure 3) is also easily assigned, again by using BDDH as a model in conjunction with simple additivity rules.[9] These results are also given in Table I. On the basis of the chemical shift of the lone methyl group, the diimine contribution to chemical shifts must be about 10–11 ppm, so that the connecting methylene resonance should be near 24 ppm, as observed. The central methylene sees a small

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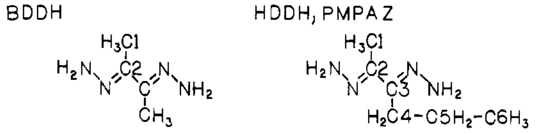
(9) Abraham, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR spectroscopy*; Wiley: Chichester, 1988.

Table I. NMR Assignments for 2,3-Butanedione Dihydrazone (BDDH), 2,3-Hexanedione Dihydrazone (HDDH), and Propylmethylpolyazine (PMPAZ)[a]



	BDDH		HDDH		PMPAZ	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
NH_2	5.51		5.29, 5.36			
C1	1.84	8.4	1.81	8.3	2.08, 2.11	13.0, 13.1
C2		147.5		147.6		154.8, 155.8
C3				151.5		159.6, 160.4
C4			2.37	24.4	2.65	28.9, 29.2
C5			1.35	18.4	1.51	20.2, 20.5
C6			0.84	14.2	0.93	14.5, 14.6

[a] All chemical shifts are given vs TMS.

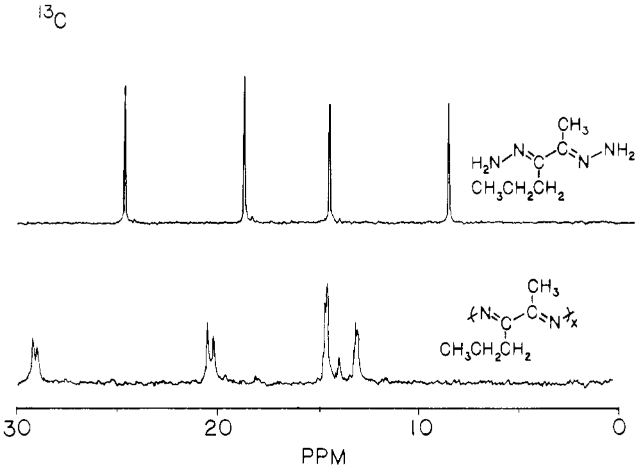


Figure 3. ^{13}C NMR spectra of 2,3-hexanedione dihydrazone (upper spectrum) and propylmethylpolyazine (lower spectrum) between 0 and 30 ppm (vs TMS) in $CDCl_3$ solution.

deshielding effect from the π system, and the terminal methyl group is sufficiently remote to be nearly unaffected by the conjugation.

Two peaks are seen in the imine region of the HDDH spectrum at 151.5 and 147.6 ppm (shown as the top spectrum in Figure 4). BDDH has an imine resonance at 147.5 ppm, so the 147.6 ppm peak found in HDDH is assigned to the imine carbon bearing the methyl group, leaving the 151.5 ppm for the carbon with the propyl substituent.

Because PMPAZ is soluble in common organic solvents, high-resolution NMR spectra can be obtained. This can be used as a sensitive test of the sequence of the alkyl substitutions at the carbon positions along the polymer chain.

The proton NMR spectrum of PMPAZ shows very broad peaks. No resonances due to NH_2 protons are observed, as expected on the basis of the elemental analysis and IR spectrum. Bands at 2.65, 1.51, and 0.93 ppm are due to propyl groups on the polymer chain. The more extensive conjugation of the polyazine π system leads to increased deshielding of the protons so that the observed resonances are all downfield of the corresponding chemical shift of the monomer HDDH. Thus, in the polymer, the resonance of the methylene adjacent to the chain is shifted about 0.3 ppm downfield from the monomer, the central methylene resonances is shifted about 0.2 ppm downfield, and the terminal methyl resonance is shifted only about 0.1 ppm downfield. Likewise, the peak for the lone methyl group directly bonded to the polyazine chain is shifted downfield about 0.3 ppm relative to the monomer resonance but, unlike the propyl resonances, is split into two peaks, reflecting the two different types of sequences possible for the substituent groups along the polymer chain.

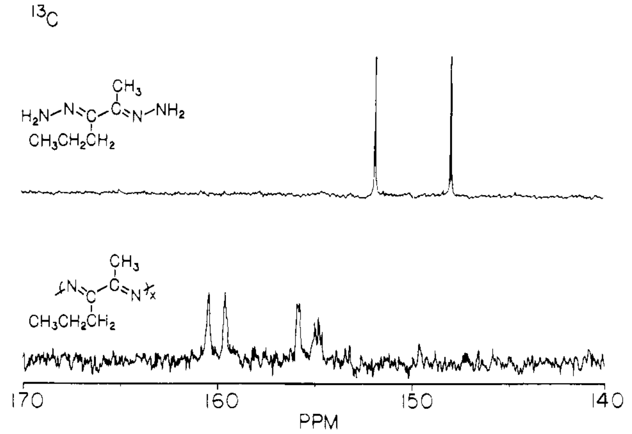


Figure 4. ^{13}C NMR spectra of 2,3-hexanedione dihydrazone (upper spectrum) and propylmethylpolyazine (lower spectrum) between 140 and 170 ppm (vs TMS) in $CDCl_3$ solution.

The carbon NMR more distinctly resolves the two types of sequences. All the carbon resonances show up in pairs, as shown in Table I, except for a peak at 13.9 ppm, which is unassigned. As with the proton spectrum, all of the peaks for the polymer are deshielded relative to the monomer resonances. This deshielding is more pronounced in the imine region of the spectrum than in the alkyl region, consistent with the deshielding being due to resonance of the π electrons in the extended conjugation of the chain. The alkyl region of the ^{13}C NMR spectrum of PMPAZ is shown in Figure 3, while the imine region is displayed in Figure 4. No peak is seen that can be attributed to the carbonyl end groups, either in the 180–200 ppm region due to carbonyls or in the 24–25 ppm region due to methyl groups bonded to a carbonyl. Given the signal to noise ratio of about 20/1 in these spectra, this observation implies that the polymers have chain lengths in excess of 20 repeat units, in agreement with the conclusions deduced from the elemental analysis and IR spectroscopy.

UV–Visible Spectroscopy. Unlike the permethyl-substituted polyazines studied previously, PMPAZ is sufficiently soluble to study the polymer by electronic spectroscopy. The solution UV–visible spectra of the monomers BDDH and HDDH and of the polymer PMPAZ are reported here.

The UV spectra of BDDH and HDDH in absolute ethanol are nearly identical. Both have peaks at 266 nm (37 600 cm^{-1}) with molar absorptivities of about 20 000 (ϵ = 19 800 L/(mol cm) for BDDH, ϵ = 20 500 L/(mol cm) for HDDH). In both cases the peak is quite asymmetric to the high-energy side, indicating the presence of a weaker second absorption, although no clearly discernible shoulder is observed. Calculations at the Hartree–Fock level indicate that the lowest energy transition in BDDH should be of the π–π^* type,[10] and clearly the π system cannot distinguish the effects of the substitution, be it methyl or propyl.

The PMPAZ solution spectrum has two peaks, located at 320 nm (31 300 cm^{-1}, ϵ = 10 900 L/(mol cm)) and at 280 nm (35 700 cm^{-1}, ϵ = 9300 L/(mol cm)), shown as spectrum

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[10] Schmitz, B. K.; Euler, W. B., work in progress.

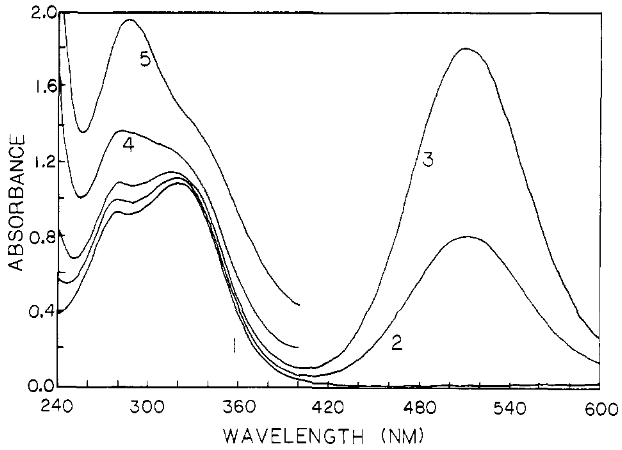

Figure 5. UV-visible spectra of propylmethylpolyazine as a function of iodine doping: 1, 98.8 μM propylmethylpolyazine in chloroform; 2, iodine/polymer ratio = 5.6; 3, iodine/polymer ratio = 14; 4, iodine/polymer ratio = 42; 5, iodine/polymer ratio = 70.

1 in Figure 5. Beer's law is followed at least up to a 0.1 mM concentration. Relative to the monomer, HDDH, the polymer peaks are red shifted by 2000–5000 cm^{-1}, another indication of the extended conjugation of the π system in the polyazines.

Figure 5 shows the results of an optical titration of a 0.1 mM solution of PMPAZ in chloroform. As iodine is added, features at 511 and 295 nm grow while the PMPAZ peaks at 280 and 320 nm become unresolved. The peak at 511 nm is due to free I_2 in solution, while the peak at 295 nm is associated with the polymer or possibly due to I_3^-. The solution spectrum of triiodide (in CH_2Cl_2) is reported to have intense peaks at 294 nm (ϵ = 43 320 L/(mol cm)) and 364 nm (ϵ = 25 250 L/(mol cm)) with weaker peaks at 440 nm (ϵ = 3000 L/(mol cm)) and 565 nm (ϵ = 250 L/(mol cm)).[11] The observed peak in the iodine-doped polymer at 295 nm matches well with the most intense triiodide peak at 294 nm, and the concentrations are probably too low to observe the visible peaks, but no distinguishable peak or shoulder is seen at 364 nm that would be expected for triiodide, so the presence of I_3^- is not certain. As iodine is added to the polymer solution, there is also evidence of a peak growing in below 240 nm; unfortunately, the solvent window limits further investigation of this part of the UV. No solvent was found that gave sufficient solubility to the reactants and was transparent below 240 nm. This region of the electronic spectrum will be explored as thin films and reported elsewhere.

The data from the optical titration can be used to estimate an equilibrium constant for the reaction between iodine and the polymer in chloroform solution. However, this requires the assumption that the doping process leads to a single product, so that any level of doping represents a mixture of reacted and unreacted polymer and not a uniform solution of partially reacted polymer. Thus, the reaction can be written as

$$(C_6H_{10}N_2)_x + zI_2 \rightarrow (C_6H_{10}N_2I_{2z})_x$$

and the equilibrium constant for this reaction is

$$K = \frac{[(C_6H_{10}N_2I_{2z})x]}{[(C_6H_{10}N_2)_x][I_2]^z}$$

where both K and z must be determined. The best fit to the data gave $z = 1$ and $K = 800\ \mathrm{M}^{-1}$, and while the overall fit was not especially good (see Figure 6), this is in part due to the large errors associated with the concentrations for the two polymer components, which were found as differences. The fit to the iodine concentrations, which were found directly from the 511-nm absorbance, is quite satisfactory. Also, the assumption of a single product may not be valid, since the largest deviations in the fit are noted at high iodine concentrations.

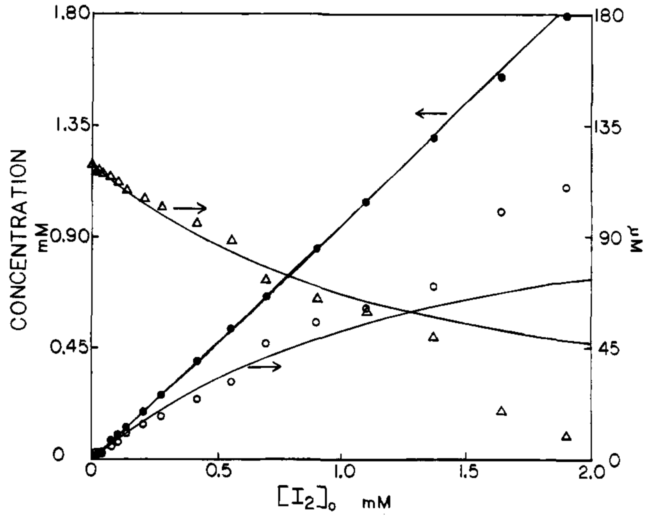

Figure 6. Reactant and product concentrations of an iodine titration of a 11.9 μM propylmethylpolyazine solution. Solid circles are iodine, open circles are the charge-transfer product, and triangles are the polymer. The solid lines are the theoretical fit using $K = 800\ \mathrm{M}^{-1}$ and $z = 1$.

Conclusions

Substitution of a propyl group onto the polyazine backbone has a number of significant effects. The desired property of solubility in organic solvents is readily achieved. Further, the conjugation along the polymer backbone appears to be relatively unaffected by the presence of the propyl group, at least in the undoped state. This is evidenced by the red shift in the electronic spectrum relative to the monomer, the downfield shift of the NMR resonances relative to the monomer, and the low-energy imine vibrational energy in the IR spectrum. These same effects are also seen in the permethyl-substituted polymer. Thus, it seems likely that the propyl methyl polyazine has a structure similar to the permethylpolyazine, i.e., a linear polymer with double bonds in the *E* conformation and single bonds in the anti (s-trans) conformation. The synthetic method does lead to a statistical distribution of sequences of methyl groups and propyl groups along the polymer backbone that is not a consideration in the permethyl case.

Upon treatment with iodine both the IR and UV–vis spectra clearly show that reaction occurs and the effects of the propyl group become more notable. The propyl group alters the reactivity with iodine significantly. No oxidative chemistry can be observed, thereby preventing the formation of charge carriers. The addition of the propyl group has made the polyazine chain much more chemically robust so that more powerful oxidizing agents must be used to form charge carriers. Investigations into this chemistry is in progress.

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